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Magnetkis i betongtilslag

Effekt på betongs bestandighet

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Børge Johannes Wigum

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Forfatter
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Sammendrag

Sulfidmineraler og spesielt magnetkis kan bidra til nedbrytning av betong. Det har siden 1950-tallet vært rapportert om skader i en rekke land. Gjennomgang av historiske data fra ulike norske forekomster har vist at ca. 10 % av prøvene har innhold av magnetkis og svovel som gjør at de ikke er godkjent iht. gjeldende regelverk. De fleste av disse er fra forekom-ster av knust berg. Rapporten gir en oversikt over skademekanismene, analysemetoder for å detektere magnetkis og svovel i tillegg til metoder for å prøve ut egnethet i betong. Rapporten peker også på behov for videre forskning.

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Summary

Sulphide minerals and especially pyrrhotite can contribute to the decomposition of concrete. Damage has been reported in several countries since the 1950s. Review of historical data for Norwegian aggregates has shown that approx. 10% of the samples have a pyrrhotite and sulphur content which means that they are not approved according to the current regulations. Most of these samples are from hard rock quarries. The report provides an overview of the damage mechanisms, methods for detecting pyrrhotite and sulphur as well as methods for testing suitability in concrete. The report also points to the need for further research.

Pages 30 + 4 appendices

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State-of-the-art rapport:

Magnetkis i betongtilslag. Betydning for betongs bestandighet

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Forord

Rapporten er utarbeidet av en prosjektgruppe som har sitt utspring fra arbeidet med revidert NB- publikasjon nr. 18 «Tilslagsmaterialer for betongformål». Målsetningen med rapporten har vært å gi en kortfattet og relativt lettlest oversikt over fagområdet, med fokus på følgende områder:

- Presentere hovedtrekkene i det vi vet per i dag
- Peke på de områdene hvor vi mener kunnskapen er utilstrekkelig
- Peke på viktige temaer hvor det er behov for å sette i gang forskning

Prosjektgruppen har vært aktiv siden mars 2018. I denne perioden har det vært avholdt 9 møter i tillegg til at det har vært arrangert en egen Nordisk workshop (se Appendix IV). Følgende personer har vært aktive i arbeidet:

- Bård Pedersen, Statens vegvesen Vegdirektoratet
- Svein Willy Danielsen, Geomaterials Consultant
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- Jan Lindgård, SINTEF
- Silje Gystad Ytterdal, Multiconsult/Bane NOR (til juni 2019)
- Viggo Jensen, NBTL/VJe Holding (til april 2019)

Arbeidet har hatt finansiering fra Norsk betongforening, Statens vegvesen og Heidelberg Cement Northern Europe, og i form av egeninnsats fra prosjektdeltagerne.

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Appendix IV:	Rapport fra workshop i Oslo, november 2018: The Nordic Concrete Federation (2018): Workshop Proceedings No. 14. “Impact of sulphide minerals (pyrrhotite) in concrete aggregate on concrete behaviour”.

1 Innledning

1.1 Bakgrunn

Internasjonalt har det vært kjent siden 1950-årene at sulfidholdige tilslag (kismineraler) kan bidra til nedbrytning av betongkonstruksjoner. Det har vært rapportert saker fra en rekke land, hvor først og fremst mineralet magnetkis ($Fe_{1-x}S$) har blitt identifisert som en hovedårsak til problemene. Magnetkis (men også svovelkis) kan reagere når det er vann og oksygen tilstede. Dette fører til oksidasjon der det dannes sulfationer (SO_4^{2-}), svovelsyre og jern-oksihydroksider. Dette fører til forskjellige former for internt sulfatangrep på herdet betong. Sulfationer og vann reagerer med portlanditt ($Ca(OH)_2$) og kalsium aluminathydrater i sementpastaen og det dannes ettringitt. Svovelsyre reagerer med portlanditt og det dannes gips. Begge disse mineralene kan føre til ekspansjon og oppsprekking. I tillegg forekommer thaumasitt sulfatangrep i fuktig og relativt kaldt miljø (< 15°C) ved samtidig god tilgang på karbonationer fra CO_2 eller kalsiumkarbonat. Thaumasitt dannes og «eter opp» sementpastaens C-S-H og kan føre til svekkelse eller total omvandling av sementpastaen, vanligvis uten stor ekspansjon. Utfellinger av jernforbindelser bidrar i liten grad til total ekspansjon.

Det gjenstår imidlertid fremdeles mange spørsmål når det gjelder magnetkis – bestemmelse av innhold, forståelse av mekanismer og forskjellige former for magnetkis, samvirket med andre sulfidformer og andre mineraler, eksponeringsbetingelser, betydning av betongsammensetningen, og ikke minst forholdsregler for å unngå reaksjoner.

I Norge har magnetkis i betong blitt et fokusert spørsmål forholdsvis nylig. En viktig årsak til at dette spørsmålet har fått ny oppmerksomhet er Follobaneprosjektet. Her skulle i utgangspunktet knuste steinmasser fra driving av jernbanetunnelen bli prosessert til tilslag for betongen som ble brukt til tunnelelementer. Det viste seg imidlertid at ca. 60 % av tilslagsprøvene hadde indikasjoner på magnetkis, i tillegg til relativt høyt svovelinnhold. Det ble derfor besluttet å ikke bruke dette steinmaterialet, men i stedet kjøpe inn et kommersielt levert tilslag. Dette hadde store økonomiske konsekvenser.

Norsk Betongforenings Publikasjon nr. 18 – Tilslagsmaterialer for betong – er under revisjon. I løpet av dette arbeidet er det blitt klart at to viktige bestandighetshensyn må fokuseres. Det ene er alkalireaksjoner (ASR) hvor vi har veletablert kunnskap etter 30 år med forskning i Norge, og også er sterkt involvert i internasjonalt fagmiljø. Det andre bestandighetstemaet er sulfidholdige tilslagsmaterialer (kismineraler). Her må vi erkjenne at det mangler en del på kunnskapene, selv om problemstillingen, som nevnt ovenfor, ble erkjent allerede på 50-tallet. Revisjonskomiteen for NB 18 initierte derfor et forprosjekt i 2018 med mål å samle kunnskap på dette området og presentere en oversikt med fokus på norske forhold. Arbeidet presentert i denne rapporten viser at økt kunnskap om denne tematikken er nødvendig. Komiteen vil derfor ta initiativ til å få finansiert og gjennomført et større nasjonalt prosjekt som kan gi grunnlag for nye retningslinjer.

En viktig del av forprosjektet var et nordisk fagseminar med internasjonal deltagelse (Europa og Nord-Amerika), som ble avholdt i Oslo i november 2018. Det var også et mål å benytte denne anledningen til å knytte internasjonale kontakter for fremtidig felles forskningsinnsats. Det ble gitt 13 presentasjoner. Disse er i sin helhet vedlagt som Appendix IV til denne rapporten, sammen med en oppsummering fra prosjektets side.

1.2 Internasjonale erfaringer

Pågående forskning knyttet til magnetkis i betongtilslag er i stor grad begrenset til noen få land og fagmiljøer. Dette kan avspeile regionale forskjeller når det gjelder alvorlighetsgraden av problemet – eller kanskje også forskjeller i fagmiljøenes anerkjennelse av problemstillingen. Suverent høyest forskningsaktivitet på dette området, og også det største antallet publiserte skadetilfeller, finner vi i Canada. Her er det også en konsentrasjon innenfor et begrenset område – distriktet Trois Riviéres – med forskningsinnsatsen konsentrert hos Laval University. Det foreligger et bredt utvalg av publikasjoner fra forskningsinnsatsen ved Laval. Dette er med i litteraturoversikten i Appendix I. En særs viktig rapport derfra er doktorgraden til Rodrigues (Rodrigues A. (2016)), hvor vi har inkludert state-of-the-art-kapitlet som Appendix III i den foreliggende rapporten.

Rapporten fra seminaret i Oslo (Appendix IV) viser også aktualiteten av denne problemstillingen i en del andre land. Selv om det internasjonale aktivitetsnivået og fokuset på dette temaet i dag er begrenset, finnes det relevant litteratur og forskningsresultater fra en rekke land. En god oversikt er gitt i Appendix III, og det er også referert til et stort utvalg av litteratur i Appendix I.

Tidlige skadeobservasjoner er rapportert fra Norge (først og fremst knyttet til alunskiferproblematikken), Canada (Montreal og Ottawa), Spania, Sør-Afrika, Australia, England, Namibia, Sverige og Skottland.

Nyere observasjoner er først og fremst gjort i Canada (se ovenfor), men også i Sveits, USA, UK og Finnland. I Norge ble problemstillingen nylig aktualisert i forbindelse med Follobanen som nevnt foran, men det har vært få konkrete skadeobservasjoner i betongkonstruksjoner.

Testing av svovel/ sulfidinnhold i tilslag foretas rutinemessig her hjemme (kapittel 3 og kapittel 4) og ikke minst i Canada, dessuten bl.a. i Sverige, Sør-Afrika, Spania, UK, Brasil og Sveits. I Europa er krav til slik testing nedfelt i EN 12620, se også kapittel 4 og 5.

2 Geologi og mekanismer

2.1 Innledning

Dette kapitlet gir en kortfattet beskrivelse av geologiske forhold og mekanismer. I tillegg er hovedmekanismene beskrevet i kapittel 1.1, mens utvidet informasjon om mekanismer er gitt i Appendix II.

2.2 Geologiske forhold

Jernsulfider er en fellesbetegnelse på en rekke forbindelser mellom jern og svovel, og er blant de mest vanlige metalliske mineraler. De finnes i utgangspunktet i alle mulige typer bergarter.

Jern(II)disulfider finnes som det hyppig forekommende mineralet ***svovelkis*** (en. *pyrite*), med en uniform sammensetning; **FeS_2**. I håndstykke viser mineralet en gylden, messing-gul farge (narregull). Svovelkis er Norges viktigste mineralforekomst og dannet tidligere grunnlag for jernproduksjon.

Jern(II)sulfider kan forekomme som det litt mindre hyppige mineralet ***magnetkis*** (en. *pyrrhotite*), som har en variabel kjemisk sammensetning; **$Fe_{1-x}S$**, der x kan variere mellom 0 og 0,125. Magnetkis er generelt ansett å være mye mer utsatt for oksidasjon enn svovelkis, og det oksiderer ofte veldig raskt. I håndstykke sees magnetkis som mørke, sterkt metallisk glinsende korn.

Det er et bredt spekter av bergarter fra ulike forekomster som i laboratorieundersøkelsene (kapittel 3) er påvist å ikke tilfredsstille kravene i standarden: Gabbro, grønnstein, amfibolitt, gneis, granitt, gråvakke, sandstein, silt-leirstein, rombeporfyr, rhyolitt, kalkstein. Dette viser at magnetkis, under gitte betingelser, kan forekomme i de fleste aktuelle bergarter. Men mineralet finnes oftest i tilknytning til mafiske- og ultramafiske bergarter, og sjeldnere i felsiske (granittiske) bergarter. Det er også vanlig å finne mineralet i metamorfoserte sedimentære bergarter, spesielt svarte skifre.

2.3 Mekanismer og reaktivitet

Reaktiviteten (oksidasjonshastigheten) til magnetkis ($Fe_{1-x}S$) er komplisert, fordi:

- magnetkis forekommer i ulike krystallkjemiske varianter med forskjellig syre- og sulfatpotensial
- når andre sulfidmineraler forekommer sammen med magnetkis, som for eksempel svovelkis (FeS_2), vil dette vanligvis gi høyere totalt syre- og sulfatpotensial enn når magnetkis opptrer alene på grunn av galvaniske spenningsforskjeller mellom de forskjellige sulfidmineralene
- andre komponenter og mineraler kan påvirke prosessen, bl.a. er det fra Canada nevnt at biotittinnhold kan påvirke reaksjonsforløpet.

Potensiell reaktivitet øker med økende x (i den kjemiske formelen for magnetkis, $Fe_{1-x}S$). Varianter med lite jern i forhold til svovel er med andre ord de mest reaktive, mens magnetkis med relativt mye jern er mindre reaktive. Parallelt med endringen i sammensetningen skjer en forandring av de magnetiske egenskaper. Reaktiv magnetkis er magnetisk, mens de mindre reaktive variantene er svakt magnetiske eller ikke-magnetiske. Liten mineralkornstørrelse og høy spesifikk overflate gir høyere reaktivitet enn større kornstørrelse/lavere spesifikk overflate. Den spesifikke overflata til magnetkis er 2-10 ganger høyere enn svovelkis, og magnetkis regnes derfor å være mer reaktiv enn svovelkis (MEND 1998, Belzile mfl. 2004). Økende spesifikk overflate til et mineral bidrar alltid til økende reaktivitet når alle andre egenskaper holdes konstant.

Betongtilslaget fra Trois-Rivier i Quebec, som har ført til store bygningsmessige skader, inneholder både magnetkis og svovelkis. Petrografiske undersøkelser av skadet betong har vist at *magnetkisen er vesentlig mer nedbrutt enn svovelkis*, og en antar derfor at magnetkisen er den viktige reaktive bestanddelen (Rodriguez 2016). Men fordi magnetkis representerer anoden (offeranode) i dette elektrokjemiske systemet *er ikke dette i seg selv grunn til å hevde at magnetkis alltid er mye mer reaktiv enn svovelkis.* Magnetkis av samme type som i Quebec er ikke nødvendigvis like skadelig i tilfeller der dette er eneste sulfid. Undersøkelser av reaktiviteten til ren magnetkis ved ulike pH- betingelser viser ifølge Belzile mfl. (2004) inkonsistente resultater, mens Divet & Davy (1996) finner at ren svovelkis er mest reaktiv ved høy pH.

Mekaniske og kjemiske forhold kan påvirke inntrengning av alkalisk porevann fra sementpastaen

Dersom det totale svovelinnholdet i to tilslag er relativt høyt, og sulfidinnhold, mineralkornstørrelse og fordeling av sulfidmineraler gir like resultatet, vil tilgjengeligheten på alkalisk porevann fra sementpastaen kunne bli avgjørende med hensyn til skadeutvikling. Ser vi bort fra at ulike sementtyper vil ha noe forskjellig porevannssammensetning så vil inntrengningsdypet av porevannet være styrt av:

- styrken til tilslaget, dvs. motstanden mot mikro-oppsprekking
- løseligheten til eventuelle sekundære sulfatmineraler, samt kvarts og feltspat ved høy pH
- absorpsjonsevne av tilslag

Et mekanisk sterkt tilslag vil ha liten grad av mikro-oppsprekking og etter alt å dømme motvirke dyp inntrenging av porevann fra sementpastaen, der sulfat og syrebidraget vil være begrenset til magnetkis og andre sulfidmineraler på tilslagets overflate. Svakere tilslag med større grad av mikro-oppsprekking vil være mer utsatt for reaksjoner med sulfidene som ligger dypere inne i tilslagskornene. Etter hvert som den opprinnelige svært basiske porevæsken trenger dypere og dypere inn i tilslaget og påtreffer flere sulfider vil pH og sulfatkonsentrasjon i porevæsken avta. Potensialdifferansen og spenningsforskjellen mellom magnetkis og svovelkis vil øke ettersom elektrolytten (porevæsken) får lavere pH (Moslemi m.fl. 2011). Det er derfor sannsynlig at dyp inntrenging fører til stadig høyere oksidasjonshastighet i takt med økt syredannelse.

Eventuell forekomst av sekundære løselige sulfatmineraler i tilslaget er også viktig. Ved oppløsning vil dette åpne nye mikrokanaler og øke tilgjengeligheten for porevannet innover i tilslaget. På samme måte er det mulig å se for seg at mikrokanaler kan dannes ved oppløsning av mikrokvarts ved høy pH i en tidlig fase.

3 Svovelinnhold i norske tilslag

Både NBTL og SINTEF har gjennom en årrekke analysert tilslagsprøver med tanke på svovelinnhold (Haugen og Lindgård (2018 og 2019), Jensen (2018), NBTL (2019)). Resultatene, som ble presentert på workshopen i Oslo (se Appendix IV), viser at flere produsenter av tilslag har resultater som ligger over gjeldende krav til svovelinnhold for prøver med påvist magnetkisinnhold. Ca. 10 % av prøvene (i snitt av de to involverte laboratoriene, og hovedsakelig prøver av knust berg) viser både svovelinnhold > 0,14 % og tilstedeværelse av magnetkis.

Det er ikke påvist (eller rapportert) nedbrytning av betong som er støpt med norske tilslag med magnetkis. Dette kan bl. a. skyldes at det meste av betongtilslag i Norge har vært tatt fra naturgrusforekomster, hvor forvitring av kismineralene gjerne har funnet sted før det blir aktuelt å blande tilslaget inn i betong. Det må imidlertid påpekes at det ikke har vært gjennomført systematiske undersøkelser for denne skadetypen, og vi kan dermed ikke utelukke at skadetypen forekommer.

Observasjonen av ikke-forvitret magnetkis i Folloprosjektet (Gystad Ytterdal 2018) kan også indikere at dette problemet er mest relevant for knust tilslag, ikke minst tunnelstein, hvor også forundersøkelser vil være mer krevende.

4 Standarder, spesifikasjoner

4.1 Dagens regler

I den europeiske tilslagsstandarden EN 12620 er følgende angitt:

- En øvre grense for svovelinnhold på 1 vekt-%. Denne er gjeldende for alle andre tilslag (inkludert fillere) enn masovnslagg hvor grenseverdien er 2 vekt-%.
- Dersom det er kjent at mineralet magnetkis finnes i tilslaget gjelder en lavere grense på høyst 0,1 vekt-% svovel.

Merk at 0,1 vekt-% er langt mer liberalt enn 0,10 vekt-%, og vil tillate verdier opp til 0,149 vekt-%.

Det er i standarden spesifisert at svovel skal bestemmes i samsvar med NS-EN 1744-1, punkt 11. Merk at det er to alternative metoder for analyse av svovel i henhold til standarden, disse er nærmere beskrevet i kapittel 5.1.

Det er i den europeiske hovedstandarden ikke angitt hvordan magnetkis skal påvises.

<u>Det nasjonale tillegget til NS-EN 12620</u> inneholder noen formuleringer av stor betydning:

- Maksimal grense for svovel er satt til 1,0 vekt-% (i motsetning til 1 vekt-%)
- Det er spesifisert at ved svovelinnhold høyere enn 0,1 vekt-% <u>alltid</u> skal undersøkes om det er magnetkis til stede. Det er videre spesifisert at undersøkelse av magnetkis skal utføres ved bruk av DTA (differialtermisk analyse), og det er gitt en enkel beskrivelse av hvordan undersøkelsen skal gjennomføres. Se kapittel 5.2.

Prøvingshyppighet for svovel og magnetkis er satt til minimum 1 analyse per år.

<u>Regler i Nord-Amerika:</u>

I den Canadiske standarden CSA A23.1 har det siden 1973 vært advart mot jernsulfider i tilslag. I 2014-utgaven ble det innført et nytt Annex P (informativt) som ga konkrete anbefalinger som er relativt like de som er gitt i den europeiske standarden:

- Ved svovelinnhold lavere enn 0,10 vekt-% (i motsetning til 0,1 i den europeiske standarden) kan tilslaget brukes uten videre undersøkelser.
- Ved høyere svovelverdier enn 0,10 vekt-% og samtidig påvist magnetkis skal tilslaget ikke brukes.
- Dersom det er snakk om andre sulfidmineraler enn magnetkis (som ikke er følsomme for oksidasjon) og dersom det er dokumentert tilfredsstillende resultater i felt, kan tilslaget brukes.

Det er i Canada foreslått en tre-fase-evaluering som kan bli standardisert (se Rodrigues et. al. (2016) og beskrivelse i kapittel 5.3):

- Fase 1: Ren kjemisk evaluering av totalt svovel (S): under 0,10 vekt-% **tillat** – over 1 vekt-% **forkast**.
- Fase 2: (dersom S ligger i intervallet 0,10 – 1 vekt-%): «oxygen consumption test». Utfallet kan her bli enten **tillat** eller **videre prøving kreves** (Fase 3).
- Fase 3: 2-stegs mørtelprismetest, hvor utfallet kan bli **tillat** eller **forkast**.

USA: Det er ikke gitt konkrete grenseverdier for sulfidmineraler i ASTM C33-18 (Standard specification for concrete aggregates). I ASTM C294-12 er det imidlertid anmerket at markasitt og noen former for svovelkis og magnetkis er reaktive i betong og kan gi volumøkning.

4.2 Behov for å endre standarder

Prøvingsregime

NS-EN 12620 foreskriver minimum 1 prøve per år for analyse av svovelinnhold og evt. forekomst av magnetkis. En slik lav prøvingshyppighet forutsetter at man har å gjøre med en relativt homogen forekomst. Men selv i relativt homogene pukkforekomster vil det være variasjoner og i mange tilfeller flere varianter av bergarter i den samme forekomsten.

Hvis vi beveger oss over mot bruk av tilslag fra tunnelprosjekter (sprengstein eller masser fra TBM) eller andre typer prosjekter må vi forvente en meget høy variasjon i forekomst av magnetkis over tid. Sikker bruk av tilslag fra tunnelprosjekter forutsetter derfor at man får på plass et helt annet og langt strengere prøvingsregime enn det som er beskrevet i tilslagsstandarden. Det er ikke nødvendigvis sikkert at dette er egnet i et nasjonalt tillegg til NS-EN 12620, det kan være at det heller bør komme i form av nasjonale anbefalinger. En mulig løsning vil kunne være å skrive disse anbefalingene inn i NB-18 som nå er under revisjon.

Grenseverdi for svovelinnhold og magnetkis - funksjonsprøving

Per i dag har vi et regelverk som har fungert tilfredsstillende i og med at vi ikke har et kjent skadeproblem i Norge. Men kanskje er regelverket såpass strengt at det utelukker bruk av noen gode ressurser. Det er mange usikkerheter knyttet opp til blant annet: kvantifisering og karakterisering av sulfidmineraler, hvor reaktive ulike varianter av magnetkis er, hvor skadelige andre sulfider (f.eks. svovelkis) er og om det finnes effektive preventive metoder for å forhindre skadelige reaksjoner (f.eks. silikastøv, flygeaske etc.).

Per i dag har vi ikke noe vitenskapelig grunnlag for å «løse opp og differensiere» regelverket, men det er ønskelig å på sikt få på plass et prøvingsregime som vil kunne muliggjøre bruk av tilslagsmaterialer som ligger noe utenfor dagens krav. Det foreslåtte Canadiske prøvingsregimet (se Kapittel 5.3) er interessant, og bruk av mørtelprismeprøving for å karakterisere skadepotensialet kan være en mulig vei å gå. Det er også interessant å tenke seg bruk av «funksjonsprøving» hvor man tester ut konkrete blandinger av tilslag og bindemidler – omtrent tilsvarende som vi gjør for alkalireaksjoner. Det vil imidlertid kreve en betydelig forskningsinnsats å komme dit.

5 Analysemetoder

5.1 Bestemmelse av svovel i tilslag

***Svovelanalyser** (elementanalyse) i h.h.t. dagens standard NS-EN 1744-1:1988 artikkel 11 (se kapittel 4.1):*

Syreløsning av svovel (referansemetode)

Reagenser som brukes er Hydrogenperoksid (H_2O_2) og saltsyre (HCl) til oppløsning og bariumklorid til utfelling.

Alle svovelforbindelser i tilslagsprøven løses opp i syre og danner sulfater. Alle sulfater i løsningen felles så ut som bariumsulfat $BaSO_4$. Bariumsulfatet tørkes og veies.

Svovelinnholdet uttrykkes som vekt-% av den totale tilslagsprøven.

Ved eventuell tørking av prøve før analyse, må ikke dette skje over 110±5 °C. Sulfider oksiderer ved høyere temperatur.

Denne prosedyren utføres per dags dato av SINTEF.

Forbrenningsanalyse for svovel (alternativ metode)

Typisk utstyr for slike analyser er «Leco ovn».

En liten del av prøven varmes opp i ren oksygenatmosfære i et forbrenningskammer. All svovel i prøven vil oksidere til SO_2. Mengden SO_2 i avgassen måles med infrarød detektor.

Denne prosedyren utføres per dags dato av NBTL.

5.2 Mineralanalyser

Differensialtermisk analyse (DTA)

Det er kun NTNU/SINTEF som utfører DTA-analyse på tilslagsmateriale i Norge.

Analysene utføres på en ikke-kommersiell DTA som opprinnelig ble bygget på NTH i løpet av 1950-tallet men er oppgradert med årene.

En liten prøve legges i en nikkeldigel og varmes opp til 700 °C mens energien leses av kontinuerlig. Sulfider (her svovelkis og magnetkis) har typisk utslag mellom 430 og 520 °C som følge av oksidasjon. Totalt sulfidinnhold kan beregnes fra arealet under utslaget på kurven, mens magnetkis kan påvises basert på formen på energikurvene.

Røntgenfluorescense - XRF

Dette er den vanligste metoden til kjemisk analyse av bergarter. To ulike teknikker benyttes for henholdsvis hoved- og sporelementer. Hovedelementene analyseres på en smeltet «pille» hvor hele bergartsprøven er homogenisert. I forkant av smelting av prøven «glødes» prøven på 1000 °C for å måle innhold av flyktige bestanddeler. Dette gir ikke spesifikk analyse per element, men rapporteres som «glødetap» eller «LOI» som typisk er et mål på for eksempel fuktighet, organisk materiale, krystallbundet vann, karbon og svovel. Analyse på smeltet pille vil derfor ikke kunne gi en korrekt analyse av svovelinnholdet. Sporelementanalysen utføres derimot på presset pille av finmalt prøvemateriale. En slik analyse kan gi et bilde av innholdet av svovel og det finnes eksempler på resultater med analyse av S ned til 0.05 vekt-% (95% konfidensnivå innenfor +/-3.5%) (Pasitschniak, 1986).

Røntgendiffraksjon (XRD)

En mikronisert (-10 µm) prøve presses til en pille med helt plan og feilfri overflate som deretter analyseres ved hjelp av røntgenstråle. Røntgenstrålen vil i interaksjon med prøvens overlate diffrakteres og vinkelen θ måles av en detektor. Ved hjelp av Braggs lov $n\lambda=2d*\sin\theta$ kan man så finne gitteravstanden d og bestemme de krystallografiske egenskapene og dermed identifisere mineralene.

XRD har utfordringer med analysenøyaktighet og oppløsning på lave mineralkonsentrasjoner. Dette gjør at deteksjonsgrensen ofte er satt til ±1 vekt%. Alle resultater oppgitt i lavere verdier kan kun anses som en indikasjon på mineralet.

Automatisk mineralanalyse

Automatisk mineralanalyse er basert på elektronmikroskop og røntgenanalyse. Et gråtonebilde (BSE) av prøven tas opp av prøveoverflata. Gråtonebildet skiller mellom faser (mineraler) med ulikt gjennomsnittlig atomnummer og porøsitet. Denne informasjonen brukes til å definere korn og partikler i prøven som deretter analyseres kjemisk. Resultatet av den kjemiske analysen brukes deretter til å klassifisere korn/partikler til mineralklasser etter forhåndsdefinert oppskrift. Sulfidmineraler i prøven kan detekteres så fremt det er et sulfidkorn tilstede som er større enn ca. 2-4 µm. Deteksjon av sulfidkorn < 1 µm er også mulig ved siste generasjons elektronmikroskop.

5.3 Canadisk 3-fase evaluering

Dersom standardundersøkelsene av et tilslag i henhold til NS-EN 1744-1, punkt 11 viser et innhold av svovel > 0,1 vekt-% og DTA-analysen samtidig viser spor av magnetkis er det som angitt i kapittel 4.1 ikke tillatt å benytte tilslaget til betongformål.

Verken i Norge eller i Europa finnes det standardiserte prøvingsmetoder for å undersøke nærmere hvorvidt et tilslag som faller utenfor akseptkriteriene evt. kan "frikjennes" for bruk i betong. Basert på forskning utført i Canada har de imidlertid foreslått en tre-fase evaluering som de på sikt håper kan standardiseres (se Rodrigues et al. (2016)):

Fase 1:

Evaluering basert på bestemmelse av totalt svovelinnhold (se 5.1): under 0,10 vekt-% tillat – over 1 vekt-% forkast.

Fase 2:

«Oxygen concumption test»; Prinsippet er å male ned tilslaget til kornstørrelse < 150 µm, legge et kompaktert lag av det nedmalte materialet (med beskrevet tykkelse og vanninnhold) i bunnen av en beholder, og så eksponere materialet for ren oksygen-gass. Under forsøket måles forbruket av oksygen. Et økende innhold av jernsulfid (som kan være svovelkis, magnetkis eller andre kismineraler) vil føre til økende oksygenforbruk når jernsulfiden oksideres. Hvis oksygenforbruket er mindre enn foreslått grenseverdi anbefales tilslaget benyttet til betongformål. I motsatt fall anbefales videre prøving i henhold til fase 3.

Fase 3:

Denne fasen består av en to-trinns mørtelprismetest. I trinn 1 eksponeres tynne mørtelprismer (25x25x285 mm) for 80^{o}C og 80 % RF i 90 døgn med to tre-timers perioder per uke hvor prismene neddykkes i et nøye beskrevet blekemiddel (6% natriumhypokloritt løsning) for å oksidere evt. jernsulfid i tilslaget. Målt ekspansjon etter 90 døgn over en gitt grenseverdi indikerer et skadelig innhold av jernsulfid og/eller at tilslaget er alkalireaktivt. Derfor bør årsaken til ekspansjonen undersøkes nærmere. Ved 90 døgns ekspansjon under grenseverdien eksponeres mørtelprismene ytterligere 90 døgn i 4^{o}C og 100 % RF (trinn 2). Også i trinn 2 inkluderes to tre-timers perioder per uke hvor prismene neddykkes i blekemiddelet. Hvis ekspansjonen av prismene øker, indikerer dette at thaumasitt dannes (pga innhold av skadelig sulfid og karbonat), og tilslaget anbefales da ikke benyttet i betong. Hvis prismene ikke ekspanderer videre som følge av trinn 2, anbefales tilslaget akseptert for bruk i betong.

Det pågår for tiden et stort forskningsprosjekt i Canada hvor blant annet disse metodene blir videreutviklet (se kapittel 7).

6 Strategi for sikrere avbøtende tiltak

Pr i dag foreligger det ikke tilfredsstillende og dokumenterte avbøtende tiltak for eksisterende betongkonstruksjoner som står i fare for å nedbrytes pga. sulfidangrep.

Heller ikke når det gjelder nystøpt betong foreligger det tilfredsstillende og dokumenterte tiltak for å forhindre sulfidangrep dersom det benyttes tilslag med magnetkis. Det fremgår av kapitlene foran, og ikke minst av kapittel 2, at vi her har å gjøre med svært komplekse kjemiske, mineralogiske og materialtekniske forhold. Det hele kompliseres av det faktum at skadelige reaksjoner synes å kunne tilskrives veldig små innhold av reaktive mineraler, som også er vanskelige å både bestemme og kvantifisere. Til tross for at det foreligger en stor mengde forskningslitteratur (Appendix I) har det pr i dag ikke lykkes å få en full oversikt over dette fagområdet. Utvikling av avbøtende tiltak vil først og fremst fordre at en slik totalforståelse blir etablert. Initiativet til fokusert forskning (kapittel 7) har nettopp som siktemål å få frem en slik forståelse, som i sin tur både kan være grunnlag for akseptkriterier når det gjelder materialvalg, og også være en forutsetning for avbøtende tiltak i eksisterende betong.

7 Videre forskning

Som angitt i kapittel 4 vet man ikke i dag hvilke innhold av magnetkis som kan gi skader i betong. Analysemetodene er også usikre. Videre er de fleste skadetilfellene som er observert relatert til betong av meget dårlig kvalitet (høyt v/c-tall), men vi kan ikke utelukke at skader vil oppstå i "vanlig betong". Det er derfor et stort behov for å forske videre på ulike problemstillinger knyttet til magnetkis, som beskrevet i de fire deltemaene nedenfor. Punkt 1 og 2 skal gjøre oss i stand til å vurdere om et tilslag har potensiale for å utvikle skadelige ekspansjoner i betong. Punkt 3 og 4 skal gi oss prøvingsmetoder, akseptkriterier og retningslinjer for pålitelig bruk av tilslag med et begrenset innhold av sulfidmineraler.

Analyse og karakterisering av svovel- og sulfidinnhold i bergartsmaterialer (tilslag) kan være meget krevende. Ofte er grenseverdiene det opereres med når tilslaget skal brukes til betong forsvinnende lave. Dersom det kun er svovelkis i tilslaget tilsvarer et svovelinnhold (S) på 1 vekt-% (grenseverdien i standarden) et innhold av svovelkis (FeS_2) i prøven på ca. 1,8 vekt-%. Dersom det finnes indikasjon på magnetkis i tilslaget vil grenseverdien droppe til 0,1 vekt-%. Dersom prøven kun inneholder magnetkis (her FeS – det minst svovelrike endeleddet av $Fe_{1-x}S$) tilsvarer dette 0,25 vekt-% FeS i prøven. Det er utfordrende med så lave innhold av sulfider når det samtidig er krav om å skille veldig like materialer (FeS og FeS_2). Utfordringene er formulert i følgende to forskningsområder:

1. Hvordan forekommer magnetkis i ulike bergarter?
    1.1. Hvilke geologiske prosesser bestemmer dannelse og konservering av magnetkis i ulike bergarter?
    1.2. Ved valg av tilslag, kan den geologiske historien til bergarten være avgjørende for om tilslaget vil kunne inneholde spor av magnetkis?
2. Hvordan karakterisere / analysere svovel (element) og sulfider (mineraler) i tilslaget?
    2.1. Hvilke metoder er best egnet og vil kunne gi det beste (mest riktige) analyseresultatet? Og hva er det riktige analyseresultatet?
    2.2. Utvikling av metodikk og prosedyrer for analyse av magnetkis og andre sulfider i tilslagsmateriale

Etter nøye klassifisering av tilslagsmaterialene (pkt. 1 og 2) er de neste utfordringene å;

3. Utvikle akselererte laboratoriemetoder for å bestemme hvilke innhold av magnetkis som er skadelig i betong (akseptkriterier) med utgangspunkt i;
    3.1. De foreløpige metodene som er utviklet ved Laval University i Canada (se kapittel 5.3)
    3.2. Økt forståelse for mekanismene som styrer nedbrytningsprosessene
    3.3. Dokumentert sammenheng mellom resultater fra akselererte laboratorieforsøk versus oppførsel i felt (feltstasjoner og virkelige konstruksjoner)

4. Utvikle funksjonsprøvingsmetoder for å dokumentere hvordan man pålitelig kan benytte et tilslag med et begrenset innhold av sulfidmineraler. Følgende problemstillinger er relevant å undersøke;
    4.1. Hvilke metoder kan være egnet?
    4.2. Hvilke akseptkriterier skal settes (dvs. validering av sammenhengen mellom labresultater og feltoppførsel)?
    4.3. Vil det oppstå skadelige ekspansjoner for betong med god kvalitet (lave v/c-tall)?
    4.4. Kan ulike tilsetninger så som flygeaske, silikastøv, slagg og andre alternative/pozzolane bindemidler, og i hvilke mengder, forhindre utvikling av skadelige reaksjoner?

Det vil være fordelaktig å samarbeide tett med det store FoU-prosjektet som nylig er startet opp i Canada.

8 Sammendrag

Små mengder kismineraler i betongtilslag kan bidra til nedbrytning av betongkonstruksjoner. Spesielt mineralet magnetkis har blitt identifisert som hovedårsaken til problemet. Magnetkis har formel $Fe_{1-x}S$, og forekommer i ulike krystallkjemiske varianter som har varierende reaktivitet. Andre kismineraler som svovelkis kan forverre problemet pga. galvaniske spenningsforskjeller mellom de ulike mineralene. Skademekanismen består av oksidasjon og dannelse av sulfationer, svovelsyre og jernhydroksider, etterfulgt av ulike former for interne sulfatangrep på betongen. Dette gir seg utslag i svekkelse av sementpastaen, samt ekspansjon med påfølgende oppsprekking av betongen.

Mekanismen har vært kjent siden 1950-tallet, og det er rapportert skader i mange land. I Norge er skadeobservasjoner først og fremst knyttet til alunskiferproblematikken. Pågående forskning er begrenset til noen få land og fagmiljøer. Den høyeste forskningsaktiviteten finner vi i Canada ved Laval University i Quebec, dette er i stor grad knyttet opp mot et stort antall rapporterte skadetilfeller i distriktet Trois-Rivieres.

I Norge har magnetkis blitt aktualisert i forbindelse med Follobaneprosjektet. Her skulle i utgangspunktet knuste steinmasser fra driving av jernbanetunnelen bli prosessert til tilslag for betongen brukt til tunnelelementer. Det viste seg imidlertid at ca. 60 % av tilslagsprøvene hadde indikasjoner på magnetkis, i tillegg til relativt høyt svovelinnhold. Det ble derfor besluttet å ikke bruke dette steinmaterialet som betongtilslag.

Gjennomgang av historiske data fra en rekke ulike forekomster har vist at for ca. 10 % av prøvene er det påvist magnetkis og svovelinnhold > 0,14 %, noe som innebærer at materialene ikke er godkjent i henhold til gjeldende europeiske regelverk. Majoriteten av prøvene med verdier utenfor kravene var produsert fra knust berg. Et bredt spekter av bergarter var representert i prøvene som ikke tilfredsstilte kravene: Gabbro, grønnstein, amfibolitt, gneis, granitt, gråvakke, sandstein, silt-leirstein, rombeporfyr, rhyolitt, kalkstein. Magnetkis kan altså under gitte betingelser forekomme i de fleste aktuelle bergarter. Men mineralet finnes oftest i tilknytning til mafiske- og ultramafiske bergarter, og sjeldnere i felsiske (granittiske) bergarter.

Analyse og karakterisering av svovel og sulfidinnhold i tilslag kan være meget krevende. Ofte er grenseverdiene det opereres med når tilslaget skal brukes til betong forsvinnende lave. Dersom det kun er svovelkis i tilslaget tilsvarer et svovelinnhold (S) på 1 vekt-% (grenseverdien i standarden) et innhold av svovelkis (FeS_2) i prøven på ca. 1,8 vekt-%. Dersom det finnes indikasjon på magnetkis i tilslaget vil grenseverdien droppe til 0,1 vekt-%. Dersom prøven kun inneholder magnetkis (her FeS – det minst svovelrike endeleddet av $Fe_{1-x}S$) tilsvarer dette 0,25 vekt-% FeS i prøven. Det er utfordrende med så lave innhold av sulfider når det samtidig er krav om å skille veldig like materialer (FeS og FeS_2).

I Norge benyttes i dag differensialtermisk analyse (DTA) ved rutinemessig analyse av tilslag. Metoden er ikke nøyaktig og gir ikke en virkelig kvantifisering av magnetkis, men i større grad en kvantifisering av totalt innhold av sulfidmineraler. Det er viktig å finne de riktige metoder og å utvikle metodikk og prosedyrer for å kunne gi en fullgod kvantifisering og karakterisering av sulfidmineralene.

Noen øvrige viktige forskningsområder er:

- utvikling av akselererte laboratoriemetoder for å kunne prøve ut hvilke mengder (og varianter av) kismineraler som er skadelige i betong. Det er i denne sammenheng viktig å validere sammenhengene mellom laboratorie og feltoppførsel
- fastsette akseptkriterier
- fastslå sammenhenger mellom materialsammensetning (i form av v/c-tall, type sement og tilsetningsmaterialer som flygeaske, slagg, silikastøv) og skadepotensialet i betong

Det er pekt på at det vil være fordelaktig å samarbeide tett med det store FoU-prosjektet som nylig er startet opp i Canada.

APPENDIX I

Literature overview

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- Marit Haugen and Jan Lindgård: "Determination of total sulphur content in aggregates (2004 – 2018) – results from SINTEF"
- Viggo Jensen: "Total S and Pyrrhotite in Norwegian concrete aggregate deposits. Statistical assessment from NBTL´s database over projects"
- Magnus Döse: "Cases in Sweden were sulphide minerals may contribute to damages in concrete"
- Hannu Pyy: "Cases in Finland where sulphide minerals in aggregate have caused damages in concrete structures"
- Josée Duchesne and Benoit Fournier: "Overview of the deterioration mechanisms: Cases of deterioration in Canada and US"
- Per Hagelia: "Mineralogical properties pyrrhotite, pyrite and associated weathering products"

- Terje Bjerkgård: “Iron sulphides: Formation and conditions for occurrence in bedrock”
- Andreas Leemann: “Simultanious iron sulphide oxidation and alkali silica reaction in a Swiss dam”
- Roland Weiss: “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”
- Ian Sims and Philip Santo: “Managing the Mundic problem in South-West England”
- Benoit Fournier and Josée Duchesne: “The development of accelerated test methods and the content of a new Canadian R&D project”
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Appendix II Mekanismer (utvidet kapittel) – og noen synspunkter på veien videre

Forfattet av Per Hagelia, Statens vegvesen Vegdirektoratet

1 Innledning

Hovedutfordringen i magnetkisprosjektet er å komme fram til grenseverdier for betongtilslag, slik at vi unngår tilslag som fører til internt sulfat- og syreangrep. Reaktiviteten (oksidasjonshastigheten) til magnetkis ($Fe_{1-x}S$) er komplisert, fordi:

- magnetkis forekommer i ulike krystallkjemiske varianter med forskjellig syre- og sulfatpotensial
- når andre sulfidmineraler forekommer sammen med magnetkis, som for eksempel svovelkis, vil dette vanligvis gi høyere totalt syre- og sulfatpotensial enn når magnetkis opptrer alene på grunn av galvaniske spenningsforskjeller mellom de forskjellige sulfidmineralene

Regelverket fanger ikke opp alle variabler som kan føre til sulfat og syreangrep på betong. Dagens norske grenseverdier for betongtilslag er basert på analyse av totalt svovel og differensialtermisk analyse (DTA). Dersom DTA gir «indikasjoner på magnetkis» er grenseverdien for totalt svovel 0,1 vekt %. Uten magnetkis er grenseverdien 1,0 vekt % (se kapittel 4). DTA er ingen nøyaktig metode og instrumentet som er tilgjengelig her i landet, fra 1950-talet, er ikke godt kalibrert (Aasly mfl. 2018). DTA gir derfor ikke et absolutt tall på innhold av magnetkis, men et tall på totalt innhold av sulfider (inkludert svovelkis og magnetkis).

Vanlige former for magnetkis i norsk berggrunn varierer fra meget reaktive til mindre reaktive. Men det er også flere andre forhold som virker inn. Det er stort behov for grundige undersøkinger ved hjelp av moderne analyseteknikker. Generelt er reaktiviteten til et tilslag med sulfider; potensialet for internt sulfatangrep på betong, avhengig av:

- prosentvist innhold av magnetkis (monokline-, heksagonale-, ortorombiske varianter)
- prosentvist innhold av sulfidmineraler sammen med magnetkis
- kontaktrelasjoner mellom de forskjellige sulfidmineralene
- mineralenes spesifikke overflate, mineralkornstørrelse & tekstur
- forvitringstilstand (grad av sulfidoksidasjon fra naturens side og forekomst av sekundære sulfater og jernoksider)
- temperatur (reaktiviteten øker proporsjonalt)
- pH
- mekaniske og kjemiske forhold som påvirker inntrengning av porevann fra sementpastaen (motstand mot mikro-oppsprekking og tilstedeværelse av løselige mineraler)

2 Magnetkis

Magnetkis er en samlebetegnelse for en gruppe sulfider med varierende egenskaper. Ikke-støkiometriske varianter med relativt lite jern i forhold til svovel har lite ordnet krystallstruktur (monokline varianter med x = 0,1-0,125) og er dermed de mest reaktive. Magnetkis med relativt mye jern (for det meste heksagonale varianter med x = 0,07-0,1) er mindre reaktive. Reaktiv magnetkis er magnetiske, mens de mindre reaktive er svakt magnetiske eller ikke-magnetiske. Avblandinger bestående av både monokline og heksagonale varianter er vanlig (Neumann 1985). Liten mineralkornstørrelse og høy spesifikk overflate gir høyere reaktivitet enn høyere kornstørrelse/lavere spesifikk overflate. Den spesifikke overflata til magnetkis er 2-10 ganger høyere enn svovelkis, og magnetkis regnes derfor å være mer reaktiv enn svovelkis (MEND 1998, Belzile mfl. 2004). Problemstillingen er i prinsipp analog med reaktiviteten til kvarts i forbindelse med alkalireaksjoner i betong, i den forstand at økende spesifikk overflate til et mineral alltid bidrar til økende reaktivitet når alle andre egenskaper holdes konstant.

Kinetiske tester viser derimot at oksidasjonsraten til forskjellige typer magnetkis i ren form bare delvis reagerer raskere enn svovelkis (Chopard mfl. 2015). Effekter av bakteriell oksidasjon på en rekke norske sulfider viste at mens svovelkis ble 100 % oksidert så ble bare 35 % av uspesifisert magnetkis oksidert (Efraimsen mfl. 1976).

Erfaringer fra områder med magnetkisførende bergarter understreker tydelig at *høyt totalinnhold av sulfid ikke generelt indikerer høy reaktivitet.* Hagelia (2018) viser et eksempel med 10 % relativt grovkornet velkrystallin magnetkis (ca. 0,5-1 mm) i hornfels med < 1 % svovelkis og < 1 % kalsitt som var svært lite reaktiv (pH = 6,2 etter 5 års statisk utlekkingstest). Eksempler fra sulfid- og sulfatførene gneiser med sur avrenning på Sørlandet viser at finkornet (mindre enn 0,1 mm) ren monoklin magnetkis gir noe lavere pH enn ren heksagonal magnetkis (hhv. pH = 3,8-4 og pH = 4,2), mens ren svovelkis ofte gir pH ned mot 2,5 (Hagelia 2018, Hagelia mfl. 2003).

3 Galvaniske effekter når flere sulfider opptrer sammen

Når et eller flere sulfidmineraler opptrer i kontakt med magnetkis dannes det galvanisk strøm som fører til en mer omfattende oksidasjon enn enkeltsulfider alene (Gottschalk & Buehler 1912, Chopard mfl. 2017). Årsaken er at sulfidmineralene har forskjellige elektriske egenskaper. Når tilslag med både magnetkis og svovelkis kommer i kontakt med vann, dannes det en elektrolytt som fører til oksidasjon av begge mineralene. Alunskiferutvalget (1943-1973) viste eksperimentelt at den kjemiske sammensetningen til elektrolytten påvirket både strømstyrke og polaritet (Bastiansen mfl. 1957). Svovelkis representerer den positive polen i både sure og basiske løsninger i oksiderende miljø. *Oksidasjonshastigheten og dannelse av sekundære jernsulfat er størst ved høy pH tilsvarende porevann i sementpasta. Utvalget fant at den skadelige effekten på betong er knyttet til forvitringsreaksjoner,* og konkluderte med at kun små mengder av svært reaktive magnetkis (x = 0,125) som ofte forekommer i alunskifer fører til katalytisk oksidasjon av svovelkis ved en elektrokjemisk prosess. *«Det som atskiller alunskiferen fra våre øvrige svovelkisførende bergarter, er at alunskiferen har det meget mere reaktive monokline magnetkismineral og at dette bevirker ekstraordinær høy reaksjonshastighet»* (Bastiansen mfl., 1957). En bør her tilføye at sulfidene i alunskifer er mye mer finkornete og reaktive (ofte mindre enn 25µm) enn i de fleste andre norske sulfidholdige bergarter.

Forsøkene til Alunskiferutvalget understøttes av nyere arbeider. Rimstidt & Vaughan (2003) har vist at *oksidasjon av svovelkis er en katodisk reaksjon. Magnetkis oppfører seg anodisk og dette gjelder i særlig grad ikke-støkiometriske monokline varianter* (Natarjan mfl. 1983, Bhatti 1993). Magnetkis i galvanisk kontakt med svovelkis representerer et elektrokjemisk system som leder til ekstraordinær reaksjonshastighet. Magnetkis bør dermed betraktes som en *offeranode*. Dette er tydelig tilfelle i en del alunskifere med både magnetkis og svovelkis. Moslemi mfl. (2011) viser at den elektriske potensialforskjellen mellom svovelkis og magnetkis er størst ved lav pH, men også tilstede ved høy pH. Lefticariu mfl. (2006) har vist at oksidasjon av svært finkornet svovelkis også kan katalyseres av radioaktiv stråling fra uran der vann omdannes til radikaler og sterkt oksiderende hydrogenperoksid. Det kan derfor ikke utelukkes at sulfidoksidasjon i uranrike alunskifervarianter i noen grad er påvirket av stråling.

Betongtilslaget fra Trois-Rivier i Quebec, som har ført til store bygningsmessige skader, inneholder både magnetkis og svovelkis. Petrografiske undersøkelser av skadet betong har vist at *magnetkisen er svært mye sterkere nedbrutt enn svovelkis*, og en antar derfor at magnetkisen er den viktige reaktive bestanddelen (Rodriguez 2016). Men fordi magnetkis representerer anoden (offeranode) i dette elektrokjemiske systemet *er ikke dette i seg selv grunn til å hevde at magnetkis alltid er mye mer reaktiv enn svovelkis.* Magnetkis av samme type som i Quebec er ikke nødvendigvis like skadelig i tilfeller der dette er eneste sulfid. Undersøkelser av reaktiviteten til ren magnetkis ved ulike pH betingelser viser ifølge Belzile mfl. (2004) inkonsistente resultater, mens Divet & Davy (1996) finner at ren svovelkis er mest reaktiv ved høy pH.

4 Mekaniske og kjemiske forhold som påvirker inntrengning av alkalisk porevann fra sementpastaen

Dersom det totale svovelinnholdet er relativt høyt og sulfidinnhold, mineralkornstørrelse, fordeling av sulfidmineraler i to tilslag gir like resultatet, vil tilgjengeligheten på alkalisk porevann fra sementpastaen bli avgjørende med hensyn til skadeutvikling. Ser vi bort fra at ulike sementtyper vil ha noe forskjellig porevann så vil inntrengningsdypet av porevannet være styrt av:

- styrken til tilslaget, dvs. motstanden mot mikro-oppsprekking
- løseligheten til eventuelle sekundære sulfatmineraler, samt kvarts og feltspat ved høy pH
- Absorpsjonsevne av tilslag

Et mekanisk sterkt tilslag vil ha liten grad av mikro-oppsprekking og etter alt å dømme motvirke dyp inntrenging av porevann fra sementpastaen, der sulfat og syrebidraget vil være begrenset til magnetkis og andre sulfidmineraler på tilslagets overflate. Svakere tilslag med større grad av mikro-oppsprekking vil være mer utsatt for reaksjoner med sulfidene dypere inne. Etter hvert som den opprinnelige svært basiske porevæsken trenger dypere og dypere inn i tilslaget og påtreffer flere sulfider vil pH og sulfatkonsentrasjon minke ytterligere. Potensialdifferansen og spenningsforskjellen mellom magnetkis og svovelkis vil øke ettersom elektrolytten får lavere pH. Det er derfor sannsynlig at dyp inntrenging fører til stadig høyere oksidasjonshastighet i takt med økt syredannelse.

Eventuell forekomst av sekundære løselige sulfatmineraler i tilslaget er også viktig. Ved oppløsning vil dette åpne nye mikrokanaler og økt tilgjengelighet for porevannet innover i tilslaget. På samme måte er det mulig å se for seg at mikrokanaler kan dannes ved oppløsning av mikrokvarts ved høy pH i en tidlig fase, selv om tilslaget er deklarert som ikke-alkalireaktivt (frikjennes < 20 % av tilslagskorn har mikrokvarts).

5 Betong og grenseverdier

Internt sulfatangrep knyttet til sulfidoksidasjon i betongtilslag omfatter flere mekanismer. Erfaringer fra Canada og andre land har vist at krakelering og oppsprekking ved sekundær ettringittdannelse, thaumasitt sulfatangrep og svovelsyreangrep er viktig. Ferrihydritt ($Fe(OH)_3$) og gøtheitt (FeOOH) dannes sekundært ved oksidasjon av magnetkis og svovelkis, og vil også bidra til ekspansjon i betong. Men denne effekten er relativt liten (Casanova mfl. 1996). En kan i denne sammenhengen se bort fra varmeindusert ettringittangrep ved herdetemperaturer over 70-80 grader (Delayed ettringite formation), som er uavhengig av tilslagets sammensetning.

Per dags dato er det ikke dokumentert noe tilfelle av internt sulfatangrep fra tilslag i moderne norsk betong. Mye tyder på at erfaringen fra alunskifer ligger til grunn for norsk regelverk for betongtilslag. Men også andre land synes å legge vekt på erfaringer med bergarter som ikke nødvendigvis kan benyttes for betongformål (Hawkins og St. John 2014). Chinchon-Paya mfl. (2012) hevder at 0.1 % total svovel kan være for strengt og føre til at brukbare tilslag blir forkasta (Follobanen?). Hawkins & St. John (2014) refererer til flere internasjonale erfaringer om påvirkning av sulfidførende grunnforhold på bygninger. Grenseverdiene varierer fra land til land, noe som antageligvis reflekterer forskjeller mellom bergartenes egenskaper.

6 Oppsummering

Etablering av sikrere grenseverdier for sulfidinnhold i betongtilslag må ta utgangspunkt i grundige undersøkelser av flere tilslag og representere en stor bredde med tanke på petrografisk-, mineralogiske- og mekaniske egenskaper, samt mulig innvirkning av løselige mineraler. Forskningen bør derfor fokusere på en best mulig beskrivelse av tilslagsmaterier i lys av etablerte mekanismer. Det bør legges vekt på omfattende mineralidentifikasjon (XRD, SEM og EPMA), undersøkelser av tekstur og mikrosprekker og mekaniske egenskaper (Los Angeles testing e.l.). Mørtelprismeforsøk eller funksjonsprøving må baseres på et representativt utvalg av fullt dokumenterte tilslag og suppleres med petrografiske undersøkelser og SEM/EPMA for å påvise skademekanismene i prismene, som må sammenlignes med skademekanismer i konstruksjonsbetong. Forskjeller mellom magnetkis og svovelkis i kombinasjon med andre sulfidmineraler er svært viktig.

Resultatene fra forskningsprosjektet vil gi grunnlag for gjennomgang og etablering av nye grenseverdier. Nye testmetoder og grenseverdier vil sannsynligvis baseres på analyser av totalt svovel, men justert for ekspansjon og et minimum av «strategisk» petrografisk/mineralogisk dokumentasjon. Målet er å oppnå en sikker håndtering for optimal økonomisk og miljømessig utnyttelse av lokale tilslag.

APPENDIX 3

Literature review: Chapter 2 from the PhD-thesis:

Andreia de Almeida Rodrigues (2016): “Concrete deterioration due to sulphide-bearing aggregates”. PhD thesis at Université Laval, Québec, Canada.

Chapter 2
Literature review

This chapter covers the available information on the iron sulfides, the mechanisms that lead to their oxidation and the associated deterioration process when they are used as concrete aggregates, as well as the resulting deterioration products.

This chapter also presents a summary of the major documented cases of damaged concrete structures involving iron sulfides, as well as the results of laboratory investigations involving the oxidation of iron sulfides when used as concrete aggregates.

2.1 The iron sulfide minerals

The iron sulfides are among the most abundant metallic minerals found in nature. They are distributed in all types of rocks from sedimentary to magmatic, and they are commonly present in most sulfide ore deposits. The following sections will focus on the main iron sulfides identified in the rocks from the Maskimo and B&B quarries (Saint-Boniface, Québec, Canada) in previous analyses, i.e. pyrrhotite, pyrite, chalcopyrite and pentlandite (as veins in the pyrrhotite).

2.1.1 Pyrrhotite

Pyrrhotite is one of the most common iron sulfide minerals in nature. Mostly found with pentlandite 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., 2000; Belzile et al., 2004). In hand sample, this mineral has a metallic luster and bronze brown, yellow or reddish color. Microscopically, pyrrhotite is a mineral with a pink cream or skin color (Deer et al., 2000).

Pyrrhotite has a non-stoichiometric chemical formula ($Fe_{1-x}S$), with x ranging from 0 (FeS) to 0.125 (Fe_7S_8) (Deer et al., 2000; Thomas et al., 2001; Mikhlin et al., 2002; Belzile et al., 2004; De Villiers and Liles, 2010) or 0 to 0.17 (Korbel and Novák, 2000), or 0 to 0.2 (Berry et al., 1983). Fe_4S_5 is a variant of the formula FeS (troilite), containing often a small percentage of nickel and cobalt, silver or even gold (Buttgenbach, 1953). The formula for pyrrhotite can also be expressed as $Fe_{n-1}S_n$ with $n > 8$, thus giving structures from Fe_7S_8 (monoclinic pyrrhotite) to $Fe_{11}S_{12}$ (hexagonal pyrrhotite). Its non-stoichiometry composition is a system of ordered vacancies within the Fe lattice (Thomas et al., 2001; Belzile et al., 2004). Depending on their chemical composition, it can crystallize in the monoclinic (pseudo-hexagonal) or hexagonal systems. The least Fe-deficient forms have hexagonal structures, whereas those with greater iron deficiencies have monoclinic symmetry (Janzen et al., 2000; Thomas et al., 2001). Pyrrhotite has a variable magnetic power, depending on the number of Fe vacancies in the crystal structure.

2.1.2 Pyrite

Pyrite is the most common iron sulfide mineral in nature, as it is present in magmatic, metamorphic and sedimentary rocks. Normally, pyrite can be found in large masses or veins of hydrothermal origin, in the form of both primary and secondary mineral. In hand sample, this mineral has a metallic luster and pale yellow tin color. Microscopically, pyrite is an isotropic mineral with a yellowish-white color in reflected light (Deer et al., 2000).

With the chemical formula FeS_2, composed by 46.6% in Fe and 53.5% in S, pyrite can also have, in its composition, arsenic, antimony, copper, nickel, cobalt, thallium, silver and gold traces. Pyrite may be well crystallized in the form of cubes, octahedrons and dodecahedrons, but frequently is in the framboidal form or as polyframboïds.

2.1.3 Chalcopyrite

Chalcopyrite occurs in all types of rocks. In hand samples, chalcopyrite has a yellow tin color, a metallic luster, and is often superficially altered and iridescent. Microscopically, chalcopyrite is slightly anisotropic with a yellowish-tin color, the chalcopyrite's yellow being brighter than the pyrite’s yellow (Deer et al., 2000). The general chemical formula is $CuFeS_2$, with 35% in Cu, 30% in Fe and 35% in S. The crystallographic system of chalcopyrite is tetragonal.

2.1.4 Pentlandite

Pentlandite is commonly associated with other sulfide minerals, such as pyrite, chalcopyrite and pyrrhotite, in basic igneous rock intrusions. With the chemical formula $(FeNi)_9S_8$, pentlandite resembles pyrrhotite, but is slightly paler. Microscopically, it presents a pale creamy yellowish color and is isotropic in reflected light (Deer et al., 2000). According to

Pearson and Buerger (1956), pentlandite crystallizes in the isometric hexo-octahedral system.

2.2 Iron sulfides oxidation reaction/process

2.2.1 Pyrrhotite oxidation reaction

There are not many studies that explain the factors responsible for the pyrrhotite oxidation. Some authors say that the mechanism is similar to that of pyrite oxidation, mechanism that will be discussed in the next section. The existing studies were mainly carried out in the acid rock drainage context (ARD), which is by far different from the pyrrhotite oxidation process occurring in concrete. In ARD, the pH is like the name says, i.e. “acid”, while the pH in concrete is highly basic, normally higher than 12.5.

The oxidation of pyrrhotite is highlighted in the following reaction (1) (Janzen et al., 2000; Mikhlin et al., 2002; Belzile et al., 2004), being oxygen and water necessary for the oxidation reaction to occur:

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

2.2.2 Pyrite oxidation reaction

Pyrite-bearing rocks are increasingly being used for concrete aggregates, because of the decreasing supply of materials with good geological conditions (Wakizaka et al., 2001).

The pyrite oxidation reaction has been described in several studies. This reaction, such as pyrrhotite oxidation reaction, needs water and oxygen to occur (Divet and Davy, 1996; Divet, 2001). According to Divet and Davy (1996), pyrite reacts with oxygen and moisture according to the following reaction (2):

$$FeS_2 + 15/4\ O_2 + 5/2\ H_2O \rightarrow FeOOH\ \text{(goethite)} + 2H_2SO_4\ \text{(sulfuric acid)} \qquad \text{(reaction 2)}$$

Due to the pyrrhotite and pyrite oxidation process, new products are formed: ferrihydrite ($Fe^{3+}{}_2O_3.1/2(H_2O)$), jarosite ($KFe^{3+}{}_3(OH)_6(SO_4)_2$), limonite ($FeO(OH).nH_2O$ and goethite ($FeOOH$) (Belzile et al., 2004; Duchesne, 2010).

2.3 Deterioration process of concrete incorporating sulfide-bearing aggregates

As mentioned before, iron sulfides have the tendency to be unstable in the presence of oxygen and water. The iron sulfide oxidation-reaction mostly studied in concrete is the pyrite oxidation (reaction 2).

When this oxidation reaction occurs in concrete aggregates, the sulfuric acid thus produced (reaction 2) lowers the pH, but the reduction will be limited by the buffering effect of portlandite, through reaction (3).

$Ca(OH)_2 + 2H^+ \leftrightarrow Ca^{++} + 2H_2O$ (reaction 3)

If the reaction (2) occurs in hardened concrete, the sulfuric acid reacts with the portlandite ($Ca(OH)_2$), which is a product of the hydration of Portland cement, and *gypsum* is formed according to reaction (4).

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

The gypsum then reacts with the aluminate phases in Portland cement concrete (anhydrous or hydrated), thus leading to the formation of potentially expansive secondary *ettringite* (reaction 5) (Tagnit-Hamou et al., 2005).

$3CaO\cdot Al_2O_3 + 3CaSO_4\cdot 2H_2O + 26H_2O \rightarrow 3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O$ (*ettringite*)

(reaction 5)

If a source of carbonate (CO_3^{2-}) is available in the system (aggregate, cement or other) *thaumasite* can be formed (reaction 6) (Thomas et al., 2003)

$2CaCO_3+2SiO_2\cdot H_2O+2(CaSO_4\cdot 2H_2O)+2Ca(OH)_2+23H_2O\rightarrow 2(CaSiO_3\cdot CaCO_3\cdot CaSO_4\cdot 15H_2O)$

(*Thaumasite*) (reaction 6)

The chain of reactions generated after the iron sulfides oxidation in the concrete can thus lead to a deleterious *sulfate attack* (Casanova el al., 1996), like it is observed in the reactions (4), (5) and (6). The extent of the sulfate attack of the paste is controlled by the composition and size of the aggregate particles, the kinetics of sulfide oxidation, the composition of the cement and the mix proportioning of concrete (Casanova el al., 1996).

Besides the above reactions/process, goethite (Moum and Rosenqvisq, 1959; Chinchón et al., 1990; Mikhlin et al., 2002), all kind of “rust” as limonite ($FeO (OH) nH_2O$), ferrihydrite ($Fe^{3+}{}_2O_3 \cdot 1/2(H_2O)$), iron hydroxides Fe(OH)2 [(Moum and Rosenqvisq, 1959, Bérard et al., 1975, Bérubé et al., 1986; Chinchón et al., 1990 Mikhlin et al., 2002)] can also be formed through the deleterious oxidation reaction of pyrite.

Many of the minerals identified as final products of the iron sulfide weathering have relatively large molar volumes (or at least, larger than the precursors) and, consequently, their formation is a source for expansive phenomena (Casanova et al., 1996).

The exterior signs of deterioration in concrete structures/elements affected by the sulfide oxidation are staining, spalling and pop-out formation (Seaton, 1948; Mielenz, 1963; Bérard et al., 1975), microcracking (Wakizaka et al., 2001) and map cracking (Bérard et al., 1975; Oberholster and Krüger, 1984; Oberholster et al., 1984; Vasquez and Toral, 1984; Chinchón et al., 1989 and 1990, 1995; Ayora et al., 1998).

2.4 Significant factors in the iron sulfides oxidation process

In addition to water and oxygen (Knipe et al., 1995; Longworth, 2003; Divet and Davy, 1996; Divet, 2001), some authors have described other factors involved in the iron sulfides oxidation process, notably their influence on the reactions kinetic. From the available literature, the bacteria’s presence (Bérard, 1970; Bérard et al., 1975; Pye and Miller, 1990; Belzile et al., 2004), the crystal structure (Janzen et al., 2000; Lehmann et al., 2000; Gerson and Jasieniak, 2008), morphology (Divet and Davy, 1996; Divet, 2001) and specific surface area of the iron sulfide mineral (Divet and Davy, 1996; Janzen et al., 2000), temperature (Divet and Davy, 1996; Steger, 1982), the pH of the system (Divet and Davy, 1996; Casanova et al., 1996; Casanova et al., 1997), and the galvanic interactions play also a role in the sulfides oxidation reaction.

2.4.1 Oxygen and water

As observed in the reactions presented in the previous sections, oxygen and water are essential to the sulfide oxidation reaction development. In the study carried out by Steger (1982), about the oxidation of sulfide minerals, the author concluded that the oxidation rate increases directly with increasing relative humidity. In 1995, Knipe and coworkers studied the interactions between pyrite and pyrrhotite and water vapour. They concluded that the oxygen is the primary oxidant, and when the iron sulfides are exposed to deoxygenated water, they do not oxidize. Divet and Davy (1996) concluded that the rate of pyrite oxidation decreases with the decrease of the dissolved oxygen concentration.

2.4.2 Bacteria's presence

Some studies suggested that the oxidation of pyrite and pyrrhotite can be promoted and catalyzed by the *Thiobacillus ferrooxidans* bacteria (Quigley and Vogan, 1970; Penner et al., 1973; Pye and Miller, 1990; Belzile et al., 2004; Suzuki el al., 1992; Chan and Suzuki, 1993; Suzuki, 1999). These organisms are widely used in the mining industry to recover metals from sulfide ores, especially from the more stable minerals like chalcopyrite and sphalerite (Bérard, 1970). These bacteria develop at low pH (Bérard et al., 1975), in a range 1.0-2.5, deriving their energy from redox reactions where Fe^{2+} or reduced sulfur compounds serve as electron donor and oxygen as electron acceptor. Thiobacilli are most active in temperatures ranging from 20 to 55°C and T. ferrooxidans is the dominant organism at temperatures below 40°C (Belzile et al., 2004).

In the case of pyrite and pyrrhotite as components of concrete aggregates, the contribution of these bacteria to those iron sulfides oxidation seems to be unlikely. The action of bacteria (thiobacillus) is not considered probable in an environment with such high pH conditions found in concrete (Bérard et al., 1975). The pH of the concrete pore solution is higher than 12.5, while the optimal conditions for the thiobacillus development and proliferation are, as mentioned before, acidic.

2.4.3 Crystal structure

As previously mentioned, pyrrhotite has a non-stoichiometric composition, ($Fe_{1-x}S$), with x ranging from 0 (FeS) to 0.125 (Fe_7S_8), that is responsible for different crystal structure that varies from pure hexagonal to pure monoclinic (Janzen et al., 2000). There is a scarcity of detailed studies on the effect of different crystal structures of pyrrhotite on the oxidation rates (Janzen et al., 2000), and the existing studies are somewhat contradictory. While Orlova et al. (1988) (in Janzen et al., 2000) noted that hexagonal pyrrhotite is more reactive than monoclinic pyrrhotite, Vanyukov and Razumovskaya (1979) (in Janzen et al., 2000) suggested the opposite. Lehmann and coworkers (2000) developed a study to compare the dissolution of hexagonal and monoclinic pyrrhotites in cyanide solution. They concluded that rate of dissolution of the monoclinic pyrrhotite under the variety of conditions evaluated was greater than that of the hexagonal pyrrhotite. In 2008, Gerson and Jasieniak, also showed that the oxidation rate of monoclinic pyrrhotite was greater than that of hexagonal pyrrhotite.

2.4.4 Specific surface area and morphology of the iron sulfide minerals

Fractures and roughness increase the iron sulfides surface area and consequently the oxidation reaction, because more surface is exposed to moisture and oxygen (Divet and Davy, 1996; Janzen et al., 2000). Pyrite, as it was mentioned before, can crystallize in the form of cubes, octahedron and dodecahedron, but frequently is in the framboidal form or as polyframboïdes.

The iron sulfide morphology can influence the oxidation reaction. In 1996, Divet and Davy studied the oxidation reaction of framboidal and massive pyrite. They concluded that the framboidal pyrite reacts more rapidly (oxidation) than the massive pyrite. The framboidal pyrite shows difficulties in developing active/reaction sites, but the later grow faster. However, the massive pyrite is attacked in numerous locations, but the velocity at which the phenomenon occurs is relatively slow. These observations are true only when the mineral size is superior to 20 μm.

2.4.5 Temperature

According to Steger (1982), Divet and Davy (1996) and Lehmann et al (2000), there is a significant increase in the oxidation rate with increasing temperature. According to Steger (1982), at a constant relative humidity, the temperature will enhance the rate of O_2 diffusion and therefore the formation of ferric oxide (as well as the SO_4^{2-} products). This relation follows the Arrhenius Law. Janzen et al. (2000) studied the oxidation of pyrrhotite at different temperatures (25°C, 35°C and 45°C), and have shown that the rate of oxidation increased with increasing temperature. Lehmann and coworkers (2000) studied the dissolution of both monoclinic and hexagonal forms of pyrrhotite and concluded that, in both cases, the dissolution increases with the increase of temperature.

2.4.6 pH system

One of the studies proving that the pH has a strong influence on the sulfides oxidation process was carried out by Divet and Davy (1996). According to the authors, the parameter that plays the major role in the pyrite's oxidation is the high OH^- ion concentration in the alkaline pore solution of concrete. For a pH greater than 12.5, the oxidation rate increases exponentially and reaches about 50 times its initial value at a pH of 13.7.

The pH can also play a significant role in the reactions that occur after the oxidation reaction starts and that are responsible for the production of secondary deterioration products. When the sulfate and hydrogen ions are released into the pore solution, they will react with the paste components (especially tricalcium aluminate and/or portlandite) to form, as mentioned before, expansive phases such as *gypsum* (reaction 4), monosulfoaluminate and eventually *ettringite* (reaction 5). The predominance of one or the other reaction will be controlled by the pH (Casanova et al., 1996, 1997). The formation of gypsum is preferentially occurring at $pH<10.5$, ettringite will be favoured at $10.5<pH>11.5$, calcium aluminate monosulfate at $pH>11.5$ (Casanova et al., 1996) while a pH greater than 10.5 is ideal for thaumasite formation.

2.4.7 Galvanic interactions between contacting/adjacent sulfide minerals

Several studies indicate that the combined presence of different sulfide minerals is responsible for accelerating the oxidation reaction (Moum and Rosenqvist, 1959; Shuey, 1975; Eglington, 1987; Ekmekçi and Demirel, 1997; Atak et al, 1998; Kwong et al., 2003; Becker, 2009; Azizi et al., 2010, 2011).

Most of metal sulfides are semi-conductors, each characterized by a *rest potential*, which can vary as a function of the sulfide's detailed composition (Shuey, 1975). The rest potential or open circuit potential, is the equilibrium potential of the mineral at zero electric current (Becker, 2009). The ease with which the different sulfide minerals are prone to oxidation can be determined by comparing their rest potential (Becker, 2009). The rest potentials of a few common sulfide minerals measured in 1.0 M H_2SO_4 at room temperature (20–25°C) are given in Table 2.1. Pyrite is the sulfide mineral with the highest rest potential (V vs. SHE: Standard hydrogen electrode/Volt), thus more stable, while pyrrhotite shows the lowest rest potential and is consequently the most unstable sulfide mineral. In nature, in the presence of an electrolyte, two adjacent sulfides with different rest potentials form a galvanic cell. The sulfide with the highest rest potential becomes the cathode and that with the lowest rest potential, the anode (Kwong et al., 2003).

Table 2.1: Rest potential of some sulfide minerals (adapted from Kwong et al., 2003)

Mineral	**Formula**	**Rest Potential (V vs. SHE)***	**References**
Pyrite	FeS_2	0.63	Biegler and Swift 1979
Chalcopyrite	$CuFeS_2$	0.52	Warren 1978
Chalcocite	Cu_2S	0.44	Chizhikov and Kovylina 1956
Covellite	CuS	0.42	Majima 1969
Galena	PbS	0.28	Chizhikov and Kovylina 1956
Sphalerite	ZnS	-0.24	Chiz-hikov and Kovylina 1956
Pyrrhotite	$Fe_{(1-x)}S$	-0.28	Chizhikov and Kovylina 1956

* Standard hydrogen electrode/Volt

In an oxygenated system, a generalized anodic reaction involving a bivalent metal sulfide (MS) can be represented by Equation 1 (Kwong et al., 2003):

$$MS = M^{2+} + S^o + 2e^- \text{ (Equation 1)}$$

The cathodic reaction, however, relates to the discharge of oxygen adsorbed on the surface of the cathode sulfide, as shown in Equation 2:

$$0.5O_2 + 2H^+ + 2e^- = H_2O \text{ (Equation 2)}$$

In other words, oxidative dissolution of the sulfide with a lower rest potential occurs at the anode while the sulfide with a higher electrode potential is protected from oxidation at the cathode. The overall galvanic reaction characterized by a mixed potential is thus given by:

$$MS + 0.5O_2 + 2H^+ = M^{2+} + S^o + H_2O \text{ (Equation 3)}$$

In the natural environment, the elemental sulfur produced is subsequently converted to sulfate. In addition to the absolute difference in rest potential between two contacting sulfides, the relative surface areas of the galvanic couple greatly affect the rate of oxidative dissolution of the anode sulfide because of the resultant current density generated. The larger the anodic area, the more widely distributed is the current generated by the galvanic cell. The low current density results in a slow dissolution of the anode sulfide (Kwong et al., 2003). For example, if pyrite and pyrrhotite coexist, the pyrite will be the cathode and pyrrhotite will be the anode, so the pyrrhotite will be the one that will be oxidized.

2.5 Deterioration products resulting from an internal sulfate attack due to sulfide-bearing aggregates

As mentioned elsewhere, the oxidation of iron sulfides in concrete can lead initially to the formation of iron oxyhydroxides and, at posteriori, to an internal sulfate attack with formation of different kinds of sulfate minerals such as gypsum, ettringite and thaumasite. These secondary products are normally considered, as well as the secondary products resulting from the iron sulfides oxidation reaction, expansive. Besides expansion, some can also lead to concrete disintegration. These sulfate minerals occur in different conditions of temperature, humidity, and pH solution. In the next sections, the essential conditions to the formation of these sulfates will be presented.

2.5.1 Gypsum

Gypsum is a calcium sulfate dihydrate ($CaSO_4.2(H_2O)$). In concrete, gypsum can occur as a constituting mineral in the aggregate material, as additive in the cement or as secondary product resulting from sulfate attack.

When sulfate and hydrogen ions are released into the pore solution, they will react with the paste components (especially tricalcium aluminate (C_3A) and/or portlandite) and will form additional expansive phases such as gypsum. Normally, the formation of gypsum occurs at a pH lower than 10.5 (Casanova et al., 1996).

The exact nature of disruption in concrete caused by gypsum formation is not well established (Tian and Cohen, 2000; Santhanam et al., 2003). Softening of the concrete surface (Cohen and Mather, 1991), rather than expansion (Tian and Cohen, 2000, Neville and Brooks, 2010), has been attributed to the effect of gypsum formation.

2.5.2 Ettringite

Ettringite ($3CaO.Al_2O_3.3CaSO_4.32H_2O$) is an hydrous calcium trisulfoaluminate. It is produced, in concrete, by a reaction that requires excess of sulfate ions SO_4^{2-} over the aluminate phase in the pore solution (St John et al., 1998). The source of sulfate ions in excess can be either the cement or other constituents of the concrete (Brown and Taylor, 1999), such as the result of the oxidation process of pyrite and/or pyrrhotite present in the aggregates (Divet, 2001; Moum and Rosenqvist, 1959; Chinchón et al., 1989, 1990, 1995; Bérard et al., 1975), late release of sulfates from the clinker, dissolution and re-precipitation of ettringite resulting from normal hydration of cement.

In concrete, ettringite can be formed in two different stages, and the consequences of that formation are completely different (Divet, 2001). Ettringite is generally formed during the early stages of the hydration of Portland cement in a plastic fresh mixture. In this case, it is called early ettringite formation and does not produce any damaging expansion (Collepardi, 2003). When ettringite occurs at later ages and is related with *heterogeneous* cement paste expansion that can result in excessive cracking and spalling of the hardened concrete, it is called delayed ettringite formation (DEF). This form of internal sulfate attack is generally related to excessive thermal effects during the early stages of the concrete hardening process.

2.5.3 Thaumasite

Thaumasite ($CaSiO_3.CaCO_3.CaSO_4.15H_2O$) is a complex mineral that contains different anions in its composition: carbonate (CO_3^{2-}), sulfate (SO_4^{2-}) and silicate as $Si(OH)_6^{2-}$. These three anions are associated with the Ca^{2+} cation (Edge and Taylor, 1971).

The internal sulfate attack resulting in thaumasite formation (TSA) has been rarely described in the literature before the 2000's. This is probably due to the fact that the deteriorated concrete is not often subjected to a detailed petrographic examination and also due to the similar appearance of ettringite and thaumasite (needle-like shape) that in many cases can lead to an erroneous identification. The TSA is potentially more severe than the attack resulting from the gypsum and ettringite formation. In the case of thaumasite formation, the C-S-H phase of the concrete is deleteriously affected, leading to a complete loss of integrity and strength (TEG report, 1999; Chinchón-Payá, 2013).

Conditions normally considered necessary for the formation of the thaumasite are: low temperature (≈ < 15ºC; the ideal temperature being about 4°C (Crammond, 1985)), constant humidity, a source of carbonate ions, a source of sulfate and a pH greater than 10.5 (Collett et al., 2004; TEG Repport, 1999; Köhler et al., 2006; Thomas et al., 2003; Zhou et al., 2006; Newman and Choo, 2003; Skalny et al., 2003).

Even though the majority of the reported cases of thaumasite formation usually occurred under low temperature conditions, some studies and cases studies showed that there are some exceptions. In recent years, cases of TSA have been reported in locations where the average temperatures are above 15°C. In 2011, Torres et al. presented a TSA case that took place in Campina Grande (Brazil), a city where the lowest temperature recorded during the winter was over 20°C. The affected element was a concrete beam used as a top structure of an earth retaining limestone wall. The beam began to show significant signs of deterioration three years after construction.

Another case of thaumasite formation at temperatures exceeding 15°C was reported by Sahu and coworkers in 2003 for residential concrete slabs in Southern California.

In 2011, Day and Middendorf have observed thaumasite formation in the laboratory at room temperature (~ 20°C). Various mortar mixes were cast and subjected to a 0.35 M sodium sulfate solution (in accordance with the test methods CSA A3004-C8/ASTM C1012 for sulfate resistance), with a continuous soaking at room temperature (~ 20°C) or at -5° C in a refrigerator. In both cases (~ 20 and ~ 5°C), thaumasite was formed.

A study by Schmidt and colleagues in 2008 demonstrates thaumasite formation both at 8°C and 20°C. The amount of thaumasite formed at 20°C was however found to be lower than at 8°C, mainly due to the increased solubility of the thaumasite with increasing temperature.

Crammond (1985) and TEG report (1999) state that a constantly high humidity is needed for thaumasite formation. This condition seems obvious considering that thaumasite has 15 moles of H_2O in its composition.

The carbonate ions generally originate from carbonate aggregates (limestone, dolomite, etc.). However, some studies reported thaumasite to form in concrete and mortar specimens incorporating a siliceous aggregate. When analyzed in detail, it was concluded that the source of carbonate material for thaumasite formation was the atmospheric CO_2 (Thomas et al., 2003; Collett et al., 2004). Another source of carbonate ions can be the CO_2^{-3} from seawater or the carbonate material used in the manufacture of Portland limestone cements.

The source of sulfate ions is generally considered to be external, usually derived from the groundwater, where it can be associated with a number of different cations, particularly magnesium, calcium and sodium (or a combination of these). Collet and colleagues (2004) reported a case where sulfates originated from sulfate minerals present in bricks, while sulfates could also be derived from the iron sulfides (pyrite and pyrrhotite) existing in concrete aggregates.

According to the report TEG (1999), thaumasite formation is favorable at a pH of 10.5. In 2003, Jallad and colleagues tested the thaumasite formation at pH between 6 and 12 and its stability at pH greater than 12. At pH 6, small amounts of thaumasite were formed. At pH levels of 7 and 8, thaumasite and aragonite were observed and at pH levels of 12 only thaumasite was formed. The same study demonstrated that thaumasite is stable at pH = 13. At pH levels lower than 11, thaumasite reacts with the ions in solution and part is converted to calcium phosphate, calcium silicate and calcium carbonate.

2.6 Major documented cases of damaged concrete structures involving iron sulfides

There are some studies reported in the literature relating damage in concrete structures to the presence of iron sulfides aggregate or granular base materials (Moum and Rosenqvist, 1959; Hagelia et al., 2003, Hagelia and Sibbick, 2009; Pardal, 1975; Vasquez and Toral, 1984; Oberholster et al., 1984; Oberholster and Krüger, 1984; Chinchón et al., 1989; 1990 and 1995; DEC, 1991; Lugg and Probert, 1996; Schmidt et al., 2011). These "problematic" iron sulfides can be part of the concrete aggregates (Shayan, 1988) or of the bedrock foundations (Quigley and Vogan, 1970; Penner et al., 1973; Grattan-Bellew and Eden, 1975; Grattan-Bellew and and McRostie, 1982).

2.6.1 Oslo, Norway (Moum and Rosenqvist, 1959; Hagelia et al., 2003)

In the Oslo region of Norway, problems of concrete deterioration and foundation heaving seemed to be related to the presence of slightly metamorphosed shales containing pyrrhotite ($FeS_{1.14}$). In some cases, the concrete structures were transformed into mush after only 9 months.

After World War II, a semi-official "Alum Shale Committee" was set up in Oslo, and the Norwegian Geotechnical Institute was requested to look into the chemical, physical, and mineralogical phases of the problem. This committee started its investigations in a closed tunnel, the Blindtarmen tunnel, where water (with a low pH, sometimes 2.5) entering through the destroyed lining comes directly from one of the most aggressive zones in the alum shale. The tunnel was partially filled with water, with the water level varying somewhat according to precipitation and had air circulation. The water in the upper part was oxidized whereas, in the deeper part, had a low pH. The *Alum Shale Committee* placed some concrete prisms deep below the low-water level (been constantly submerged), and some between the low-water levels (exposed to fluctuation of the ground water level). After 3 to 4 years, the prisms left above the low-water level still had sharp edges and fairly good mechanical properties; however, those left deep in the tunnel were mostly destroyed, except those containing sulfate resistant cement. The "upper" specimens were covered by a brown layer of rust. In the bottom specimens, large amounts of white pulverized material were observed. Petrographic examination showed that the product was mainly *ettringite*. The authors concluded that the deleterious mechanism responsible for the deterioration was a combination of two types of attacks, a typical sulfate attack with production of *ettringite* and an acid attack. In 2001, Hagelia and coworkers (Hagelia et al., 2003; Hagelia and Sibbick, 2009), examining the descriptions of the attack proposed by Moum and Rosenqvist (1959), argued that the deterioration mechanism must represent a severe case of *thaumasite* sulfate attack (TSA). In order to prove their theory, the authors recuperated the samples left in the tunnel since 1959. XRD and petrographic analyses were carried out and it was concluded that the material that Moum and Rosenqvist (1959) identified as *ettringite* was actually *thaumasite*.

2.6.2 Ottawa, Canada (Quigley and Vogan, 1970)

In this case, Quigley and Vogan (1970) studied the processes involving the heaving of structures sitting directly on pyrite-bearing dark-grey/black shale bedrock.

A lightly loaded building founded directly on drained black shale presented three inches (7.6 cm) of differential heaving over a 20-year period, thus causing severe structural deformations. The heaving was attributed to the oxidation of disseminated iron sulfides in the shale by autotrophic bacteria (*Thiobacillus ferrooxidans* and *Ferrobacillus ferrooxidans*) to produce secondary hydrous sulfates of greater volume. To study the case, logging of a core from the rock foundation, X-ray diffraction on the rock and chemical and bacterial analyses of the water from old boreholes were carried out. The logging showed bands of orange oxidized silty shale and soil like material filling the bedding plane cleavages, and soft white gypsum crystals. Microscopic examinations showed abundant autotrophic bacteria of the *Thiobacillus ferrooxidans* and *Ferrobacillus ferrooxidans* types.

There seem to be two possible heaving mechanisms at the site: 1) hydration and expansion of swelling clay complexes, and 2) geochemical alteration of sulfides to produce secondary sulfates and heaving resulting from pressures of crystallization.

The amount of secondary gypsum that broke apart the bedding plane cleavages in the core is believed to correspond roughly to the magnitude of heaving, which is about 3 in. (7.6 cm).

It is hypothesized, therefore, that the bacteria have oxidized or catalyzed the oxidation of pyrite in the shale, thus producing sulfuric acid. This sulfuric acid then slowly dissolved calcite disseminated in the shale and in the rock cleavages, thus altering into gypsum. The gypsum has migrated through solution, eventually precipitating out as the flat crystals observed in the horizontal and inclined cleavage openings.

2.6.3 Ottawa, Canada (Penner et al., 1973)

At the end of 1969, Penner and coworkers started an investigation on the mechanism responsible for the heaving of the basement floor of a three-storey extension of the Bell Canada Building in Ottawa, founded on shale. The study was initiated when the displacement of the basement floor interfered seriously with the alignment and operation of the power and switching facilities located in this area.

The original building was constructed in 1929, and an extension was added in 1961, with all the corresponding floors located at the same elevation. Heaving of the basement floor in the extension was noticed about 4 years after the addition was completed. The affected area appeared as two rounded domes.

The object of the investigation was to establish the cause of heave and to initiate remedial measures for controlling the heave until the equipment could be relocated.

The building is founded on the Billings formation, a black pyritic, calcareous and fissile shale. The shale formation is about 6m thick at this location and lies conformably on interbedded limestones and shales of the Eastview formation. A minor fault, which appeared to have a strike in the direction of the heaving areas, was observed in an excavation immediately south of the Bell building. This fault was also uncovered during the excavation of the examination pits below the floor slab of the Bell Canada building.

The 30 cm thick reinforced concrete floor slab was placed on a 15 cm layer of crushed limestone. This levelling course, which also contained an under floor drainage tile system, had been placed directly on the shale, at about 1.5 m below the original shale level.

The maximum measured floor displacement was 5.6 cm over a period of about 32 months, which corresponds to a heave rate of approximately 0.18 cm per month. Based on the estimated floor elevation immediately after construction, the maximum total movement was 10.7 cm.

The authors tried to core the affected zone, but the recovery by drilling was poor, so that examination pits were excavated in three locations within the problematic area. The top 40 to 50 cm of shale were extremely soft and crumbly and could be removed with a hand shovel; below that, excavation was carried out with the aid of a jack hammer. Joint surfaces and shale laminae in the altered zone (top 0.5 to 1 m) were covered with a yellowish brown coating and numerous colourless crystals. The altered zone was found to be acidic and, based on numerous measurements, the pH ranged from 2.8 to 4.4. Below about 1 m, the shale appeared to be sound.

The mineralogical investigations carried out on the reaction products of the altered shale confirmed the presence of gypsum and jarosite. The mineralogical investigation of the unaltered shale showed: pyrite, calcite, ilite and quartz; no gypsum or jarosite were observed. The X-ray diffraction analysis that identified the presence of pyrite was unable to determine if other iron sulfides were present.

The existence of extensive pyrite intrusions and general pyritic content in the unaltered shale zone, the type of alterations products identified in the altered zone and the acid conditions in the altered zone, suggested that autotrophic bacteria were probably involved in the weathering and heaving process. The energy for growth and proliferation of autotrophes is obtained by the oxidation of inorganic compounds in the presence of atmospheric oxygen. The autotrophic bacteria that is believed to be responsible of the oxidation is the *Ferrobacillus-Thiobacillus.*

As the shale is calcareous, the formation of gypsum is derived from the neutralization process between the excess sulfuric acid and calcite. Jarosite, also a main reaction product in the altered zone, forms most readily under acid conditions, as found in the altered zone. The potassium content of jarosite is thought to come from the degradation of clay minerals and/or by base exchange reactions in the highly acid environment.

The above reactions caused heaving because the molar volumes of the unaltered components are less than the reaction products. The volume increase from pyrite to jarosite is 115%, and from calcite to gypsum 103%. It is also very apparent that the weathered products formed between the shale laminae, although in the rotted material, gypsum and jarosite were found to exist inside the pores of the laminae.

A remedial treatment had to be implemented to stop the heave. The authors suggested the creation of unfavourable conditions for the growth of the bacteria by neutralizing the acid conditions in the altered zone with a base and by reducing the air circulation by saturation with water. The decision was, therefore, to keep the treatment concentration below 0.1 N KOH although the exact nature of the dimensional changes resulting from treatment was not well understood.

After about 3 months of treatment, the acid conditions in the shale had been greatly reduced and the cracks were well impregnated with KOH solution although the acidic pH's still persisted near the surface. In the following months, there was a great improvement in the pH in the observation wells and the decision was made to discontinue the KOH treatment but continue to supply water to keep the water table as high as possible and maintain wet conditions beneath the slab. In the period following the start of treatment, floor movements have been controlled satisfactorily.

2.6.4 Barcelona, Spain (Pardal, 1975; Vasquez and Toral, 1984; Chinchón et al., 1989, 1990 and 1995)

Since 1970 (Vasquez and Toral, 1984), studies have been carried out on cases of deterioration of concrete incorporating pyrite-rich aggregates in the Maresme region, near Barcelona (Spain) (Chinchón et al, 1989, 1995). The affected structures consist of public buildings, houses, overpasses and dams. In 1975, more than 30 cases were reported (Pardal, 1975). In all cases, the deterioration started with expansion with resulting cracking leading to the structures destruction (Vasquez and Toral, 1984; Chinchón et al, 1989, 1990). In some cases, where the deterioration was less important, the structures presented large brown spots (Vasquez and Toral, 1984). All the affected concretes contained aggregates from the Mont Palau quarry. These aggregates basically consist of limestones and phyllites, with high content of iron sulfide minerals, mainly pyrite and pyrrhotite (Chinchón at al., 1989, 1990, 1995). The hexagonal pyrrhotite occurs disseminated in the aggregates and the pyrite, formed from the sulfurization of pyrrhotite in “bird eyes” textures that affect all the pyrrhotite, occurs in fracture areas of centimetre-sized range (Chinchón et al., 1989).

In all studies of this problem, liability was associated to the oxidation of pyrite into sulfates, thus causing internal attack in concrete. This attack was the cause of the expansion responsible for cracking and ultimate destruction (Vasquez and Toral, 1984)

2.6.5 Montreal, Canada (Bérard et al., 1975)

In 1971 and 1972, similar cases of distressed concrete structures (bridges, overpasses and houses) were brought to Bérard and coworkers' attention. Some concrete blocks fell down from bridges and overpasses, thus exhibiting fragments of black shale on their surfaces, thus giving the impression that the coarse aggregate was mainly composed of argillaceous shale. All affected structures showed map cracking, pop-outs (with fragments of shale in the center), and, in some cases, iron oxide was seeping out the fractures.

Although the coarse aggregate was composed of three types of crushed rocks, diabase or gabbro, limestone and black shale, only the shale was found to be “reactive”. In the cores drilled from the structures, it was possible to observe the shale fragments surrounded by a whitish rim, 1 or 2 mm in width, of *ettringite*. The petrographic analyses of the shale showed that pyrrhotite was present in a percentage of about 4.5%.

According to the authors, the deterioration process was due to the oxidation of pyrrhotite and the formation of sulfuric acid and rusty secondary minerals, which could be limited to *Jarosite*. The sulfuric acid would then react with the calcite within the shale or with the portlandite of the hydrated cement paste to form more gypsum; the latter was believed to be the main cause of the swelling of the shale.

2.6.6 Penge, South Africa (Oberholster and Krüger, 1984; Oberholster et al., 1984)

In South Africa, damage of concrete made with sulfide-bearing aggregates was noticed. The aggregates consisted of cummingtonite slates incorporating sulfide minerals (pyrrhotite, pyrite, arsenopyrite, and chalcopyrite) and magnetite. The oxidation of iron sulfide minerals was seen in both coarse and fine aggregates. Serious cracking of houses has been encountered where sulfide–bearing aggregates from asbestos mine tailings were used in concrete bricks and floor slabs. Expansion of the concrete floor slabs has pushed the corners of houses outwards and, in some instances, lifted the external walls off the damp proof course. The expansion of concrete bricks containing the sulfide-bearing aggregate has resulted in extensive random cracking in external wall rendering. In some cases, the houses started to show signs of deterioration within two years after construction.

The examination of the concrete bricks revealed the presence of a white powdery material around the black carbonaceous aggregate. Under the SEM, the above secondary material was found to be well-crystallised hexagonal crystals containing calcium, silicon and sulfur (*thaumasite*). The XRD showed the presence of pyrrhotite and the analyses for the mineral sulfur gave a pyrrhotite (with a molar Fe/S ratio of 0.96). The pyrrhotite content in the aggregate was small as 0.5 % by mass.

2.6.7 Australia, (Shayan, 1988)

In Australia, a case of concrete deterioration due to pyritic aggregates (shale) was reported by Shayan (1988). A 10 year-old concrete hospital floor slab, about 150mm in thickness, was laid over a water proofing membrane and covered with conventional vinyl tiles. After a few years, severe blistering occurred over an extensive area of the floor, thus disrupting the vinyl tiles. The blistering was found to be caused by the oxidation of the pyrite in the aggregate particles located near the surface of the slab.

Cores were extracted and analysed by XRD, SEM/EDS and by polarizing microscope. Some affected aggregates contained large amounts of pyrite and produced a large amount of jarosite and smaller amounts of *gypsum*. Some aggregates and mortar were covered by a greenish-yellow material that consisted mainly of *jarosite* and *gypsum* and other blistered zones showed *halotrichite*. In this case, no ettringite was observed.

2.6.8 Cornwall and Devon, England (DEC, 1991; Lugg and Probert, 1996)

Between 1900 and 1950, many buildings were constructed using inferior quality concrete blocks (Lugg and Probert, 1996); the aggregate utilized was found to be at the origin of the concrete failure. The constructors, many of them being the owners of their small building firms, utilized the aggregate that was available in the area and that was cheap, sometimes even available for free. The aggregate mainly consisted of mining tailings, specifically "mundic" and "killas" rocks. "Mundic" is the local name (Cornwall) to designate sulfide-bearing rocks, commonly found in the mining wastes, which may oxidize with the formation of sulfuric acid; the latter attacks the cement paste, thereby causing loss of bond, as well as volumetric expansion. "Killas" is the local name to designate fine-grained sedimentary rocks, containing clay minerals and micas, which undergo cyclic expansions and contractions in response to changes in moisture content, thereby leading to mechanical weakening of the concrete (Lugg and Probert, 1996).

The deleterious mechanisms involving this type of concrete made with sulfide-bearing aggregates began early after construction, but it was only in the seventies that the mechanisms started to be understood.

The number of affected structures is not known exactly; however, two surveys suggested that approximately 15% of the pre-1959 concrete building stock, in Cornwall, have "mundic" degradation (Lugg and Probert, 1996). In many cases, the strength of the blocks was deteriorated to the point where the walls were structurally unsafe and some houses had to be demolished (DEC, 1991). The sections of the houses that presented the most visible signs of deterioration were the parts most exposed to moisture (DEC, 1991; Lugg and Probert, 1996). The mechanisms that was found to be responsible for this damage are: 1) the aggregate that is very susceptible to swelling and contraction due to changing moisture conditions owing to content of recrystallized clay and related minerals, and 2) oxidation of finely disseminated pyrite causing expansion and adverse resulting effects, including sulfate and acid attack on the cement paste in the concrete.

2.6.9 Lladorre, Spain (Ayora et al., 1998)

In 1998, Ayora and coworkers published cases of two dams presenting significant durability problems. During their service life, the above structures developed map cracking in some surface areas, color changes and expansion. Some cracks had a depth of 30 cm. The aggregates used in the concrete consisted of schists that contained minor amounts of pyrrhotite (Fe_7S_8), as disseminate crystals and veinlets. The total sulfur content of the rock was up to 0.8 wt. % S.

Drilled cores were taken from the two dams and subjected to petrographic analysis, SEM/EDS and XRD. From those analyses, *ettringite* was observed as needle-shape crystals filling cavities and fractures in the cement paste; *gypsum* was found as radial aggregates of needle-shape crystals. In some samples, the pyrrhotite was surrounded by melanterite white halos.

The authors concluded that the principal cause of concrete expansion was pyrrhotite oxidation leading to an acid attack of the components of the cement paste, and the formation of iron sulfates that have a higher molar volume. The second stage of the deterioration process corresponds to the attack of the cement paste, where *ettringite* halos formed and promoted the disintegration of the bounds in the interfacial paste/aggregate zone.

2.6.10 Eastern Canada (Tagnit-Hamou et al., 2005)

Tagnit-Hamou et al. (2005) reported the results of laboratory investigations carried out to elucidate the cause of the premature deterioration of house and building foundations and slabs that occurred in one region of Eastern Canada. The concrete made with the sulfide-bearing grey anorthosite aggregates have caused a large range of damage to the above structures as early as two years after construction. Concrete cores extracted from the deteriorated structures were analysed by XRD, SEM/EDXS, while petrographic examination was conducted using a stereomicroscope.

The observations allowed identifying large deposits of *goethite* around several aggregate particles and a very porous cement paste in some locations. *Ettringite* was identified in all samples, generally very close to the weathered aggregate particles and in the cement paste near sound aggregate particles.

Cracks that reached up to 2 mm in width were observed in the aggregate particles and in the cement paste. Cracks in the cement paste skirt around aggregate particles; however, in some heavily weathered cases, cracks were found to run through the aggregate particles. In the cracked aggregate particles, pyrrhotite exhibits a rusty aspect and, sometimes, the crystals seemed to be completely dissolved. Most of the time, weathered micas are observed within these reacted zones.

In this case, it was shown that the presence of chemically unstable iron sulfides (pyrrhotite) in aggregates would have caused the early cracking of concrete. The oxidation of the iron sulfides provokes a series of chemical reactions leading to the precipitation of iron hydroxides and *ettringite*. The most deteriorated zones were observed where pyrrhotite was associated to micas, the latter having probably contributed to accelerating and enhancing the deterioration process by absorbing water and oxygen.

2.6.11 Switzerland (Schmidt et al., 2011)

Schmidt et al. (2011) published the results of a study carried out on a concrete dam, constructed in the beginning of the 1970s in Switzerland that was found to suffer from steady expansion since the early 1980s. The overall expansion in the upper part of the dam is estimated to be 0.025%. The authors also reported deposits of "rust" (iron oxides and hydroxides) accumulated in the galleries of the dam, and there was also a smell of sulfurous compounds. The rocks utilized as aggregate in this construction mainly consisted of schists. The foliation layers had a thickness of 0.5–2.0 mm. The schists were mainly composed of feldspar, quartz, biotite, and muscovite. Iron sulfides were found to be randomly dispersed and agglomerated within the aggregates. Pyrite/marcasite (80%) and pyrrhotite (20%) were analysed to be about 0.3 to 0.4% by volume. The ore particles were within a range of 30 to 200μm in size, while minor amounts of ilmenite ($FeTiO_3$) were also noticed. The concrete was produced with an ordinary Portland cement (equivalent to present day CEM 1 32.5: a blended cement with: 65% ≥ Clinker ≤ 79%, 21% ≥ limestone ≤ 35% and calcium sulfate, with the chemical composition in sulfates (SO_3) ≤ 3.5 and chlorides ≤ 0.10%), using a water-to-cement ratio in the range 0.5–0.6. The samples (cores of 150 mm in diameter) were taken from the downstream face and from galleries in the inner part of the 40 year-old structure.

The investigations indicated that the deterioration process of the iron sulfide grains in various concrete samples was similar but not uniform. The oxidation or degradation process of both pyrite/marcasite and pyrrhotite usually started from the surface of the grain leading to a layer of oxidation products, which is darker than the unreacted iron sulfide. From the chemical microanalyses, the iron sulfide particles seemed to react to first form iron oxide (Fe_2O_3) and secondly iron hydroxides ($FeO(OH)$, $Fe(OH)_3$). The oxidation or degradation reaction was found to usually start from the outside inwards of the iron sulfides grains. The concrete samples showed significant cracking originating from the iron sulfide-containing regions within the aggregate particles, and then extended into the cement paste. Thus, it appears that the degradation can be directly linked to the reaction of iron sulfides, which leads to an increase in volume within the aggregate particles that, in turn, cause cracking and expansion of the concrete. The formation of secondary *ettringite*, from released sulfate, was observed, but there were no clear signs of expansion associated with the extra sulfate. It is not clear to what extent this may contribute to the macroscopic reactions. It was found that pyrrhotite reacts much faster than pyrite in alkaline concrete environments.

2.7 Tests involving the oxidation of iron sulfide-bearing aggregates when used in concrete

Since it was found that aggregate particles containing iron sulfides can be deleterious to the concrete durability, some laboratory tests have begun to be developed. The aim of these tests has been to determine a limit value of the iron sulfides (pyrite and/or pyrrhotite) content that will be safe to utilize when they are incorporated in concrete aggregates, as well as the influence of different types of cements on the durability of concrete incorporating aggregates with different contents of sulfides. Some studies tried to recreate in the laboratory the field conditions and mechanisms that lead to the concrete deterioration due to sulfide-bearing aggregates.

2.7.1 Sweden (Hagerman and Roosaar, 1955)

After having noticed some concrete deterioration problems involving sulfide-bearing aggregates in Sweden, Hagerman and Roosaar (1955) tried to evaluate the maximum tolerable pyrrhotite content in concrete aggregate.

For their tests, four different types of aggregates containing pyrrhotite, as well as an aggregate produced from crushed Stockholm Granite (without sulfides), were used for comparison purposes. In order to obtain different levels of pyrrhotite contents in the aggregates used in the trial mixes, the rocks were sorted into four series, i.e. in order to obtain samples from Pengfors with pyrrhotite contents of 1%, 5% and 10% (Series 1 to 3), and rocks from Norrforsen with 10 to 15% of pyrrhotite (Series 4). A fifth series was produced with the Stockholm Granite as a control aggregate. This tests involved measurements of the natural frequency in transversal vibrations, length measurements and visual inspections.

The experimental tests were carried out on concrete beams, 80 x 15 x 10 cm and 40 x 15 x 10 cm in size. In the case of the large specimens (80 x 15 x 10 cm), three beams of each series were stored in warm water for 3 days alternating with air storage at 75°C for 4 days, for a total of 7 days for each cycle. Two beams of each series were stored in water for 3 days, alternating with air storage for 4 days, both at room temperature, for a total of 7 days for each cycle. Lastly, three beams from each series were stored outdoors.

In the case of the small specimens (40 x 15 x 10 cm), three breams from each series were subjected to steam curing in an autoclave at 225°C for five hours. After, they were allowed to cool to 100°C in the autoclave, followed by cooling in hot water down to room temperature. This treatment was repeated four times at approximately one week intervals. Between autoclaving, the specimens were stored in air at room temperature.

Visual observations of the test beams were made at 2.5 months, 4.5 months and 7 months. After 7 months of testing, the samples made with pyrrhotite showed the presence of rust, some minor cracks and, in one set of beams (80 x 15 x 10 cm) stored in warm water for 3 days alternating with air at 75°C for 4 days, some aggregate particles close to the surface displayed evidence of swelling thus causing fine cracking in the surrounding concrete.

One of the most deteriorated samples, i.e. those stored in warm water for 3 days alternating with air at 75°C for 4 days, was deliberately broken at the end of the testing period. Upon inspection of the fractured surface, rusty aggregate particles were only present in the first 10 mm from the surface of the prism. The petrographic examination of two thin sections prepared from this sample revealed evidence of oxidation of the sulfides, together with oxidation staining in the cracks. Ettringite was not observed.

2.7.2 Montreal (Canada) (Bérard et al., 1975)

As mentioned before, in 1971 and 1972, similar cases of distressed concrete structures in Montreal were brought to the attention of Bérard and coworkers (Section 3.6.4).

In order to determine the amount of sulfide-bearing shale required to cause the unwanted oxidation reactions, twenty concrete prisms were made. Ten of those prisms were made with shale particles recycled from the deteriorated concrete (maximum aggregate particle size of 2 cm), while the other ten were made with shale extracted from the quarry (maximum aggregate particle size of 4 cm). The concrete prisms were subjected to cycles of wetting and drying. These cycles consisted of keeping the samples in a moist room at 22.8 °C for a certain period of time, after which the specimens were transferred to another room and allowed to dry for an equal period of time. All the samples suffered shrinkage, while only one specimen showed a longitudinal crack with iron oxide seeping through the crack. Although the test was unable to reproduce the distress observed in the field (expansion/cracking), the deleterious properties of the shale were somewhat highlighted since some shale particles near the surface of the test prisms generated pop-outs through the oxidation of pyrrhotite mainly visible along bedding planes.

Rock expansion tests were also carried out. Five blocks were cut from the shale and expansion measurements were carried out perpendicular to the bedding. Two of the blocks saturated in water expanded by over 0.2% in less than 100 days. Two other test blocks that were kept outdoors (so that variations due to natural weather conditions could be followed) expanded slightly less than the first two blocks. A fifth specimen, kept indoors at room temperature, showed a small shrinkage, mainly because of a small decrease in water content. Oxidation of sulfides was visible and concentrated along thin bedding planes.

2.7.3 South Africa (Oberholster and Kruger, 1984)

Laboratory investigations were carried out using prisms that were cut from bricks and prisms cast using the aggregate from Penge. In the second case, two mix designs were used, namely aggregate-to-cement ratios of 5:1 and 10:1, and these were combined with two manufacturing procedures, i.e. well compacted and poorly compacted. Some prisms were stored at 38°C, either under water or above water in sealed containers.

The prisms cut from the bricks and stored under water expanded by approximately 0.40% after 1000 days; the amount of expansion was however much less than that obtained for the specimens stored above water (more than 1% after 1000 days).

The manufactured prisms started to expand after 22 months. After that period, some of the test prisms stored above water, started expanding at a high rate, while those stored under water did not expand, even after three years. From the above results, it appeared that only the laboratory prisms cast from the low cement (aggregate-to-cement ratio 10:1) content concrete expanded, and that the well compacted prisms expanded at a higher rate than the poorly compacted ones. Expansions of more than 1% were measured. In the test prisms that were manufactured in the laboratory, no thaumasite was found, instead it was ettringite.

2.7.4 Spain (Chinchón et al., 1990)

Chinchón et al. started a testing program in 1990 in order to study the phase behaviour of aggregate minerals undergoing reaction with water and cement components. Two sets of mortars were made using a P-450 Portland cement. The first set of mortar was composed of limestone (with 4.20% hexagonal pyrrhotite and 0.70% pyrite), cement and water. The second set of mortar was composed of shale (with unknown values of pyrrhotite and pyrite), cement and 20% water. The two types of lithologies had sulfides in their composition, hexagonal pyrrhotite and pyrite 15g-samples of the mortars were separated into porcelain capsules and were maintained at 20°C and 97% of relative humidity and the mortars were monitored over a 140-day period. The formation of ettringite in the mortars made with limestone was slower than in the case of the mortars made with shale. A large production of ettringite and a reduction in the pyrrhotite and pyrite contents was noted in both cases. According to the authors, the results show that the mortar was deteriorated through the formation of ettringite resulting from the iron sulfide oxidation products and the reaction of those with the cement paste products.

2.7.5 Cornwall and Devon, England (Lugg and Probert, 1995; RICS, 2005)

During the 1980s, the market price of houses that were thought to be affected by the “Mundic” problem started to drop and, at that time, there was no effective way to determine whether the houses had the problem or not. In 1985, the Royal Institute of Chatered Surveyors (RICS), commissioned a committee to investigate the problem (Lugg and Probert, 1995). This committee thus developed a guidance note that recommended the use of chemical and petrographic analyses for the identification of the “Mundic” concrete. Besides the chemical and petrographic analyses, the RCIS implemented an experimental program to measure the unrestrained linear expansion of concrete cores taken from the “problematic” houses. This test is an accelerated weathering test where the concrete cores are subjected to a water-saturated atmosphere (100%HR) at a constant temperature of 38°C and for a period of at least 250 days. Cores showing an average expansion upon wetting exceeding 0.075% at 7 days were considered to have failed the test; on the other hand, if the expansion was less that the above limit, the test had to be pursued up to 250 days. Core specimens showing an expansion lower than 0.025% over the remaining part of the 250 day test period, are likely to remain stable under ambient conditions for many years, provided that normal levels of care are maintained.

2.7.6 Brazil (Gomides, 2009)

In Brazil, some of the bedrocks supporting hydraulic dams and some aggregates available for dams construction contain iron sulfides. Due to the lack of information on the various factors promoting and/or accelerating the oxidation of sulfides and the influence of the type of hydraulic cement on the development of pathological manifestations in concrete made with sulfide-bearing aggregates, a study was launched on this topic (Gomides, 2009). Gomides thus started a PhD to investigate the influence of five types of cements on the durability of concrete incorporating aggregates with different sulfide contents.

The experimental program was separated into two stages. In *stage 1*, the concretes were prepared with a quartz-muscovite-schist aggregate containing 3.89% of sulfides, of these sulfides 3.40% correspond to pyrrhotite, 0.31% correspond to pyrite and 0.17% to marcasite. A water-to-cement ratio of 0.45 was selected for concrete manufacturing. Three types of cements were used; one type of cement was for reference (CP II-F-32), while the other two resulted from the partial replacement of the reference cement by 40% (CP40) and 60% (CP60) of ground granulated blast-furnace slag. In *stage 2*, the concrete specimens were made with three types of cement, specifically: CP II-F-32, CP III-40-RS (sulfate resistant cement) and CP IV-32 (pozzolanic binder (25% to 40%) and 38% of fly ash). The aggregate used in *stage 2* was the same as that used in the *stage 1*, but this aggregate had previously been stored outdoors in steel drums, i.e. subject to all kinds of weathering conditions, during a period of two years. After those two years, the aggregate in question had lost approximately 86% of its sulfide content due to an oxidation process, with a remaining/residual sulfide content of 0.56%. Of this value, 0.29% corresponded to pyrrhotite and 0.27 % corresponded to pyrite.

During the two stages, the concretes specimens used for testing consisted of prisms (75 mm x 75 mm x 285 mm in size) and cylinders (100 mm in diameter x 200 mm in height). After casting, all specimens were stored, for all the time of the experimental program, in a humid chamber where the temperature was maintained between 23°C ± 2 and the relative humidity ≥ 90%.

The main purpose was to assess the performance of the concretes prepared with these different cements due to internal sulfate attack resulting from the process of sulfide oxidation of the aggregate in a high moisture environment up to approximately five years.

The results showed that pyrrhotite is the most reactive sulfide in the system, i.e. the main mineral responsible for the changes observed in the aggregates extracted from the concretes. It was found that the oxidation promotes the expansion of this material, besides interfering with its elastic-mechanical properties. In the specimens from *stage 1*, external spots of rust, white efflorescence, chipping and breakdown of aggregate particles containing high levels of sulfides were observed. These features of external deterioration resulted from the oxidation of sulfides and were more pronounced in the concrete containing higher proportions of ground granulated blast-furnace slag (CP40 and CP60). The concretes prepared in *stage 2* showed no visual pathological manifestation related with the iron sulfides. In general, the concretes had typical deleterious products of sulfate attack, i.e. ettringite and gypsum. The concrete CP40 and CP60 were those with a higher concentration of these products in *stage 1*. In *stage 2, no* information was obtained about the concentration of ettringite and gypsum. The expansion values calculated after five and a half years of testing reached a maximum value of 0.052% for the CP60 (*stage 1*), and a maximum value of 0.041% for the CPIII after four and a half years of testing (*stage 2*), suggesting that the higher the concentration of sulfides and aluminate ions present in the system, the greater the expansion or the observed levels of deterioration.

It was also verified that the higher the concentration of sulfides, especially pyrrhotite, the more intense and severe was the observed levels of deterioration. A high-moisture environment was an essential parameter to accelerate the oxidation process of these minerals in concrete aggregates.

2.7.7 Switzerland (Schmidt et al., 2011)

In order to recreate the deterioration mechanism responsible for the damage in the dam in Switzerland (section 2.7.11), concrete prisms (70 × 70 × 280 mm in size) were prepared with the same aggregate that was utilized in the dam (Schmidt et al., 2011). The cement utilized was an ordinary Portland cement (CEM I 42.5), with a water-to-cement ratio of 0.50. Those prisms were stored in water for 5 years at 60°C.

The degree of expansion could not be assessed accurately. Petrographic and SEM/EDS analyses of the prisms were performed after 4 years of testing. The laboratory concrete samples had the same appearance and reaction pattern as the dam concrete, but the extent of reaction of the iron sulfides was much lower. The reaction products observed were the same that the ones observed in the dam, i.e. iron oxide, iron hydroxides and ettringite. These observations clearly indicate a very slow reaction rate of the iron sulfide inclusions and the difficulties to reproduce the iron sulfide degradation in the laboratory conditions (immersion) used. Due to the low degree of reaction, it was not possible to assess the influence of temperature on kinetics. These findings indicate the difficulties to reproduce the specific iron sulfide degradation in the laboratory.

2.7.8 Spain (Chinchón-Payá et al., 2012)

Chinchón-Payá and coworkers in the last 20 years have studied samples of concretes from dams in which the metamorphic slate coarse aggregate very often contained oxidizable iron sulfides, usually in the form of pyrrhotite. It has been observed in practice that this combination produces conditions more harmful to concrete than other situations such as for example limestones with pyrite.

The work exposed here is the first step of a more extensive study on the role of different iron sulfide minerals when they form part of aggregates used in concrete dams, and has a twofold objective: firstly, to study the oxidation of pyrite and pyrrhotite samples under the same experimental conditions, seeking to differentiate their respective behaviors; and secondly, to investigate the effects of adding different aggregates to solutions containing pyrite and pyrrhotite in order to check the effect that the host rock has on the speed of reaction and the nature of the reaction products.

Two pyrite and pyrrhotite samples were obtained from the Catalonian Pyrenees (Spain). Approximately 500 g of each sulfide minerals was obtained by separation from the host rock. The pyrite has a composition of S 49.03% and Fe 46.37%, while the composition of the pyrrhotite is S 35.18% and Fe 61.12%. The aggregates used were a Miocene marlstone, a Cretaceous limestone and an Ordovician shale. The three aggregates were chosen taking into account their low content in sulfur. The iron sulfides and aggregate samples were ground in an agate mortar and the fraction with a particle size between 1 mm and 500 µm was used in the experiments.

Two types of experiments were carried out, with and without the addition of coarse aggregates. In the experiment without the addition of aggregates, 10 g of pyrite and 10 g of pyrrhotite were placed in two 500 ml precipitation vessels with 200 ml of water. A constant air flow was applied to the suspension by means of a pump with a pressure of ca. 120 mbar. The pH and solution potential (Eh) values were measured daily for 2 months. At the end, the reaction products were analyzed to determine the sulfate and the total Fe contents.

In the second experimental set-up, binary samples of aggregate and iron sulfide were prepared in proportions of 95% and 5% by mass respectively. The solids were placed in 500 ml precipitation vessels with 200 ml of water; a similar experiment to that described before for the sulfides without aggregates was conducted.

In the case of the dissolution of iron sulfides alone, the Eh (redox potential) during the experiments was almost constant; a significant increase was noted initially only in the case of pyrite and a constant value was reached a few days after the beginning of the experiment. Both solutions present positive potential values, though to a higher extent in the pyrite solution. The pH monitoring showed a fast decrease at the moment of placing the pyrite in contact with water (the pH decrease from 4.5 to almost 3.5), followed by a slight gradual decrease until they reached constant values (pH 3) about 50 days after the beginning of the experiment. The results obtained indicate that the reaction of pyrrhotite generates more sulfates than pyrite.

In the case of exposing the iron sulfides in combination with aggregates, it was noticed, for the three aggregates, a significant increase of pH values (between 6 and 10) when compared to those obtained for the pure sulfide oxidation experiment. In the case of the iron sulfides combined with marlstone and limestone, there was a buffer effect due to the presence of carbonate minerals. In the iron sulfides with shale case, the pH is controlled by the dissolution of feldspars and micas. The results showed no existence of Fe^{2+} in solution, meaning that the Fe has precipitated in the form of a hydroxide. In the case of SO_4^{2-} concentration, in all three cases, the values were much higher with pyrrhotite than with pyrite.

The results of the various experiments confirmed that aggregates containing pyrrhotite release more sulfates to the solution as a result of the oxidation process than those with pyrite despite the fact that the sulfur content of pyrite (53.4%) was higher than that of pyrrhotite (36.4%).

2.8 The standardization state face to the problematic of iron sulfides

Canadian standards highlight, in the following terms, the risk of using aggregates incorporating iron sulfides in concrete (Clause 4.2.3.6.2, CSA A23.2/A23.2-2014):

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

Back in 1983, the French standard NF P18-301 limited the total sulfur content in concrete aggregates to 1% as SO_3 (0.4% as S). This threshold was further increased/relaxed in the context of European standardization NF EN 12 620 (2003), which specified that the total sulfur content (S) of the aggregates and fillers, must not exceed:

•1% S by mass for aggregates other than air-cooled blast furnace slag;

•2% S by mass of S for air-cooled blast furnace slag.

Note: Special precautions need to be taken when pyrrhotite, an unstable form of iron sulfide ($Fe_{(1-x)}S$) is present in the aggregate. If the presence of this mineral is proven, a maximum total sulfur content of 0.1% (as S) shall apply.

Despite the fact that the potential problem related to the use of sulfide-bearing aggregates in concrete is highlighted in a number of concrete Standards worldwide, no precise/detailed guidelines have been proposed to evaluate the potential reactivity of such aggregates other than the application of the chemical thresholds mentioned above. While these thresholds could be used as a screening tool for concrete aggregates, they need to be supplemented by other test methods when the total sulfur content is > 0.10%. These tests would identify the type of sulfide mineral(s) present in the aggregate under test. Considering that 0.10% S represents about 0.19% by mass of pyrite or 0.27% by mass of pyrrhotite, the precise identification of such small quantities of material could represent a significant challenge for petrographers. In addition, such quantities are too small to be identified by commonly used X-Ray diffraction analysis. Also, even if the presence of pyrrhotite is identified in the aggregate under investigation, not all forms of pyrrhotite are equally “reactive” (Janzen et al., 2000; Mikhlin et al., 2002; Belzile et al., 2004) thus, other tools are needed for the routine evaluation of aggregates containing iron sulfide-bearing minerals.

2.9 Research needs

As documented in the literature review (section 2), several cases of deterioration of the concrete containing sulfide-bearing aggregates have been documented in the past decades. In the analyzed cases, problematic aggregates consisted mainly of limestone, shale and schist, porous and mechanically weak rocks (Bérard et al., 1975; Chinchón et al., 1995; Casanova et al., 1996; Ayora et al., 1998). In the case of concrete damage observed in the Trois-Rivières area, the rock used is a massive rock. A few cases documenting concrete deterioration using a similar kind of rock were published by Hagerman and Roosaar (1955), Mielenz (1963), Tagnit-Hamou et al. (2005).

In the published literature, attempts to recreate the mechanisms responsible for the oxidation of iron sulfides and damage of concrete have been made, but unfortunately without success. As well no test method capable to evaluate or predict the potential reactivity of such aggregates has been proposed to date.

As previously mentioned (section 2.4), the main parameters that contributes to the oxidation reaction of iron sulfides are presence of oxygen, moisture and high temperature. The data presented in the literature review clearly showed that immersing the mortar or concrete test specimens in water (Schmidt et al.,2011; Oberholster et al., 1984; Hagerman and Roosar, 1955) or keeping them at a high relative humidity of 100% or close to 100% (Lugg and Probert, 1996; Chinchón et al., 1989 and 1990; Gomides, 2009) would not promote expansion or the oxidation reaction will be too slow since, in both cases, the oxygen diffusion is insufficient to accelerate the oxidation of the iron sulfide minerals. Steger (1982) showed that the oxidation of sulfide minerals increases with an increase in relative humidity for values between 37 and 75% RH, while Mbonimpa et al. (2003) stressed that excessive humidity will slow down the reaction. Moreover, samples immersed in water will suffer from a significant decrease of the alkalinity of the concrete pore solution.

The samples submitted to low temperatures (20 to 38°C) (Bérard et al., 1975; Oberholster et al., 1984; Chinchón et al., 1989 and 1990; RICS, 2005; Gomides, 2009) will take long time to react since, as mentioned, sulfides oxidation rate increases significantly with increasing temperature (Steger, 1982; Divet and Davy, 1996). However, generation of ettringite will be eliminated at high temperatures, as tested by Hagerman and Roosaar (1955) (225°C) because ettringite is stable up to temperature < 80°C (Zou and Glasser, 2001).

The production of gypsum and/or ettringite was noticed in some studies (Schmidt et al., 2011, Oberholster et al., 1984; Gomides, 2009). Thaumasite, one of the deterioration products identified by Oberholster and Krüger, 1984, and by Oberholster et al., 1984 in problematic concrete was not observed in their laboratory tests; this is not surprising considering that the ideal temperature conditions for thaumasite formation is between 0 and 5°C (Aguilera et al. 2001) while the temperature tested was 38°C.

The development of an evaluation protocol capable to predict the deleterious potential of aggregates containing iron sulfides is necessary. The use of the ideal conditions of temperature and humidity as well as the use of oxidation solutions in the acceleration of the iron-sulfides oxidation and sulfates production will be tested. The development of this evaluation protocol is essential to avoid the use of reactive sulfide-bearing aggregates in concrete and as result avoid the millions of dollars of unnecessary spending in repairs and replacements of damaged structures.

APPENDIX 4

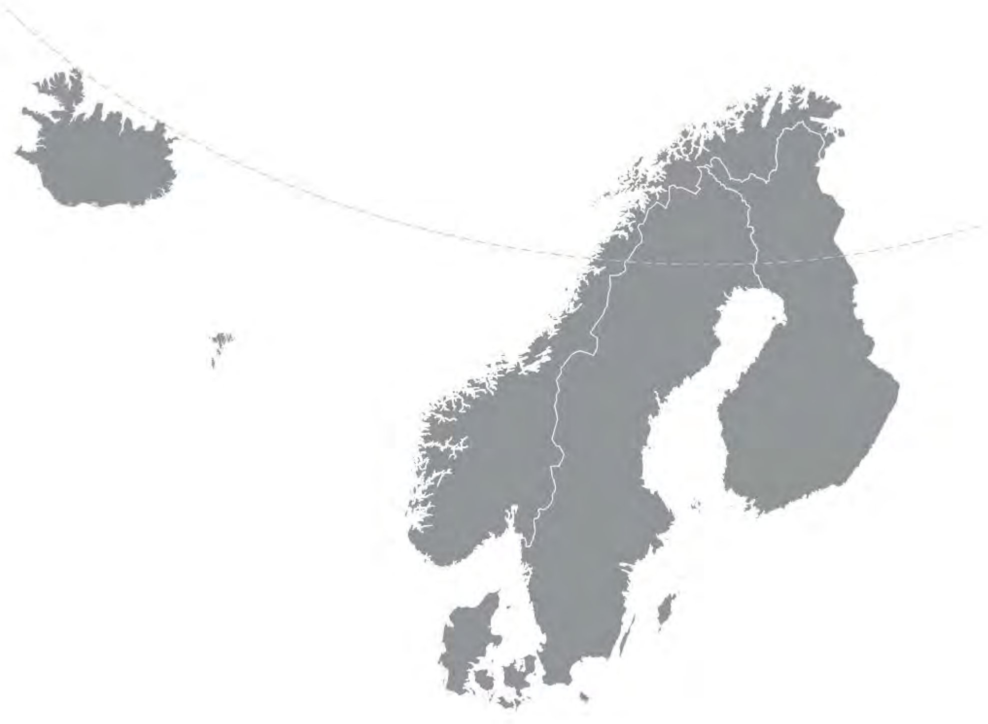
The Nordic Concrete Federation (2018): Workshop Proceedings No. 14:

Impact of sulphide minerals (pyrrhotite) in concrete aggregate on concrete behaviour. Workshop Proceedings from a Nordic workshop

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

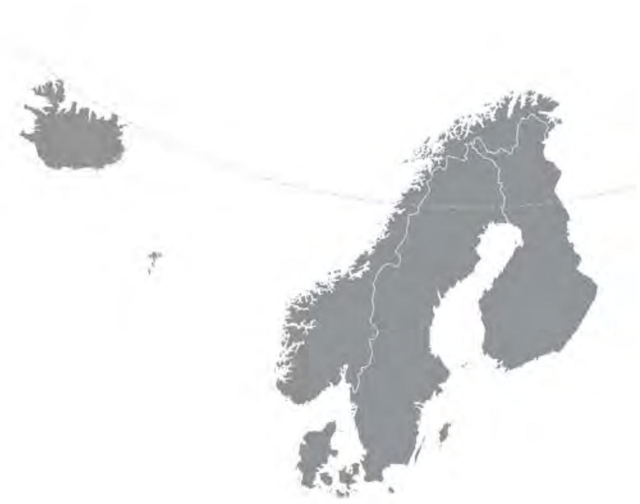
WORKSHOP PROCEEDINGS FROM A NORDIC WORKSHOP

OSLO - NORWAY, 15. – 16. NOVEMBER 2018



Nordic Concrete Federation

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



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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2	Inger Lise Ullnæss	Bane NOR SF
3	Ian Willoughby	Bane NOR SF
4	Svein Willy Danielsen	Dr. ing. S. W. Danielsen
5	Andreas Leemann	Empa
6	Espen Rudberg	Feiring Bruk AS
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9	Maarten Broekmans	Geological Survey of Norway - NGU
10	Terje Bjerkgård	Geological Survey of Norway - NGU
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12	Paul Glamo	Kontrollrådet
13	Magnus Gade Skjeggerud	NorBetong
14	Rolands Cepuritis	Norcem/NTNU
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17	Bård Pedersen	NPRA / Statens vegvesen
18	Kjersti K Dunham	NPRA / Statens vegvesen
19	Nikolas Oberhardt	NPRA / Statens vegvesen
20	Kurt Aasly	NTNU
21	Klaartje De Weerdt	NTNU
22	Petter Hemstad	NTNU
23	Philip Santo	Philip Santo
24	Øystein Mortensvik	Ribe Betong AS
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.

Abstract

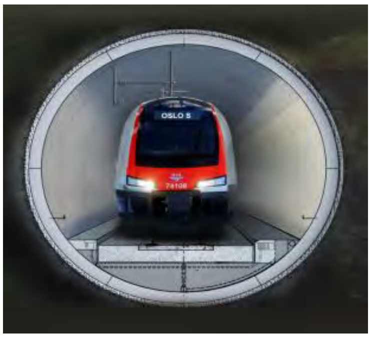
Lessons learned from the Follo Line Project –

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.

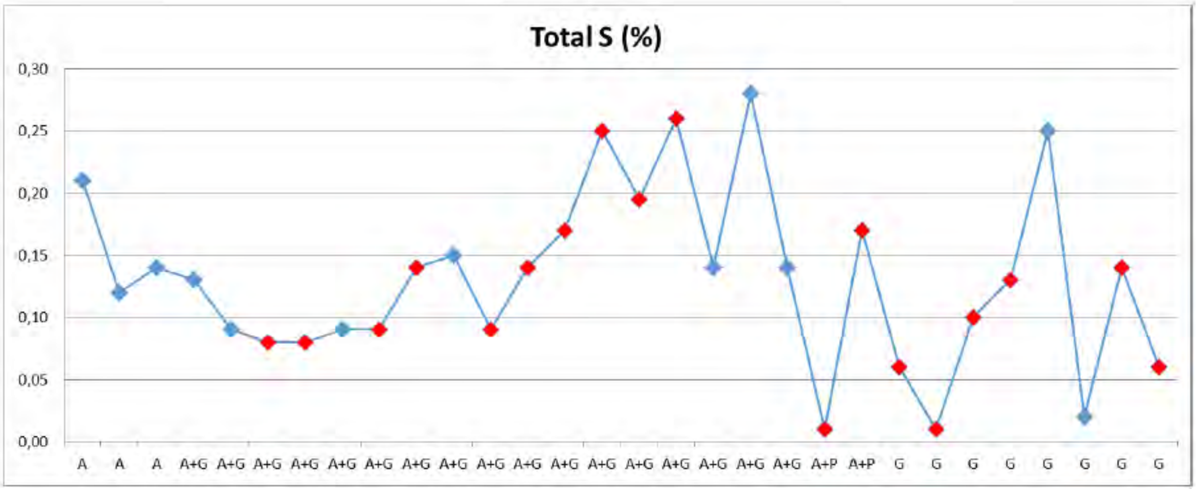


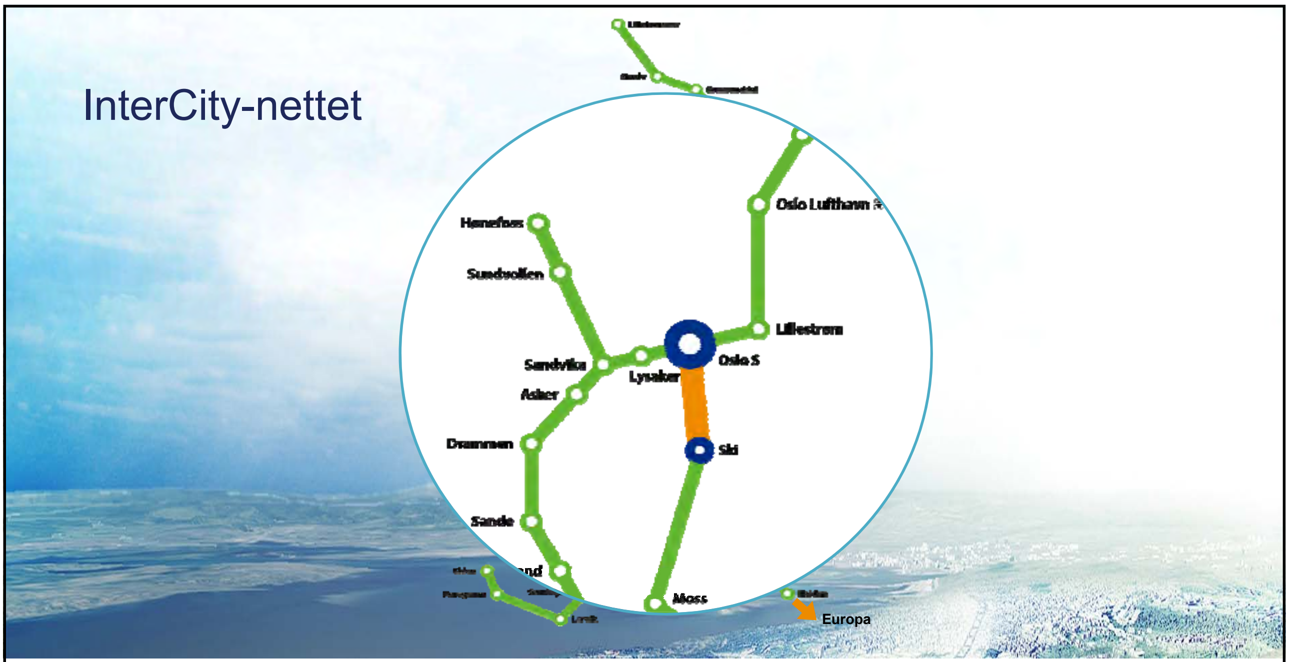
Figure 1 - Variation in pyrrhotite content in terms of geology, red dots are samples with pyrrhotite

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

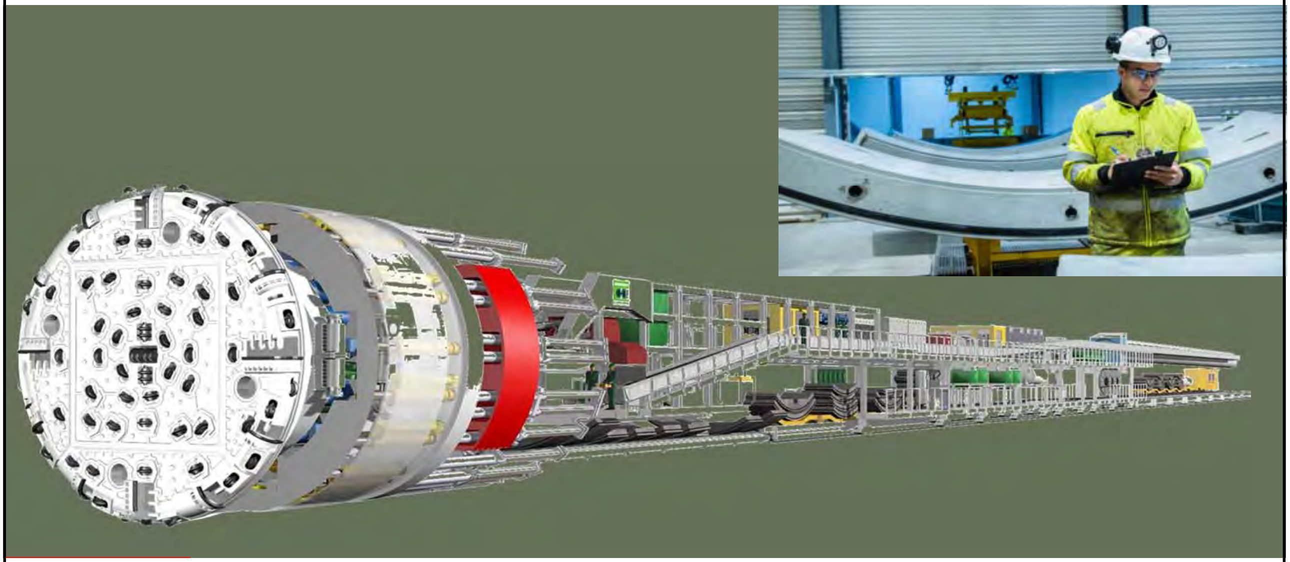
Workshop: Impact of sulphide minerals (pyrrhotite) in concrete aggregate on concrete behaviour
15.11.2018



InterCity-nettet

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

BANE NOR



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

Production of concrete aggregates from TBM-material

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

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…

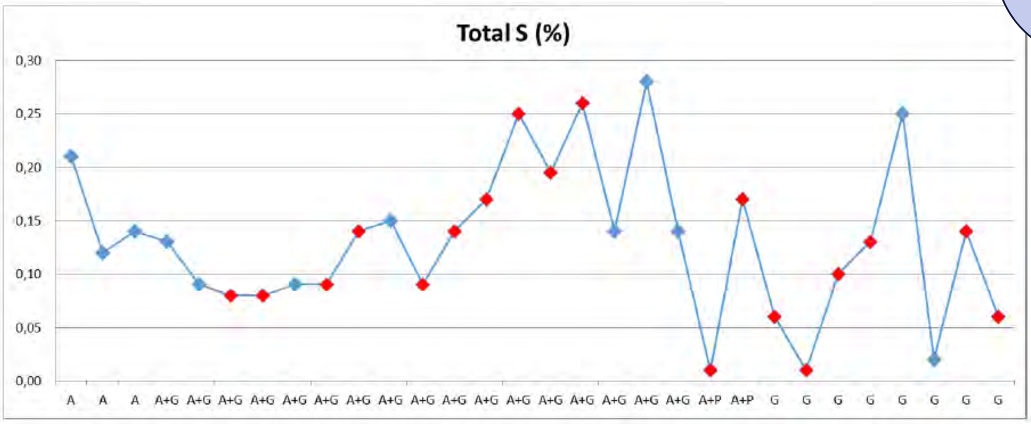
How «correct» is the limit of 0.1%?

Which contents of pyrrhotite will lead to damage?

Foto: Aftenposten Scanpix

Variation in pyrrhotite content in terms of geology

How to perform quality control? Selective production?



BANE NOR

Lessons learned

Challenges with production of concrete aggregates from TBM-material:

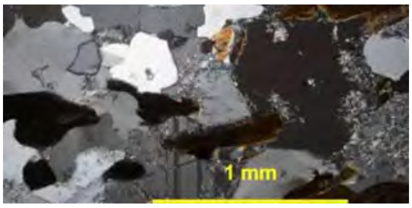
- Production: short time between production and use, production system must allow sufficient quality control
- High humidity in crushed sand due to washing
- Variation of rock quality – selective production is difficult
- NS-EN 12620+NA is not adapted to production of concrete aggregate from tunneling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

BANE NOR

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

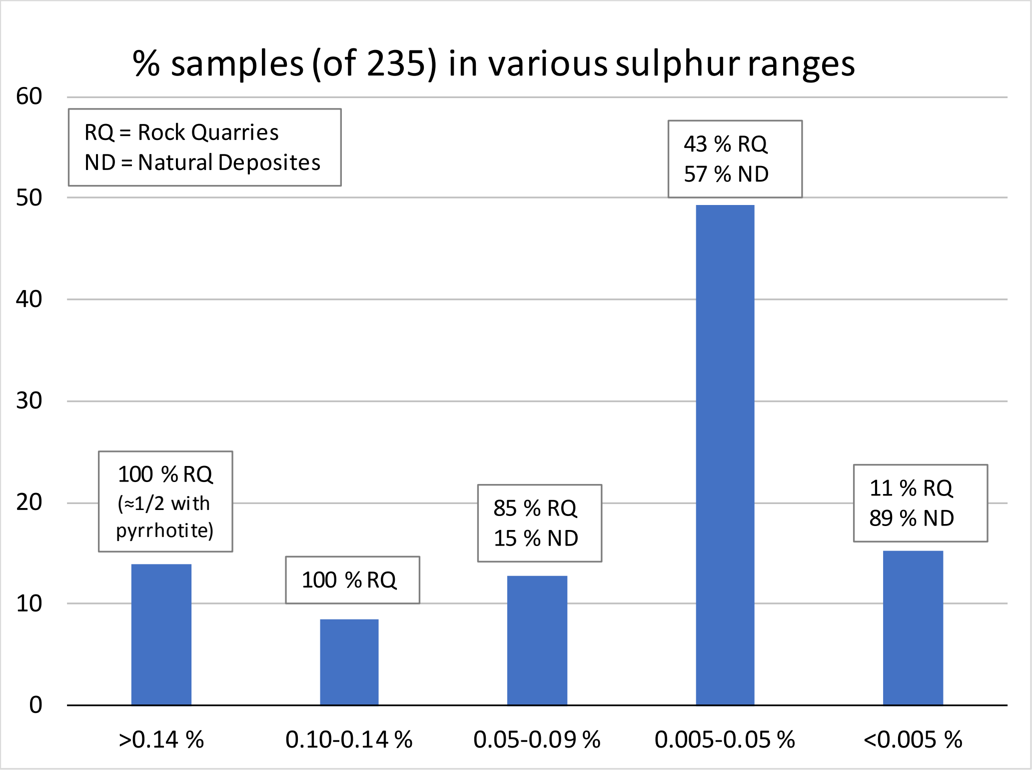
Abstract

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.

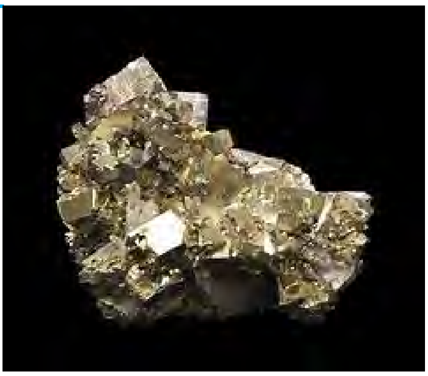
According to the review of the SINTEF results, the rock quarries that show a pyrrhotite content above the critical acceptance limit consist of limestone, dark rocks (i. e gabbro and amphibolite) or a combination of gneiss/granite and dark rocks.

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

Marit Haugen, Jan Lindgård

SINTEF Building and Infrastructure

Sulphides



Pyrite, FeS_2

Pyrrhotite, $Fe_{1-x}S$

The acceptance limit 10 x
higher than for pyrrhotite

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)

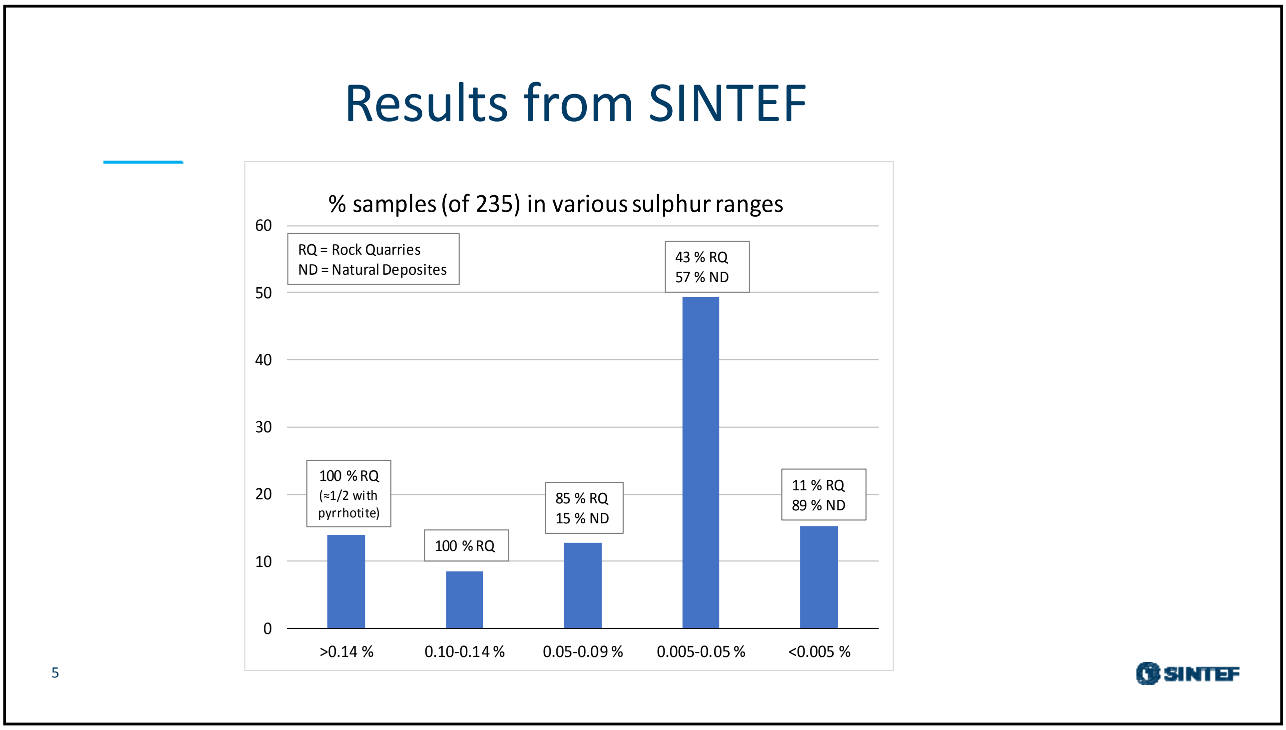
- Type of sulphide determined by DTA (if > 0.1 % S)

Sulphur analyses at SINTEF

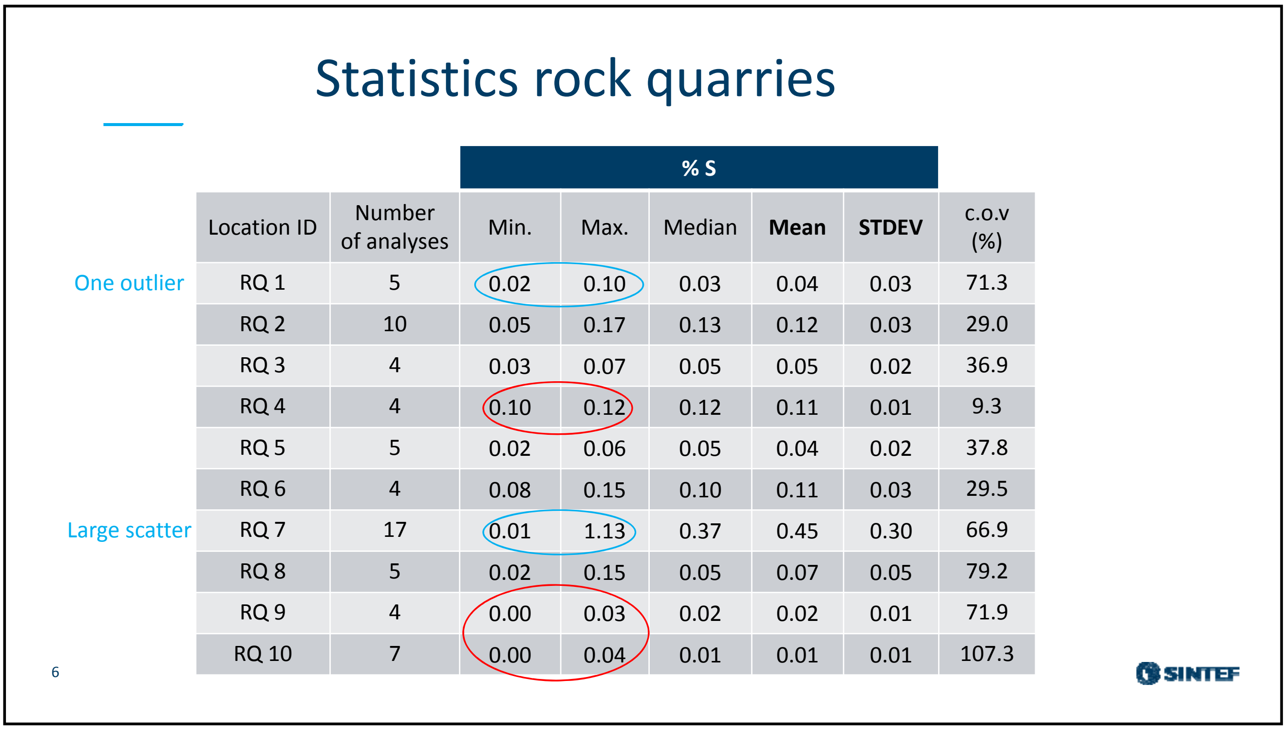
- 2004-2018: Totally 264 samples examined
  - Rock quarries (142 samples)
  - Sand - and gravel deposits (107 samples)
  - Other materials (15 samples)
    - Rock cores, rock samples, light weighted aggregates, recycled concrete and waste materials

- 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

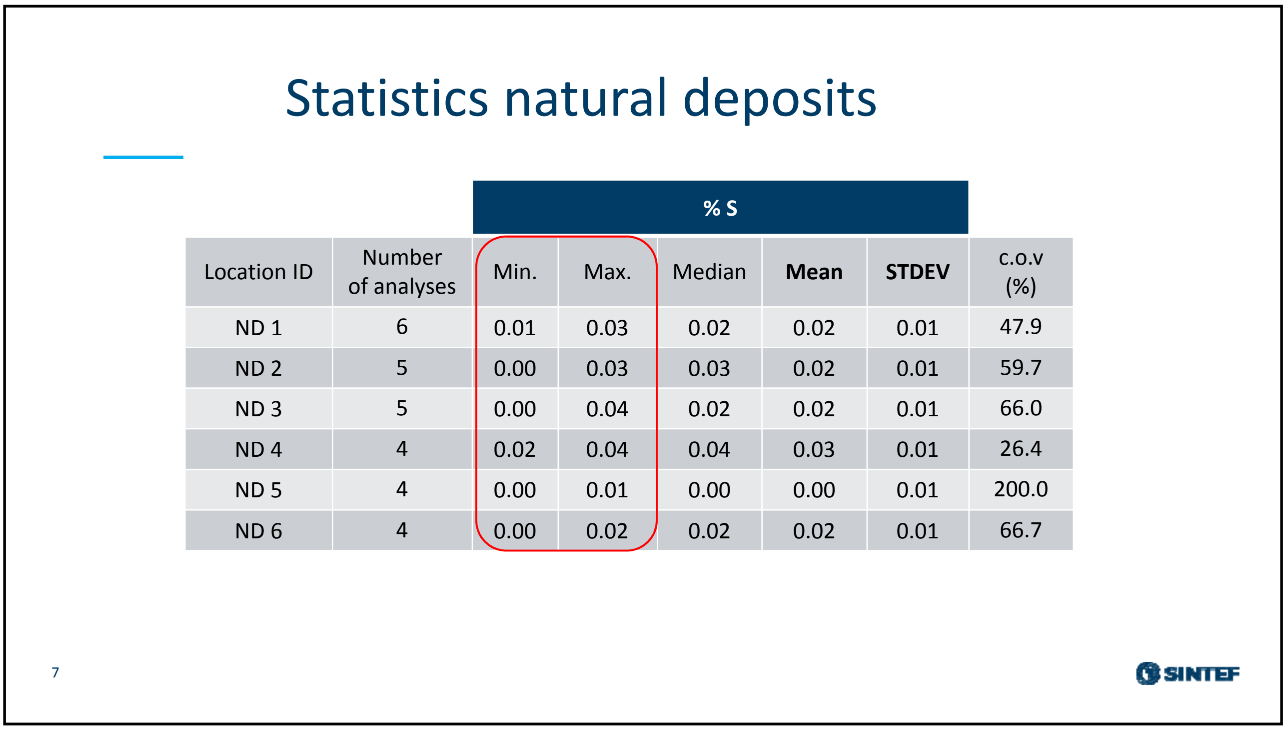


Results from SINTEF



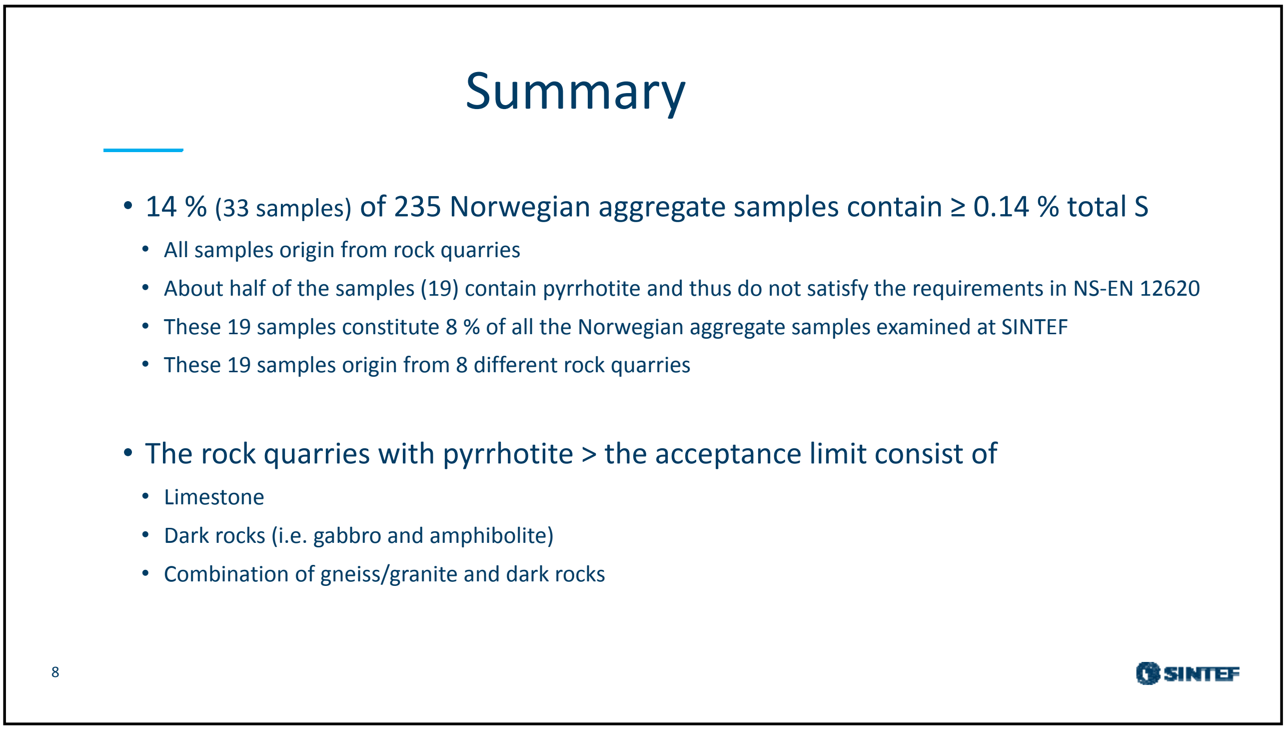
Statistics rock quarries

	Location ID	Number of analyses	% S Min.	Max.	Median	**Mean**	**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



Statistics natural deposits

		% S					
Location ID	Number of analyses	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

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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)

Total S and Pyrrhotite in Norwegian concrete aggregate deposits
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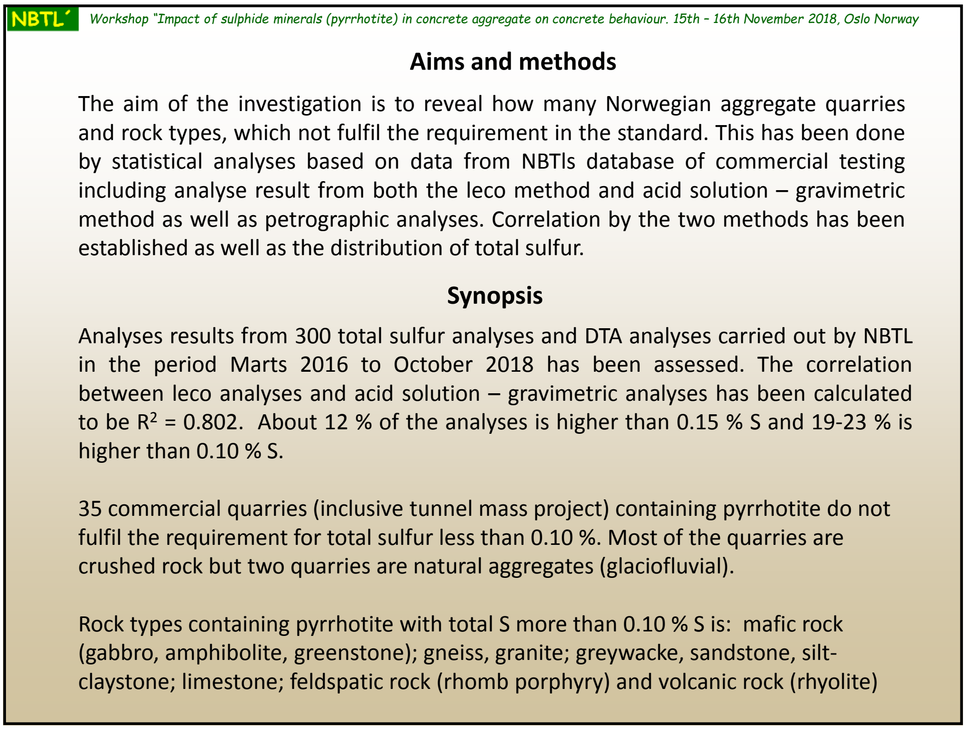
Norwegian Concrete and Aggregate Laboratory LTD (NBTL)

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))



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

Aims and methods

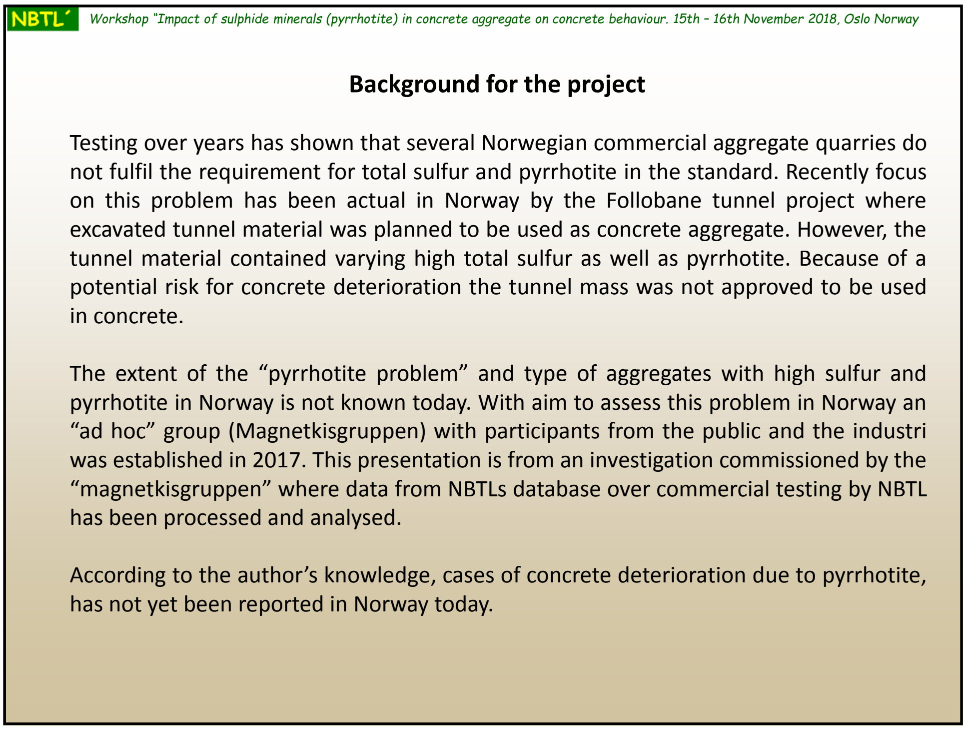
The aim of the investigation is to reveal how many Norwegian aggregate quarries and rock types, which not fulfil the requirement in the standard. This has been done by statistical analyses based on data from NBTls database of commercial testing including analyse result from both the leco method and acid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



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)*

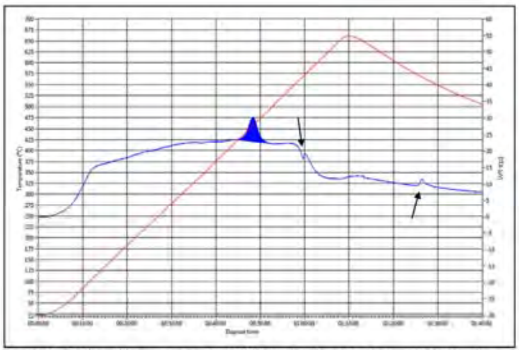
NBTL has over several years used both methods simultaneous for commercial testing of total sulfur and results are presented here.

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.

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»

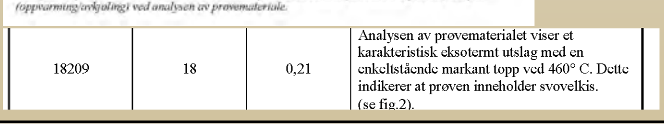


Figur 2. Grafisk fremstilling av prøve merket "18209". Det karakteristiske eksoterme utslaget, med en markant topp ved 460 °C, er markert. Det endoterme (ved oppvarming) og eksoterme (ved avkjøling) reaksjonene for kvarts ved 574 °C er indikert med piler. Den røde linjen viser temperaturforløpet (oppvarming/avkjøling)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

Result: indication of Pyrite

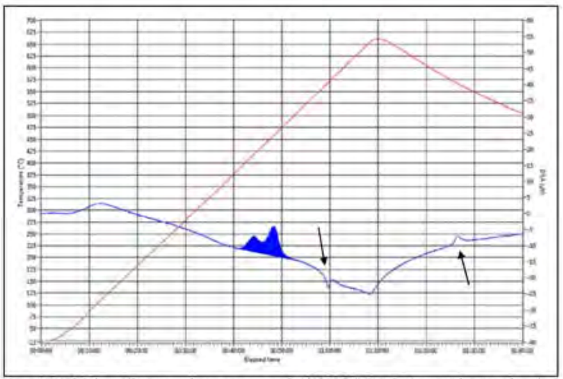
Crushed rock with 70 % gneiss, 25 % mafic rock and 5 % feldspatic rock

Total sulfur = 0.098 %

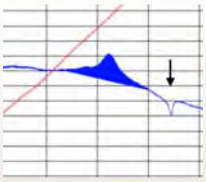


18209	18	0,21	Analysen av prøvematerialet viser et karakteristisk eksotermt utslag med en enkeltstående markant topp ved 460° C. Dette indikerer at prøven inneholder svovelkis. (se fig.2).

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.



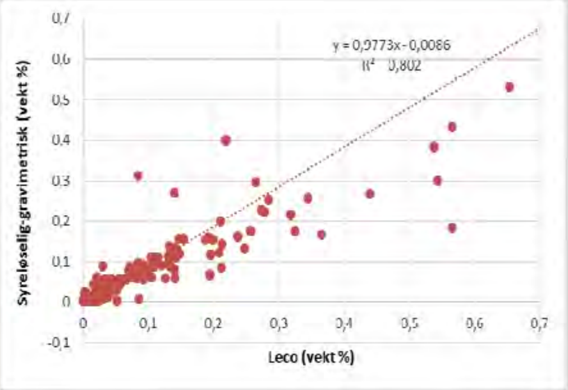
Result: indication of Pyrrhotite or a combination of different types of sulphides

DTA from sandstone

Total sulfur = 0.192 %

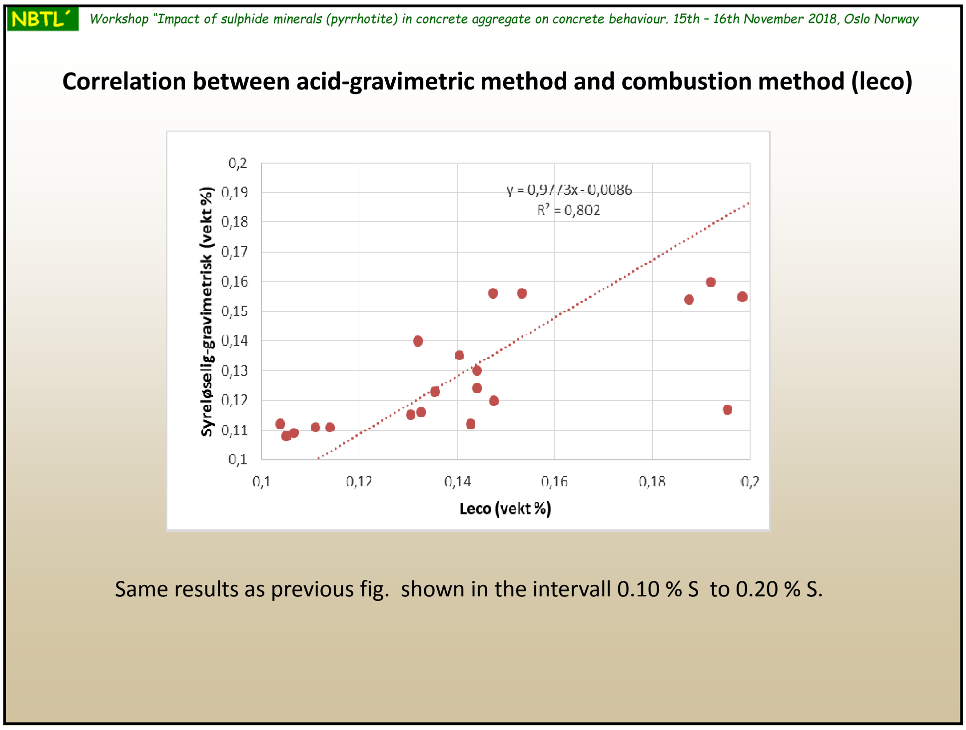
Prøvemerking	Kvarts [vekt %]	Kis [vekt %]	*Merknader:*
18213	22	0,43	Analysen av prøvematerialet viser et sammenhengende eksotermt utslag med markante topper ved 458° C og 417° C. Dette indikerer at prøven inneholder magnetkis eller en kombinasjon av ulike kistyper. (se fig.1).

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

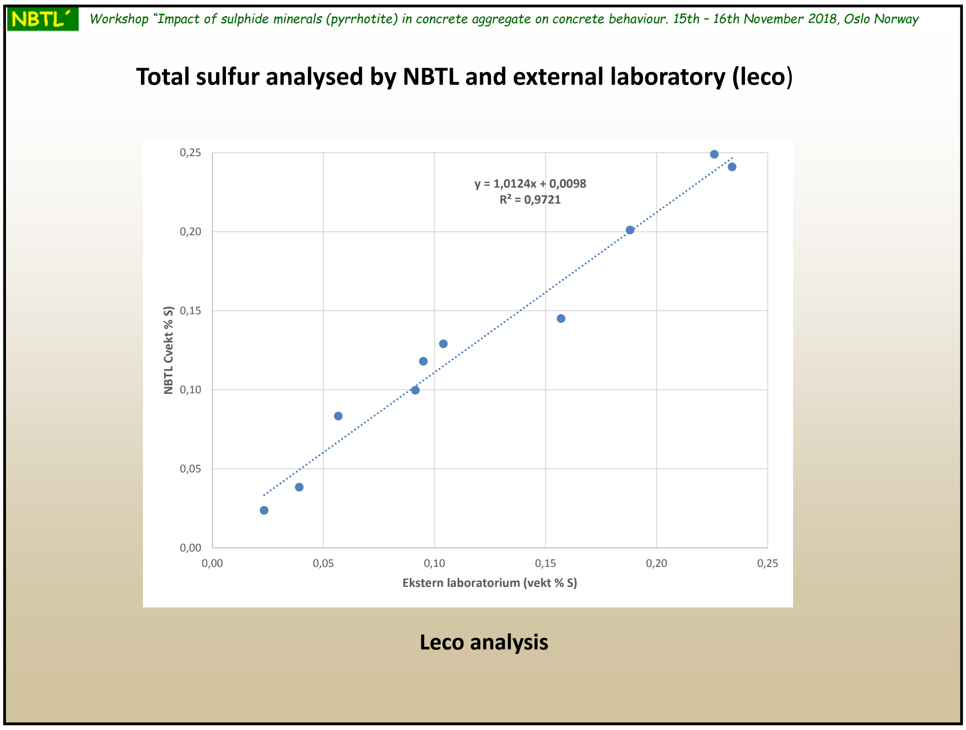
The graph is excluded results from rhomb porfyry (with pyrrhotite) where leco gived 1.25 % S and acid-gravimetric method gived 1.89 % S



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

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

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



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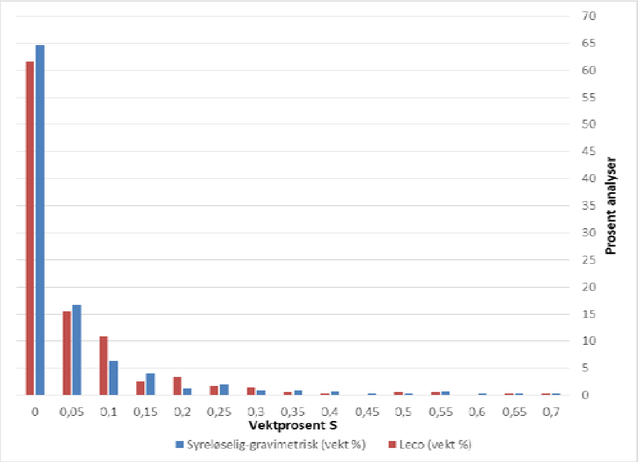
Total sulfur analysed by NBTL and external laboratory (leco)

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.

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

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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

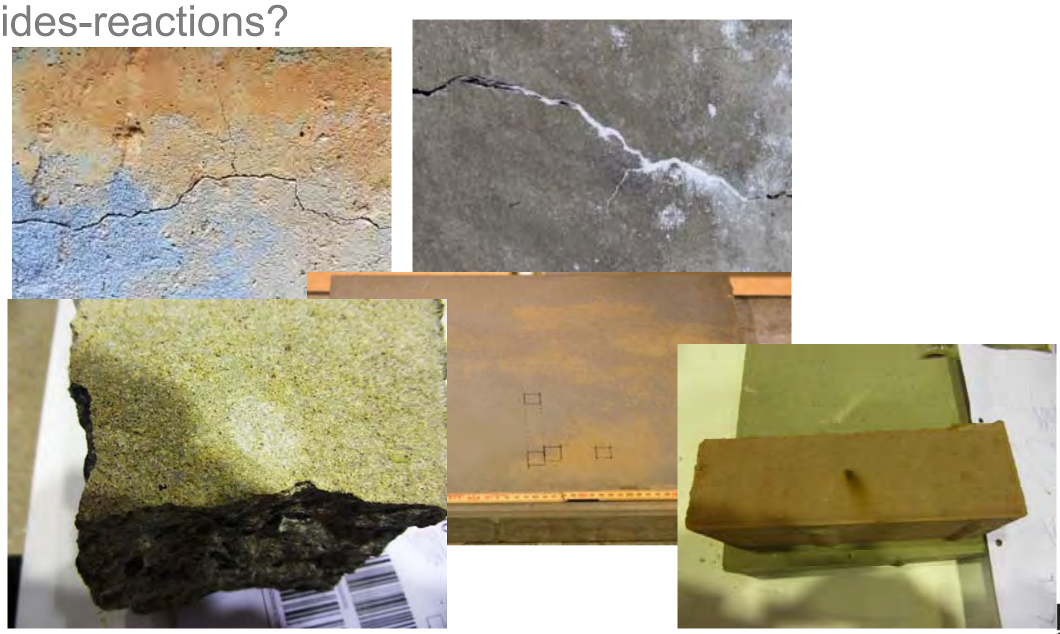
A swedish outlook..

RISE Research Institutes of Sweden

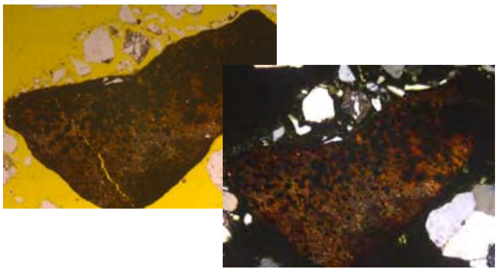
Aggregates with sulphides – issue?

Precast and cast in place?

Sulphides-reactions?

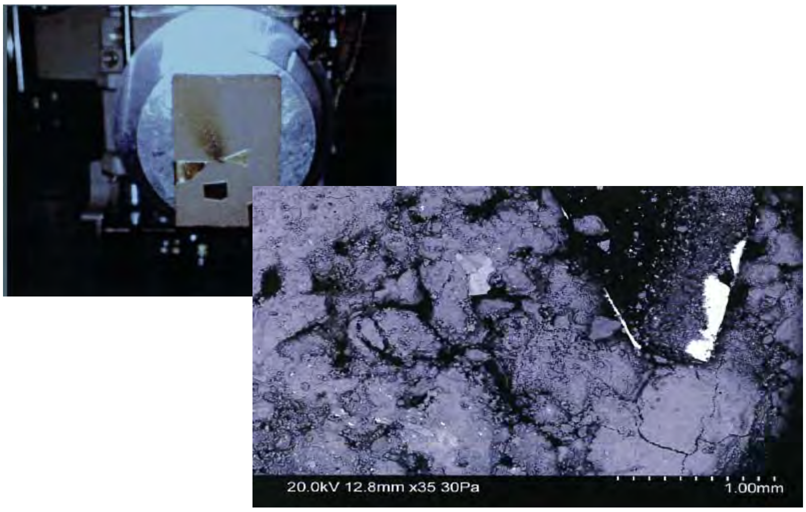


Case I – Discoloration – paving stones/tiles



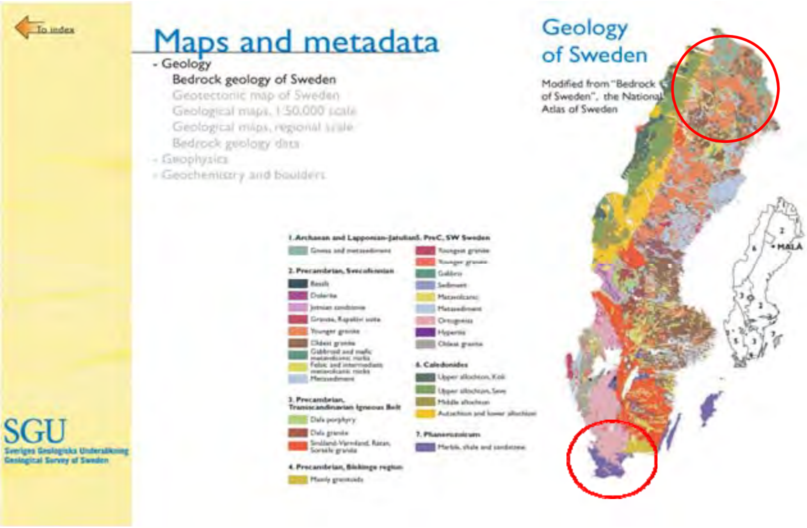
	Mg	Al	Si	S	Mn	Fe	Cu
Object_1	1,03	1,04	29,81	22,51	0,04	42,21	0,00
Object_2	0,76	1,09	25,04	27,32	0,02	39,07	0,00

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

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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Vahanen Building Physics Ltd.

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

VAHANEN

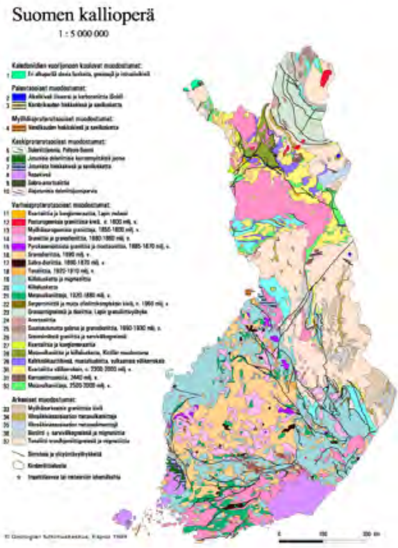
Geological background of Finnish aggregates

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.



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.

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.

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.

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).

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

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.

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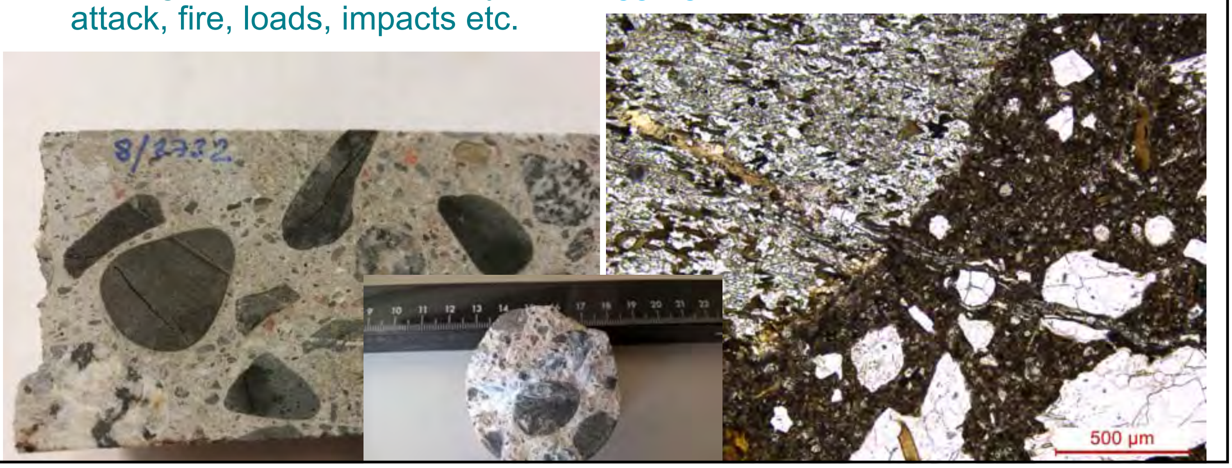
Damages in concrete

- 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

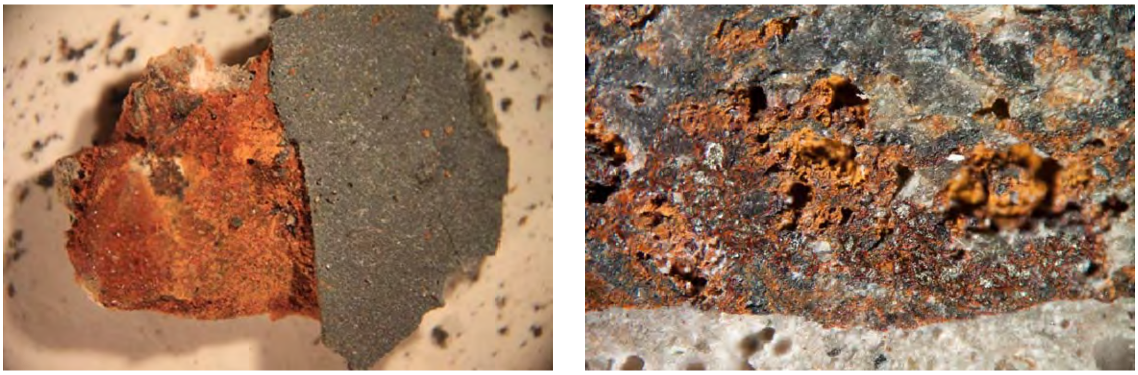
- In every case the visible signs were rusty surfaces and pop outs.
- The first thought was that it is question about rusty steel bars in the elements.
- But in every case the bars were of stainless steel and the bars were in excellent condition.
- The damages were caused by sulphide minerals in aggregate

Damages caused by sulphide minerals

- Case N:o 1 apartment house in Vantaa

Damages caused by sulphide minerals

- Case N:o 1 apartment house in Vantaa

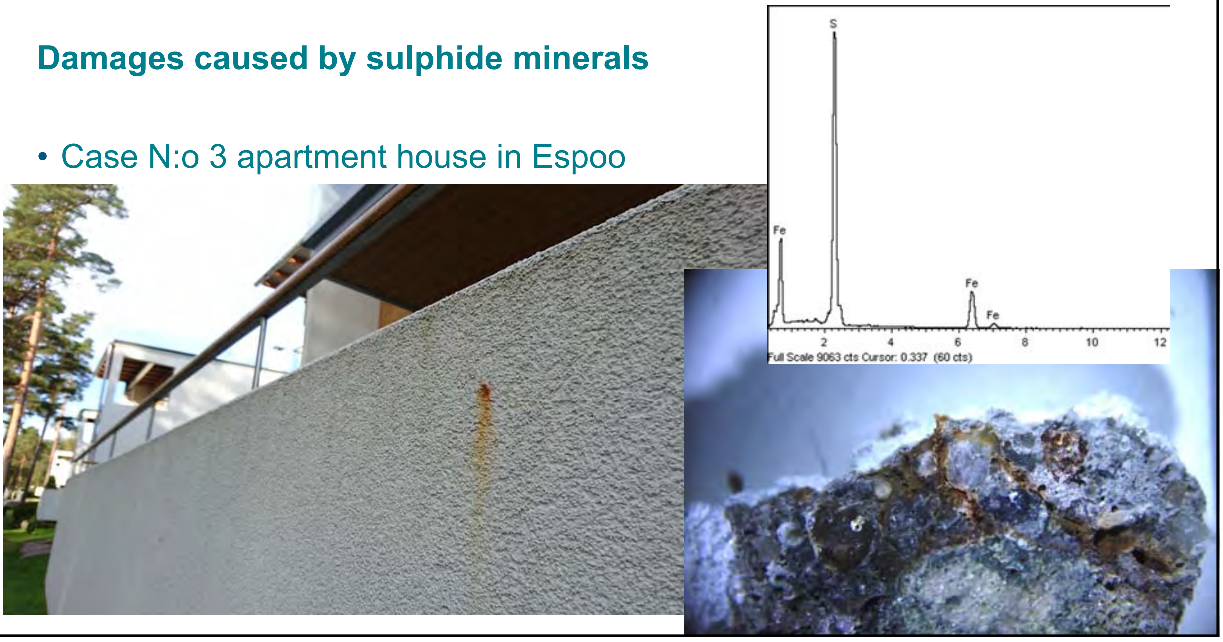


Damages caused by sulphide minerals

- Case N:o 2 apartment house in Espoo

Damages caused by sulphide minerals

- Case N:o 3 apartment house in Espoo



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.

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?

- 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.

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

THANK YOU

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VAHANEN

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

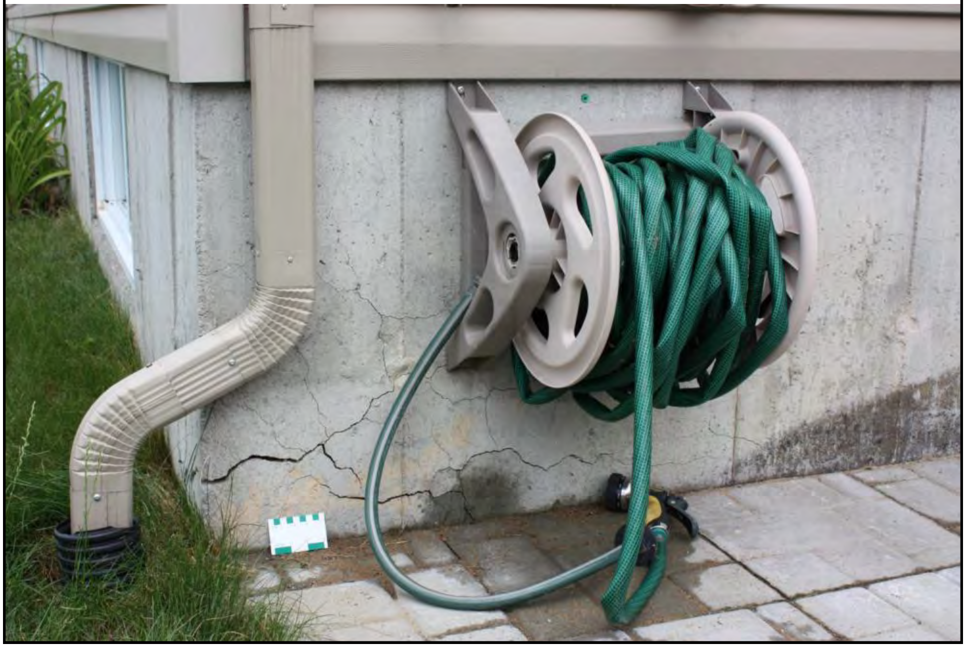
Visual Inspection of Concrete Foundation

- 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

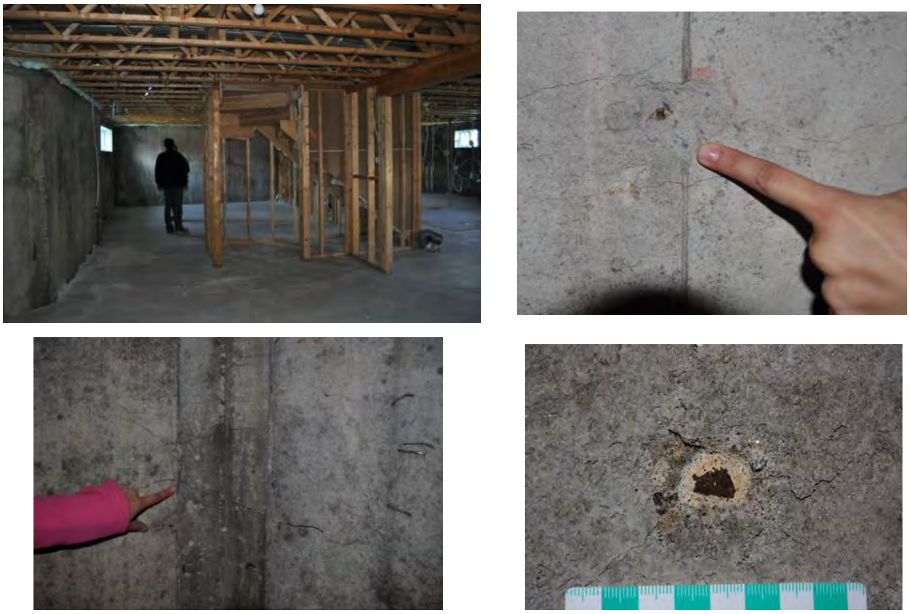


Visual Inspection - Trois-Rivières Case Study

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

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

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

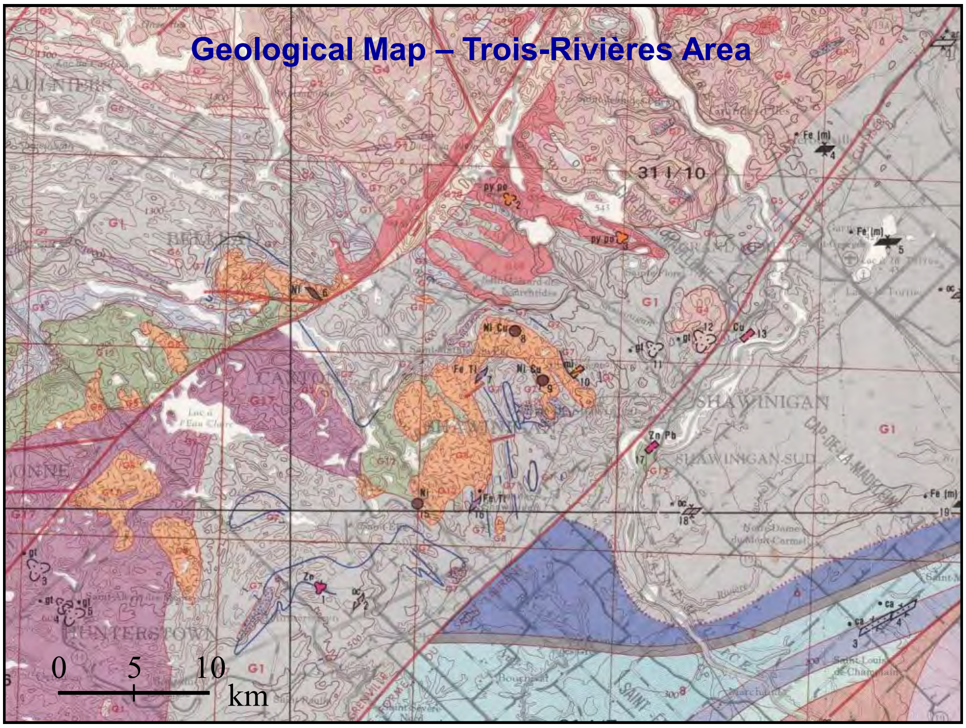
Most Common Secondary Products

- "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

Geological Map – Trois-Rivières Area



Characterisation Methods

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

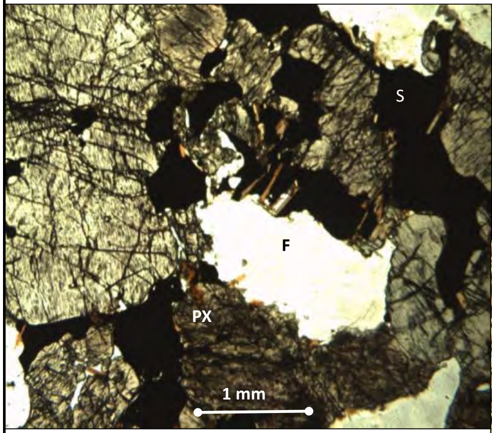
- Macroscopic examination
- Microscopic observation
  - Polarized light microscopy
    - transmitted light
    - reflected light
- Scanning Electron Microscopy (SEM/EDS)
- Electron Probe Microanalysis (EPMA)

St-Boniface Quarry - Lithology

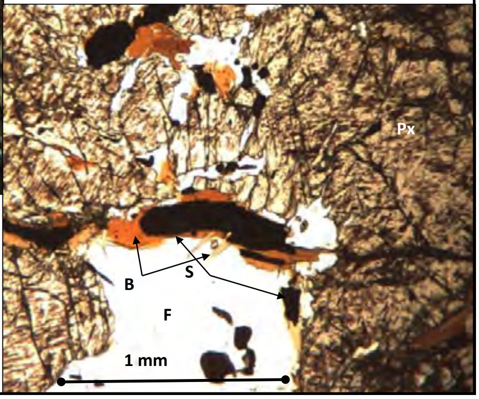
St-Boniface Quarry - Lithology

Petrography & chemistry of rocks

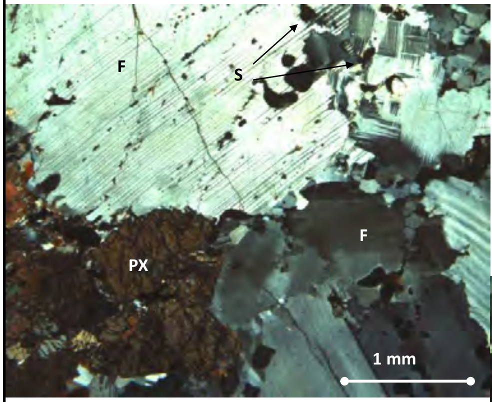
Petrographic Examination of Aggregates

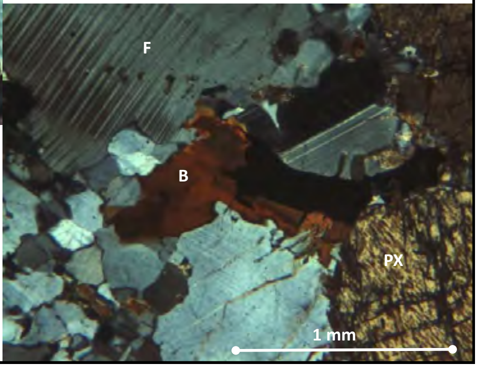


Plane polarized light



Petrographic Examination of Aggregates

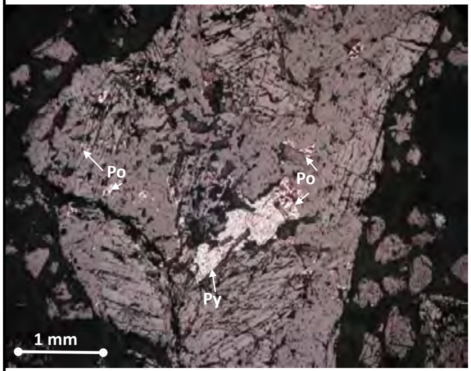


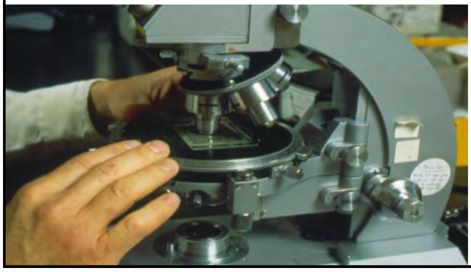


Crossed polarized light

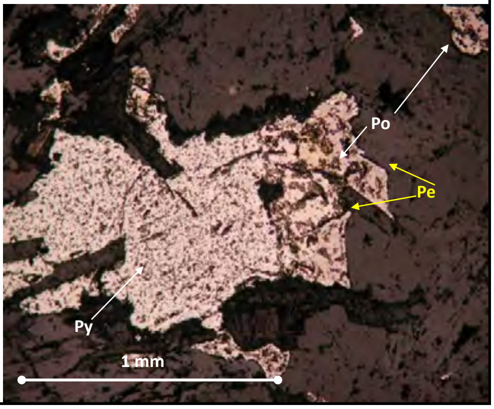
Intrusive mafic rock:
Gabbro - norite
with hypersthene

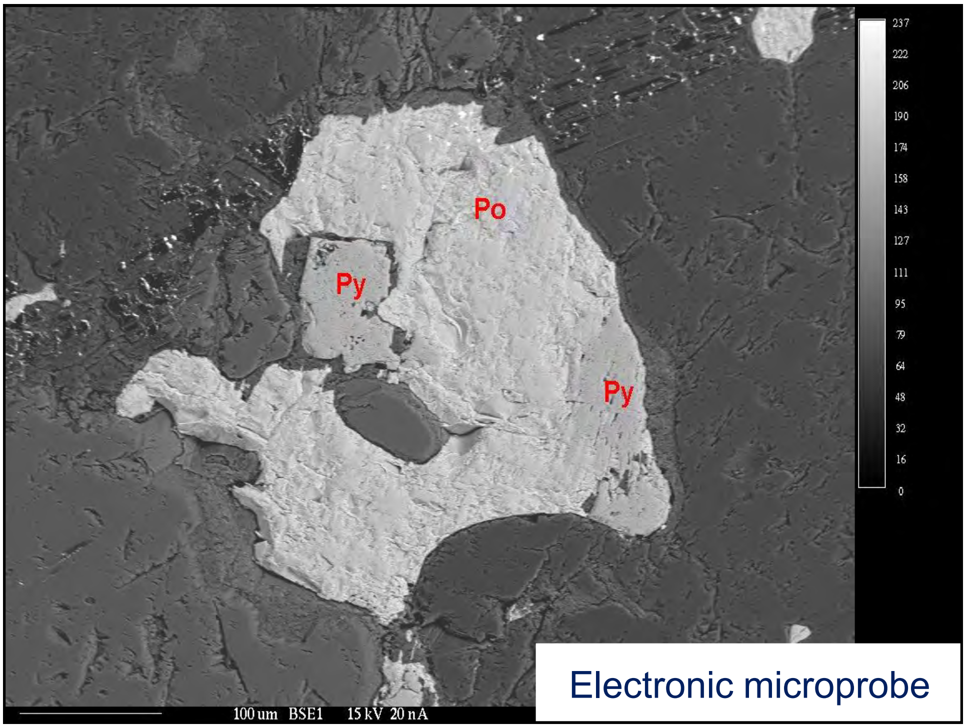
Petrographic Examination of Aggregates



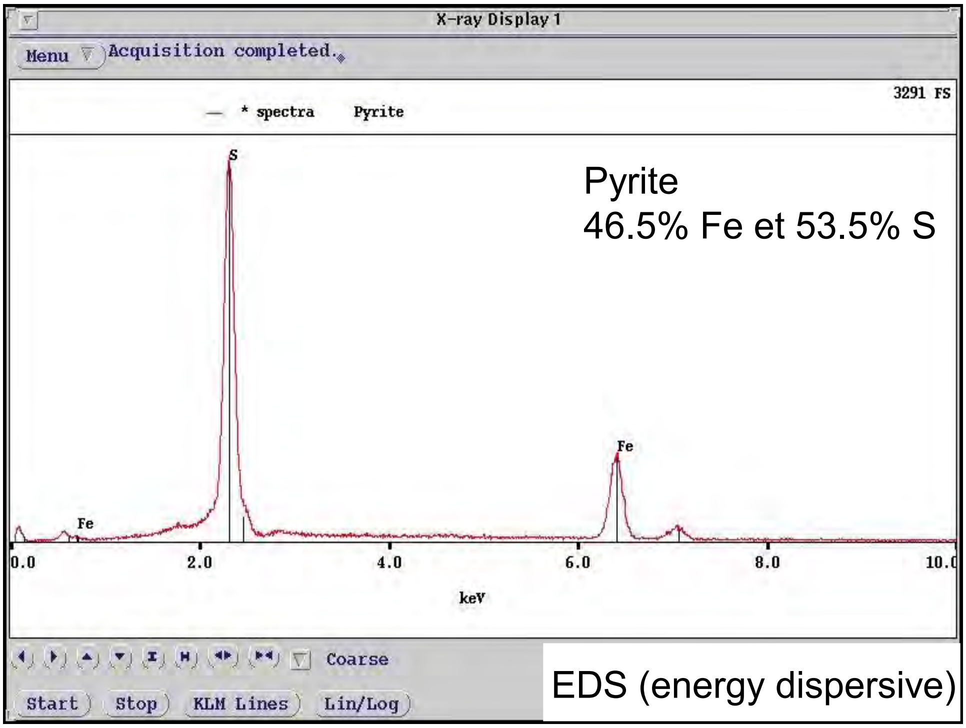


Reflected polarized light





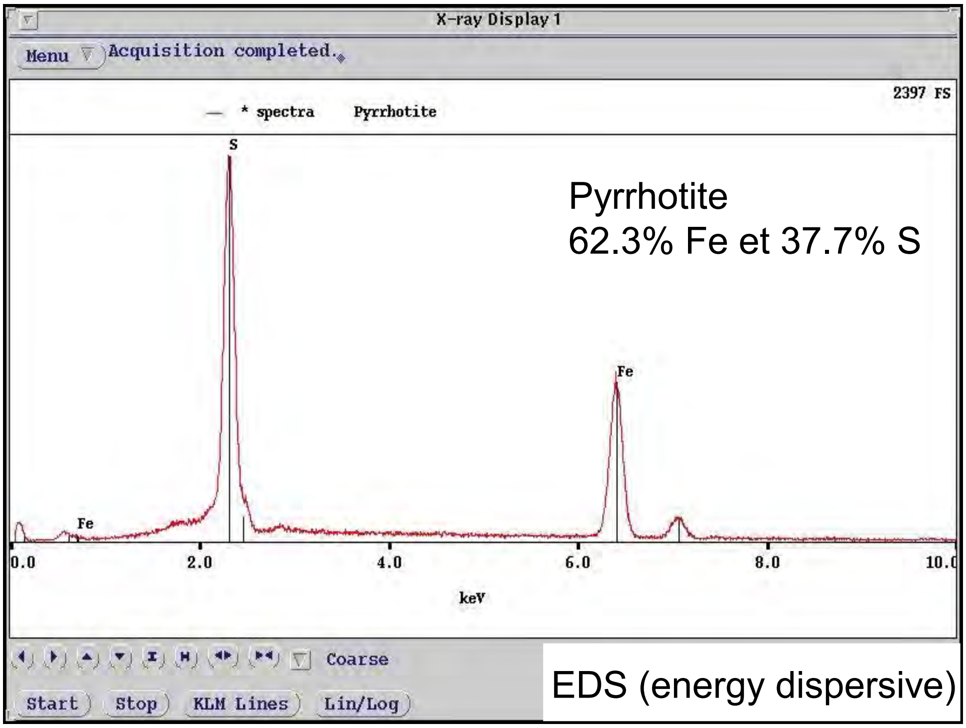
Electronic microprobe



Acquisition completed.

Pyrite
46.5% Fe et 53.5% S

EDS (energy dispersive)



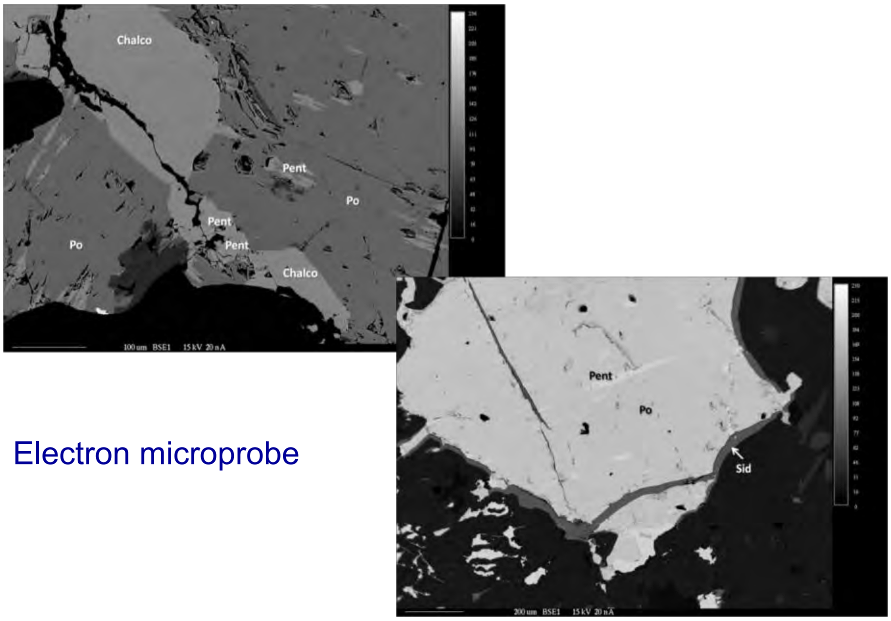
Acquisition completed.

Pyrrhotite

Pyrrhotite
62.3% Fe et 37.7% S

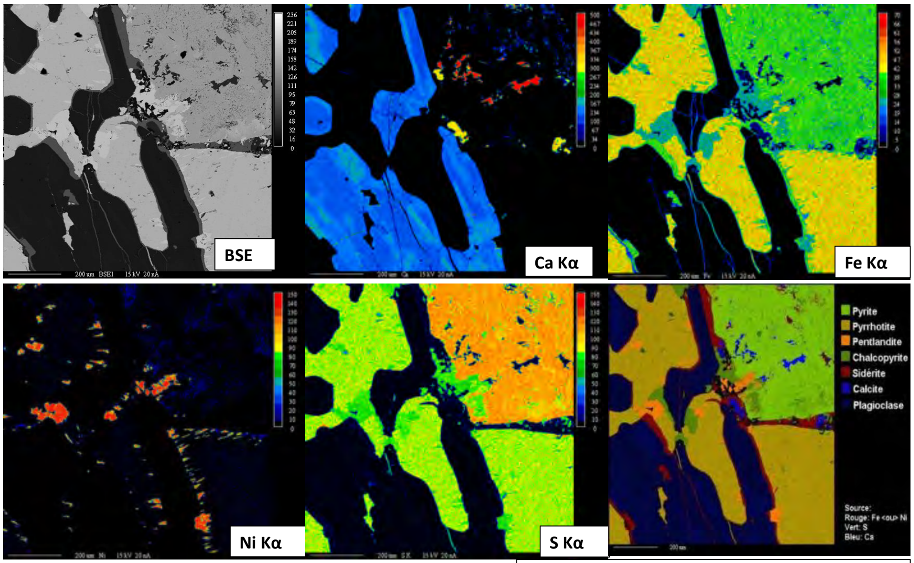
EDS (energy dispersive)

Petrographic examination of rocks



Electron microprobe

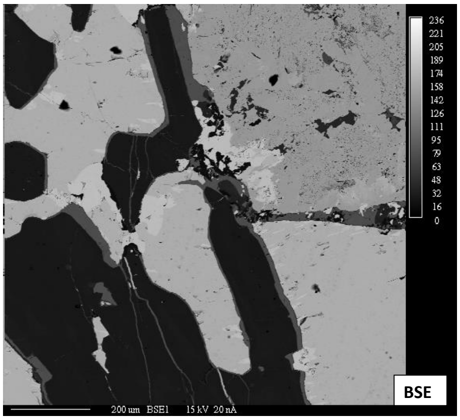
Chemical mapping (microprobe)

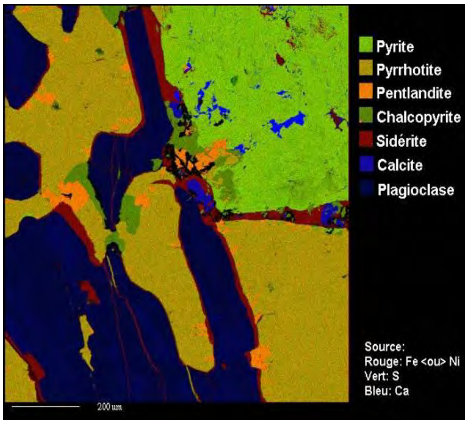


False color reconstruction image :

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

Chemical mapping (microprobe)

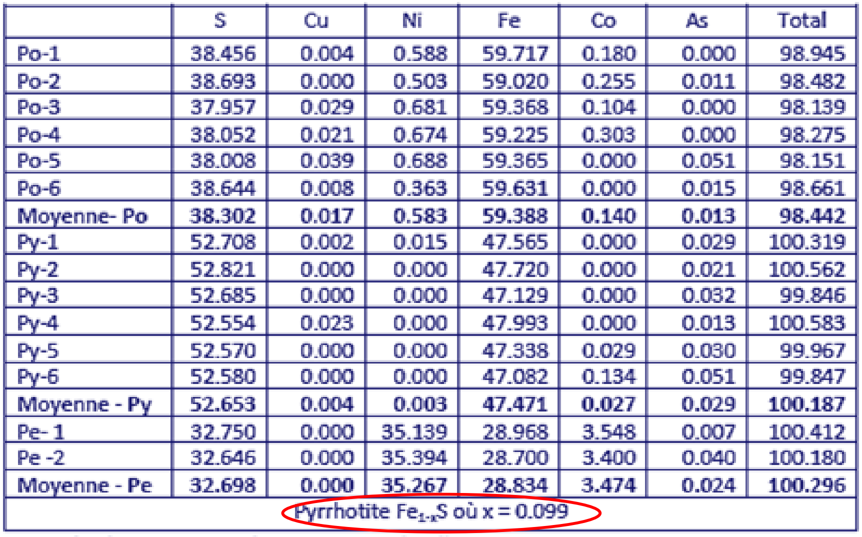




False color reconstruction image :

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

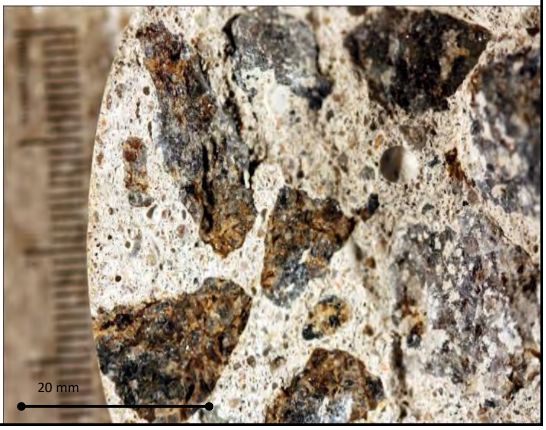
In-Situ Chemical Analysis (EPMA)

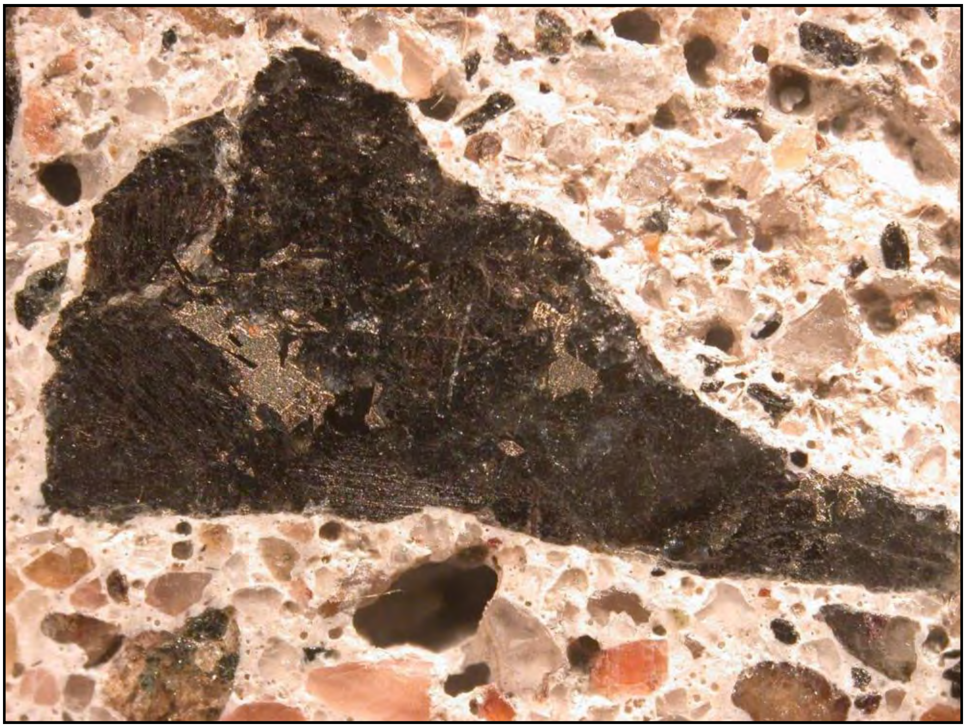


	S	Cu	Ni	Fe	Co	As	Total
Po-1	38.456	0.004	0.588	59.717	0.180	0.000	98.945
Po-2	38.693	0.000	0.503	59.020	0.255	0.011	98.482
Po-3	37.957	0.029	0.681	59.368	0.104	0.000	98.139
Po-4	38.052	0.021	0.674	59.225	0.303	0.000	98.275
Po-5	38.008	0.039	0.688	59.365	0.000	0.051	98.151
Po-6	38.644	0.008	0.363	59.631	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

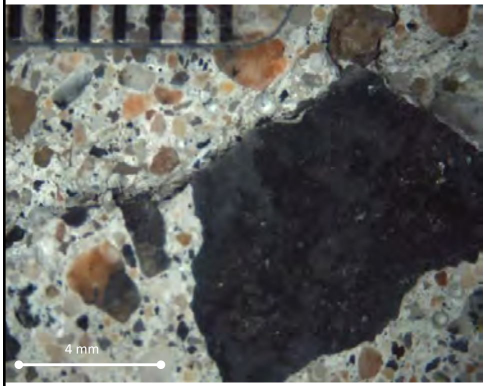
Petrographic Examination of Concrete Samples

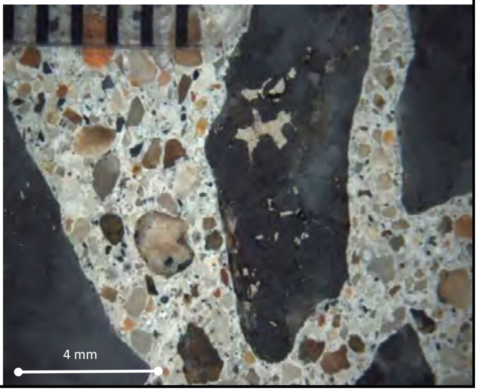





Fig

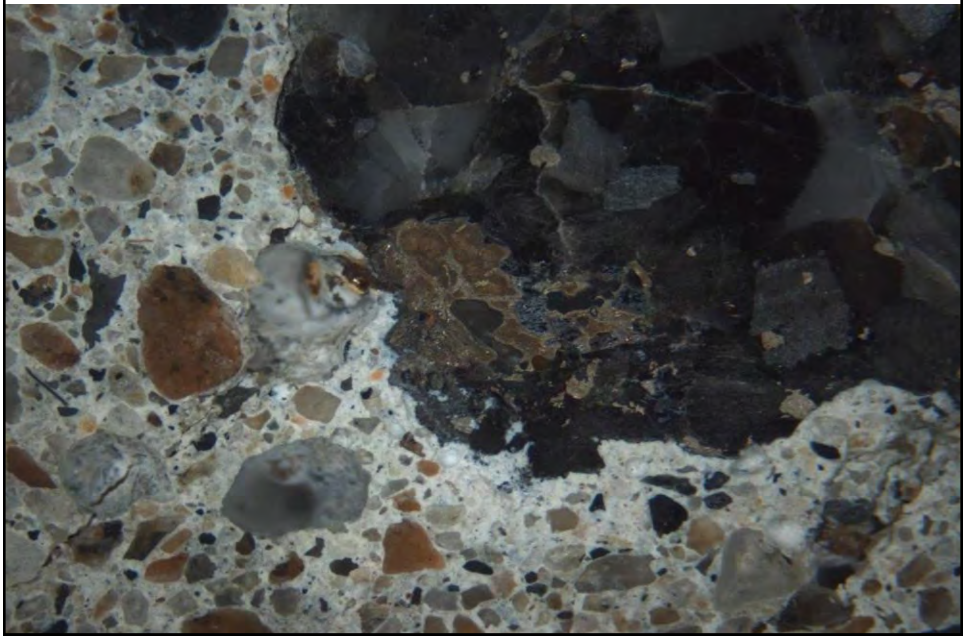
Petrographic Examination of Concrete Samples



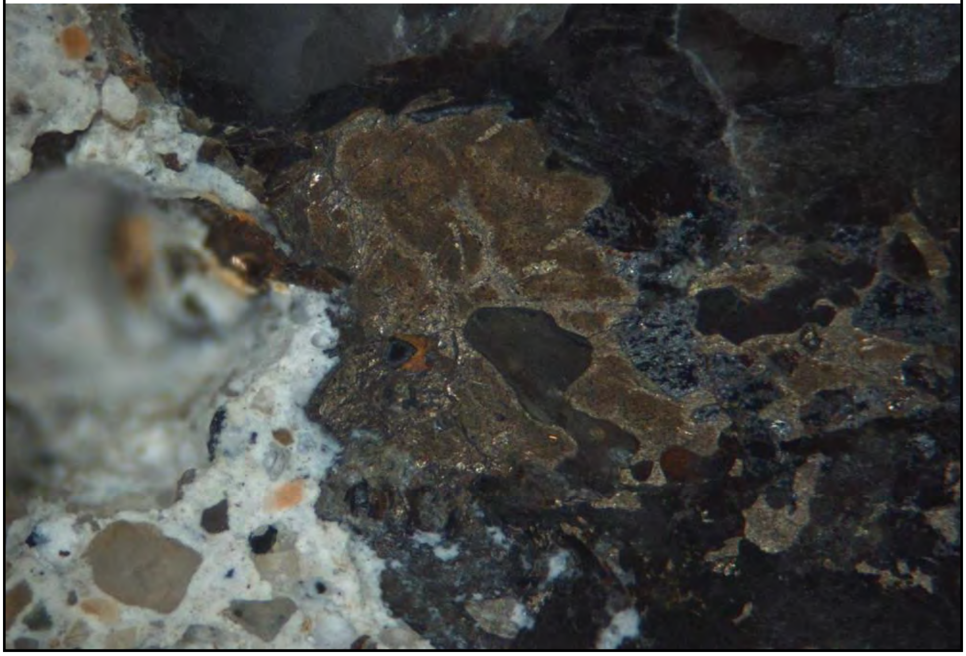


Petrographic Examination of Concrete Samples

Petrographic Examination of Concrete Samples



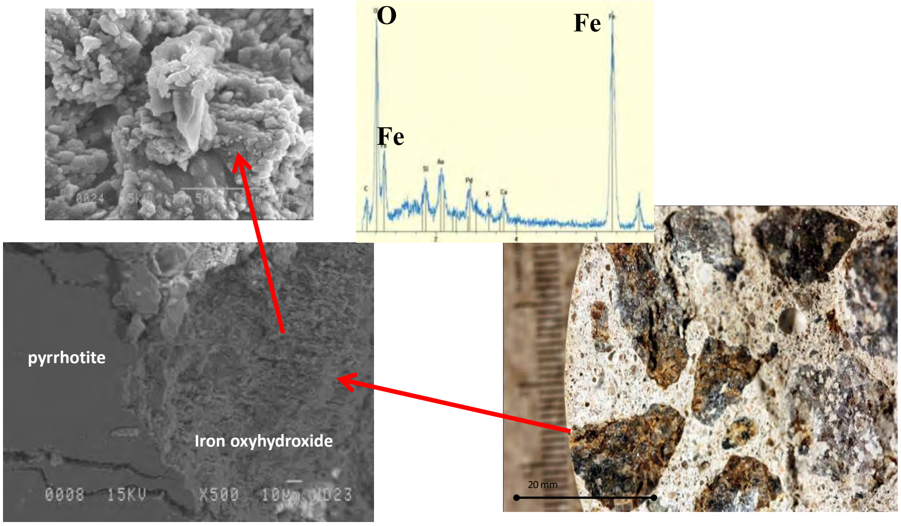
Petrographic Examination of Concrete Samples



Petrographic Examination of Concrete Samples

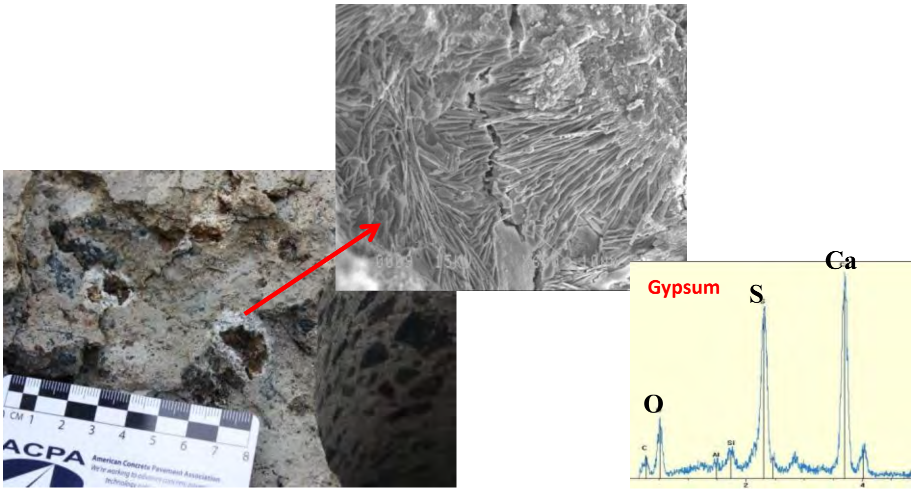
SEM examination of concrete samples

Pyrrhotite + oxygen + water → goethite + sulfuric acid



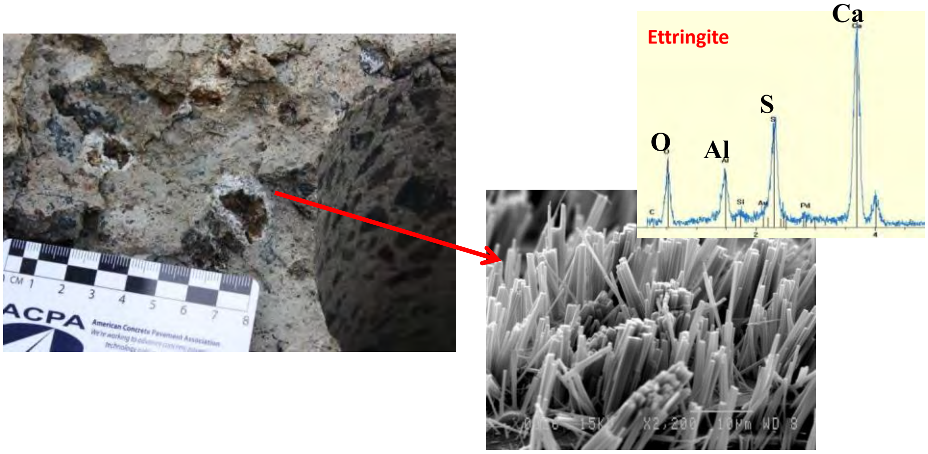
SEM examination of concrete samples

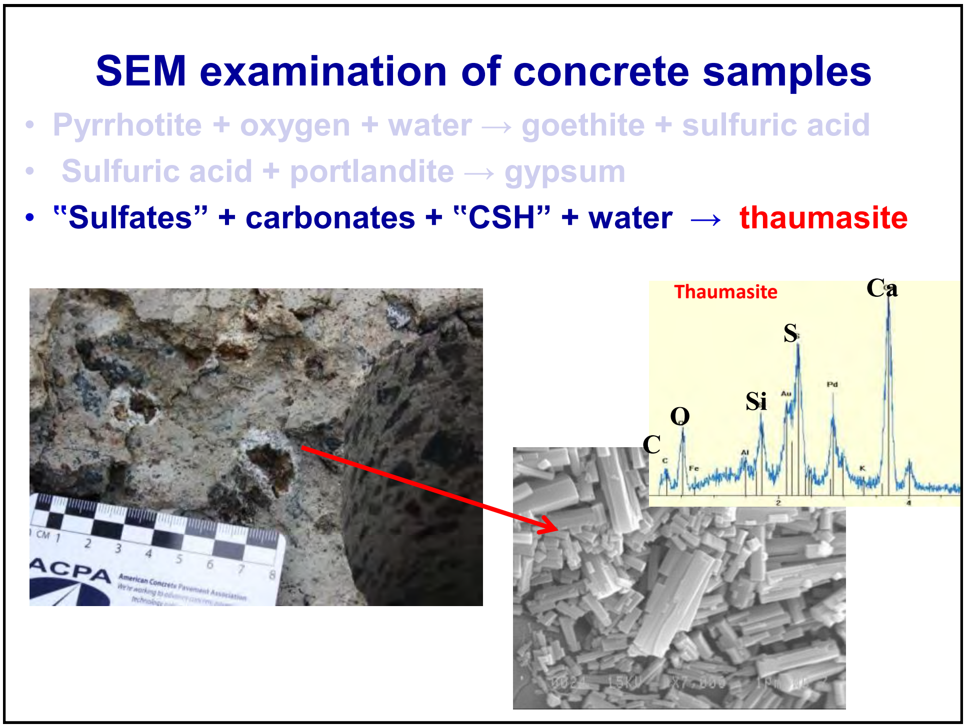
- Pyrrhotite + oxygen + water → goethite + sulfuric acid
- Sulfuric acid + portlandite (cement) → gypsum



SEM examination of concrete samples

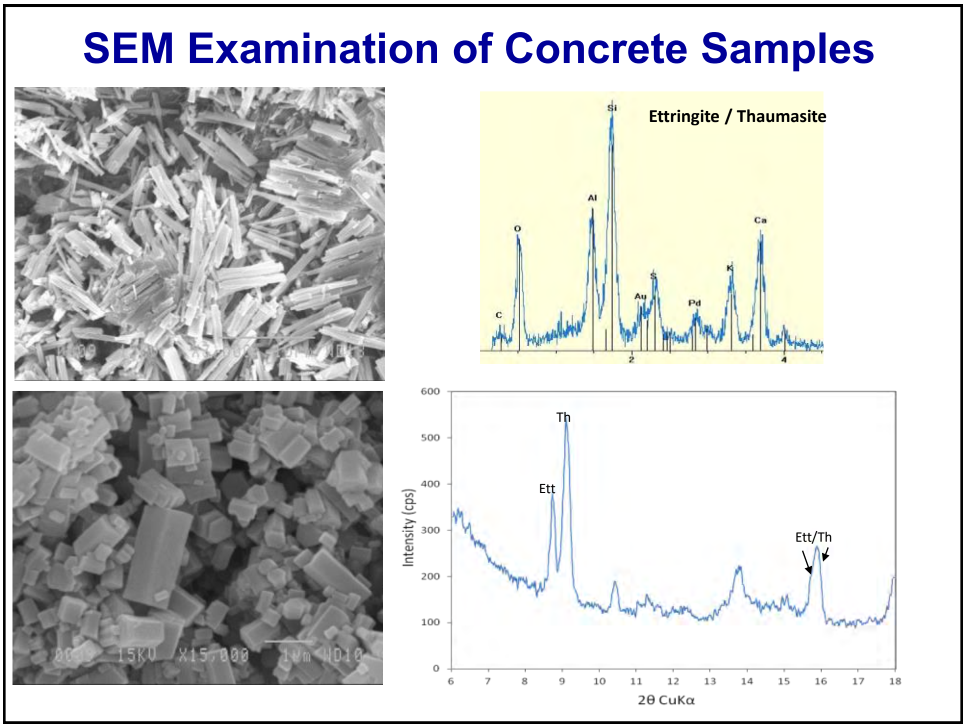
- Pyrrhotite + oxygen + water → goethite + sulfuric acid
- Sulfuric acid + portlandite → gypsum
- C_3A (cement) + gypsum "sulfates" + water → ettringite





SEM examination of concrete samples

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

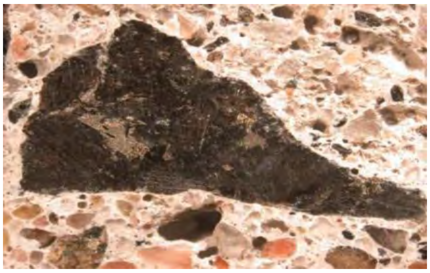


SEM Examination of Concrete Samples

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

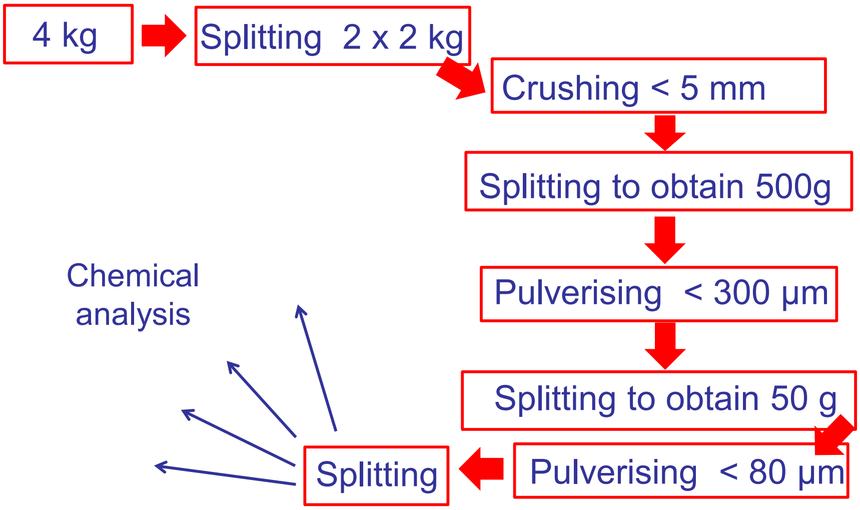
Sub-sample

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

---

Chemical approach (S_{total})

Sample preparation method



4 kg

Splitting 2 x 2 kg

Crushing < 5 mm

Splitting to obtain 500g

Pulverising < 300 µm

Splitting to obtain 50 g

Pulverising < 80 µm

Splitting

Chemical analysis

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

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Introduction

Isochemical sulfate reactions are related to sulfate availability rather than amount
F. P. Glasser 1998

- 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 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

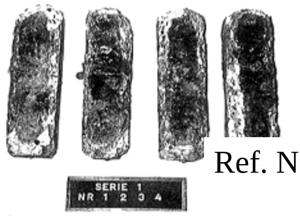
Non-oxidised ground water: pH = 5-6 ($FeSO_{4(aq)}$)
Oxidised water (Vadose): pH = <3-4 ($Fe(OH)_2 + H_2SO_4$)

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)

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

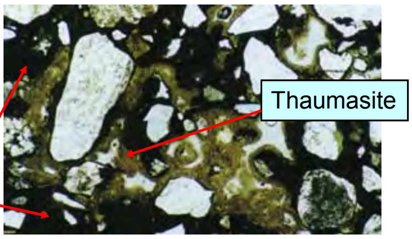
Modern sprayed concrete was attacked by thaumasite! Ettringite was unimportant (NPRA-BRE work)

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.



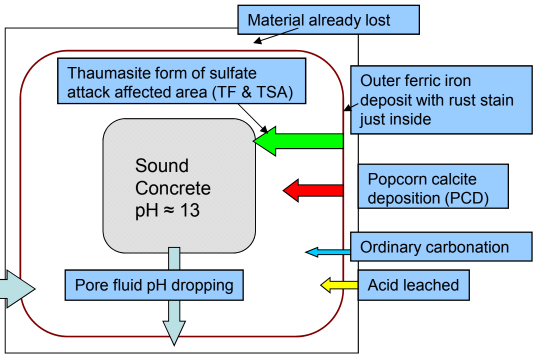
Thaumasite

Intact cement paste (C-S-H)

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



Material already lost

Thaumasite form of sulfate attack affected area (TF & TSA)

Outer ferric iron deposit with rust stain just inside

Sound Concrete pH ≈ 13

Popcorn calcite deposition (PCD)

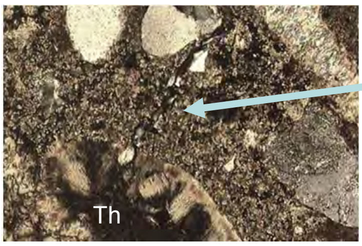
Ordinary carbonation

Pore fluid pH dropping

Acid leached

TSA-PCD in Alum shale environment

(Hagelia & Sibbick, 2009)

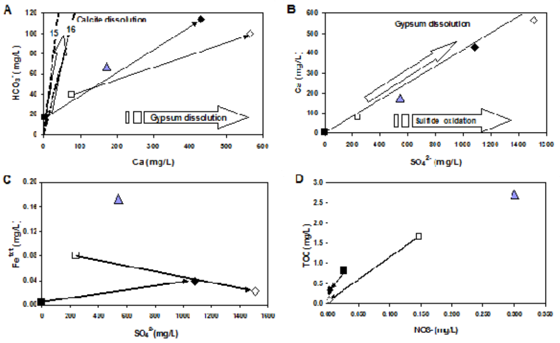


Full scale TSA most efficient at expense of PCD (internal carbonation) and strongly depleted CSH!
Fast degradation due to thaumasite is clearly linked to Ca-leaching!
Typical of mixes without pozzolana

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)

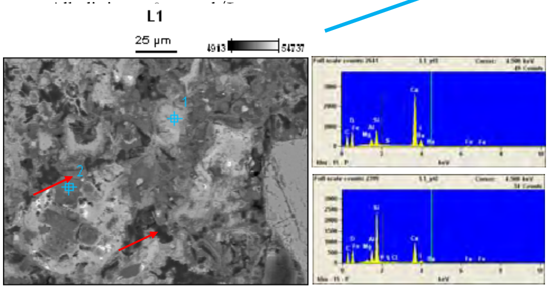
Anhydrite/gypsum may also represent source of sulfate



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)

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

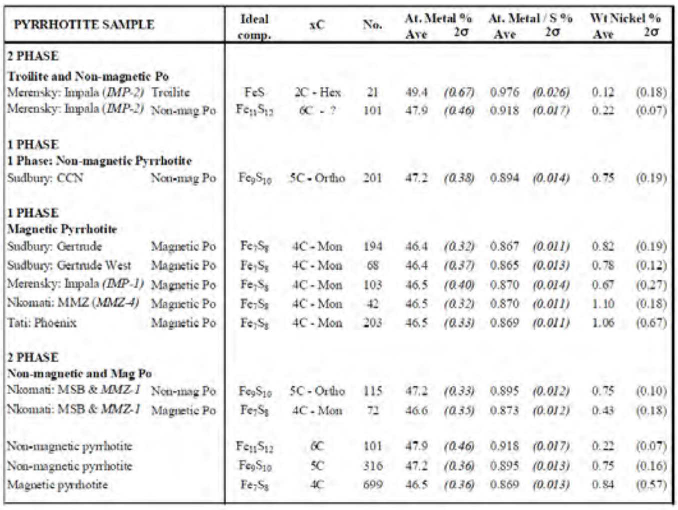
- Orthorhombic
- Hexagonal
- Monoclinic

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

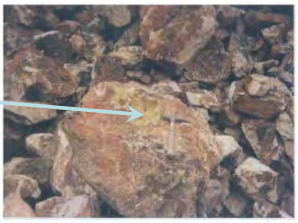
Pyrrhotite varieties (University of Pretoria)



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

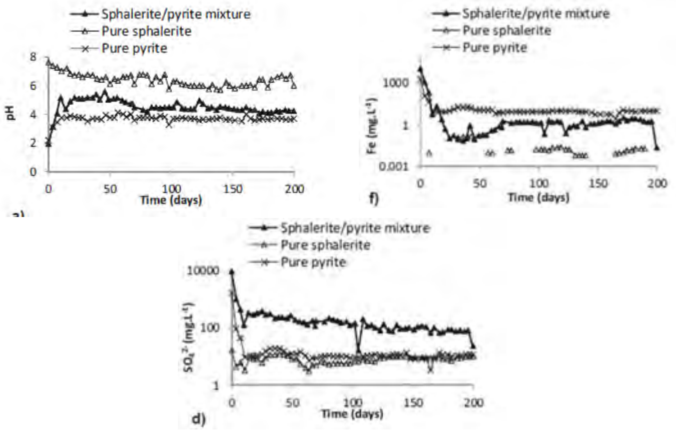
NB! May be mistaken for iron red rust in thin section

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

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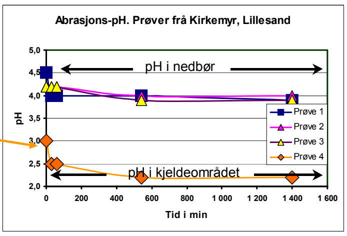
ARD example (no buffer)

Jarosite–FeOOH crust
no sulfide (Prøve 4)

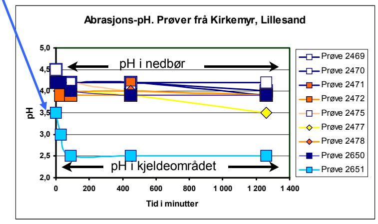
Other samples with py and po
Reached pH = 4

Selected field samples:



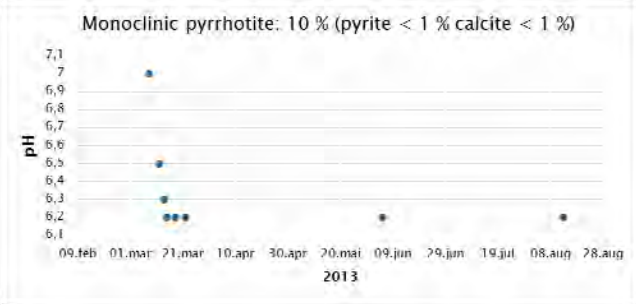
- **Fresh pyrrhotite: pH = 4.2**
- **Degraded pyrrhotite pH = 4-3.8**
- **Fresh pyrite from joints pH ca. 2.5**
- **Oxidised pyrite from joints, pH ca. 4**

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



10 wt. % pyrrhotite – yet no real acidification!

% pyrrhotite from XRD (Rietveld refinement)

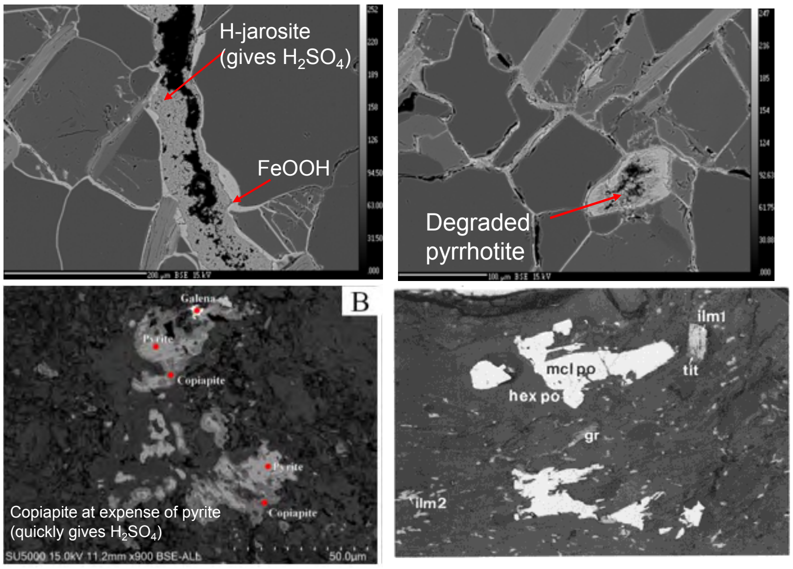


Hornfels
Very hard rock!

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



Copiapite at expense of pyrite
(quickly gives H_2SO_4)

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

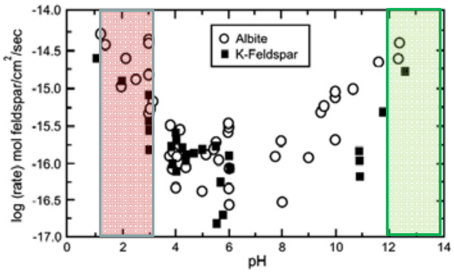
Characterisation by petrographic and other techniques is mandatory for realistic understanding!

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

ARD classification by detailed petrography gives better prediction

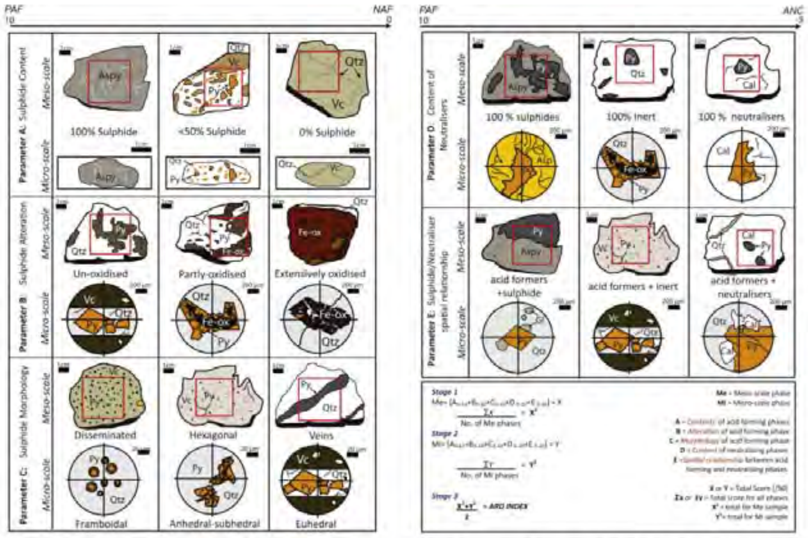


Figure 72 - Cartoon examples of ARD Index method for classification of a rocks ARD potential (Parbhakar-Fox et al., 2011)

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.

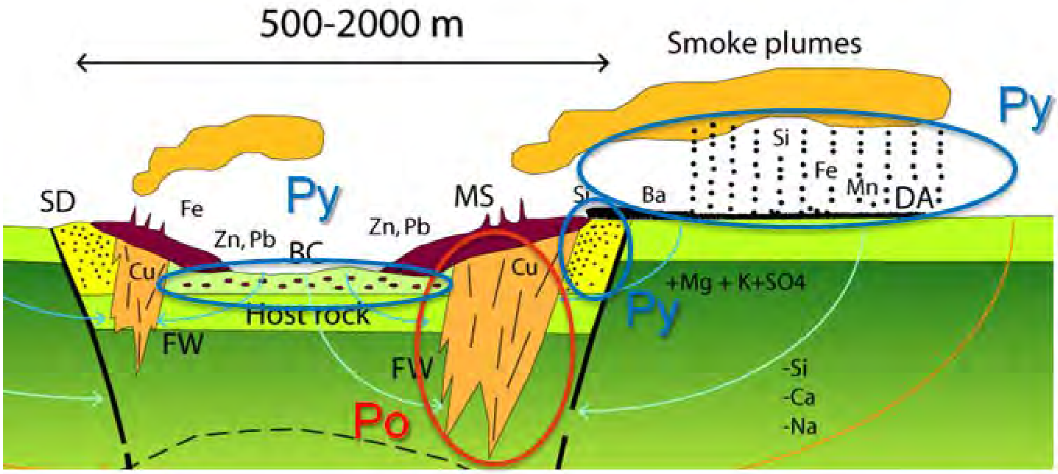
Iron sulphides: Formation and conditions for occurrence in bedrock

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.

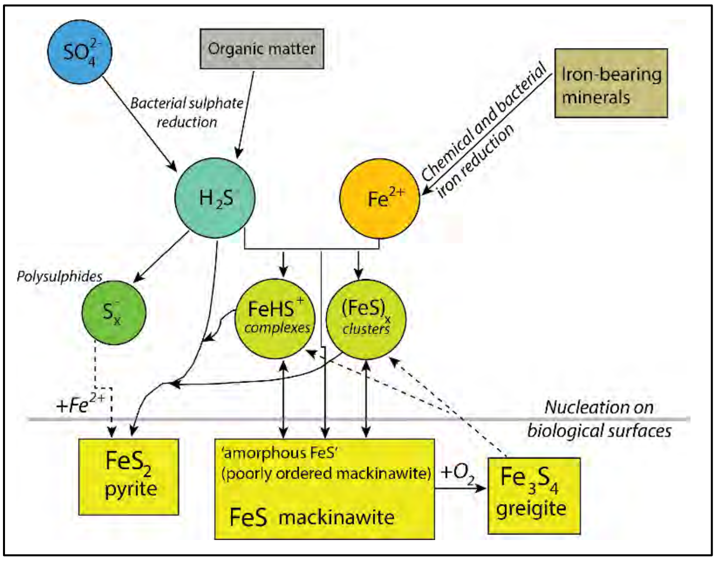


Schematic model of massive sulphide deposit (VMS), showing the main deposits of pyrite (Py) and pyrrhotite (Po) (Modified from Franklin et al. 2005).

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)

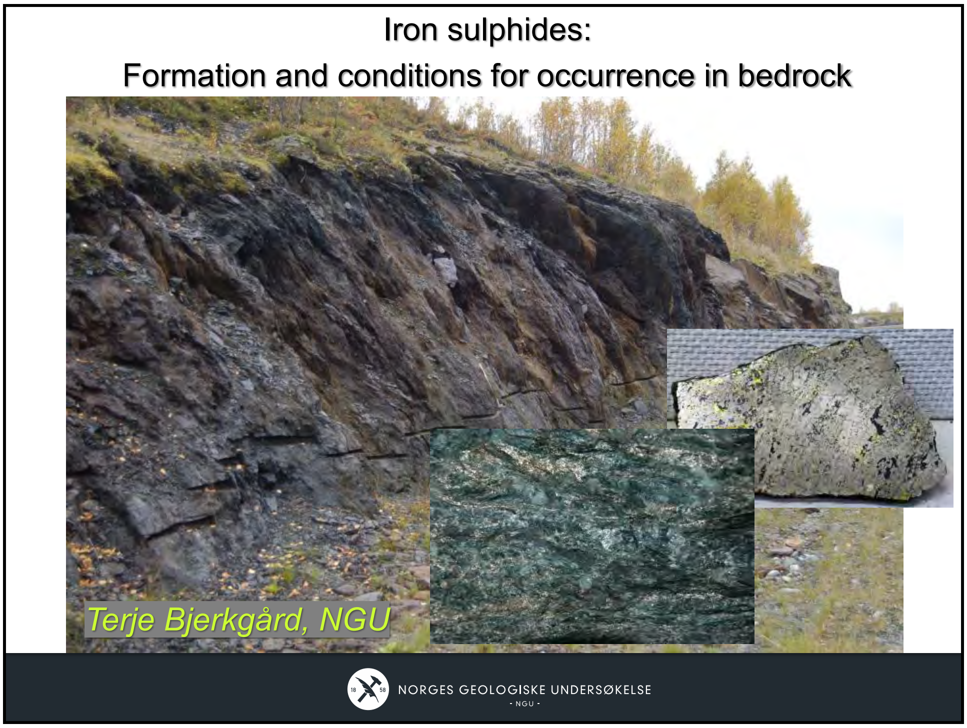
Pyrrhotite is generally much more susceptible to oxidation than pyrite, but especially sedimentary (framboidal) pyrite is readily attacked by oxidising solutions. Marcasite, mackinawite and greigite are rare, but may locally contribute to acid drainage.

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

Terje Bjerkgård, NGU

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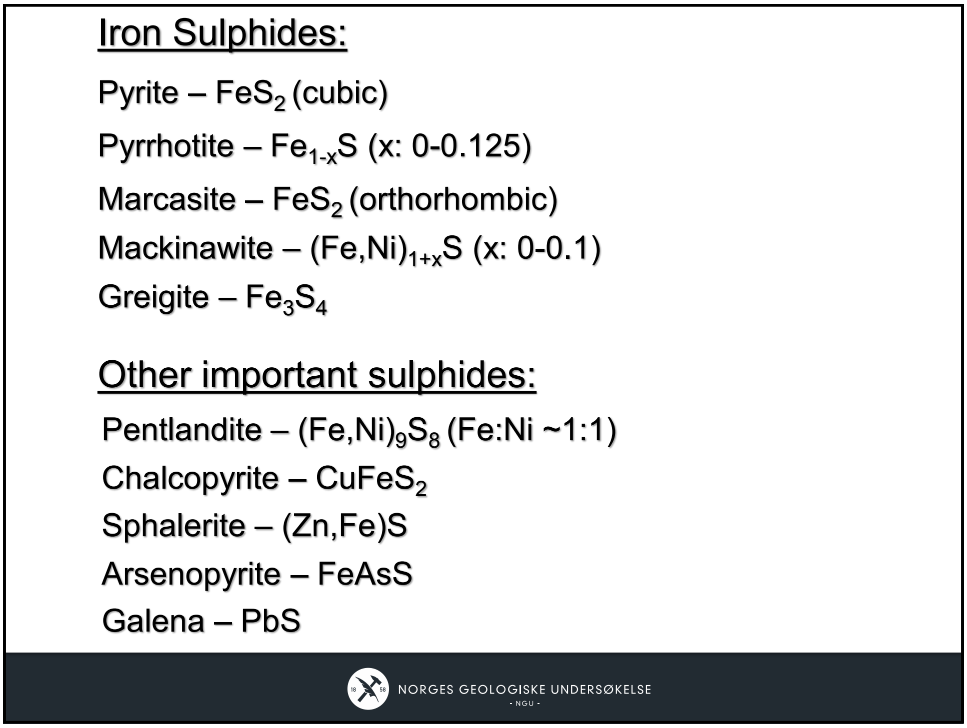

Iron Sulphides:

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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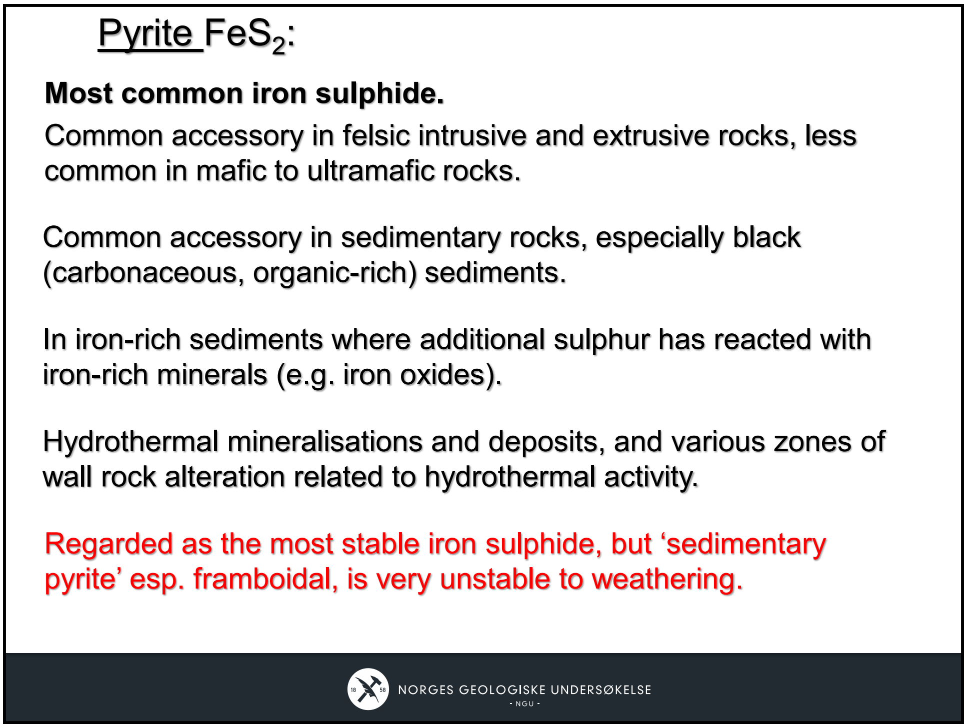
2



Pyrite 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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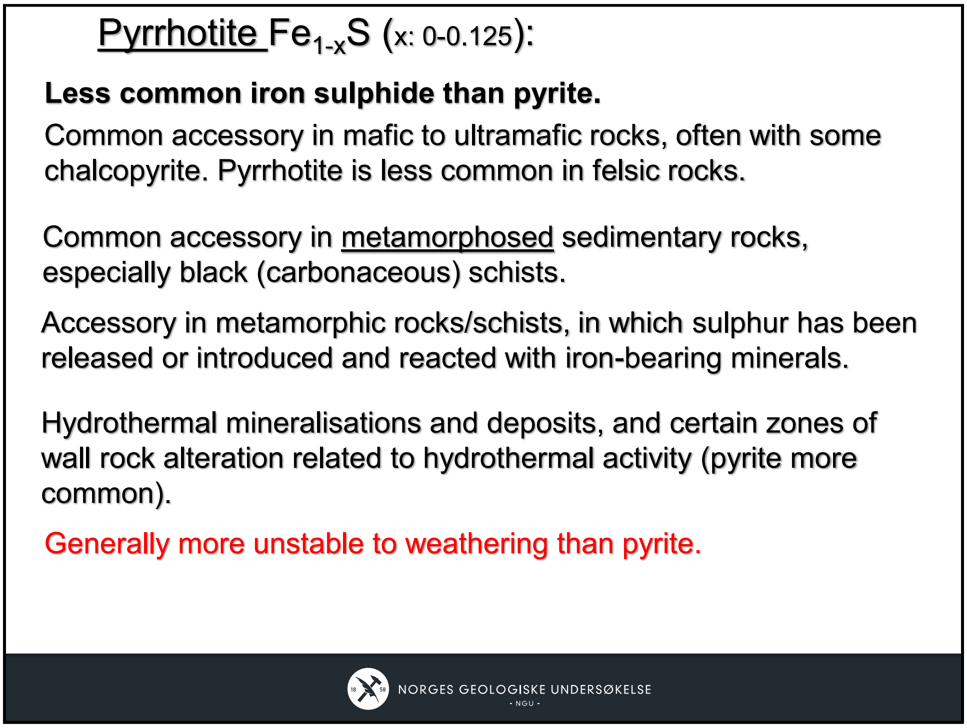

Pyrrhotite $Fe_{1-x}S$ (x: 0-0.125):

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

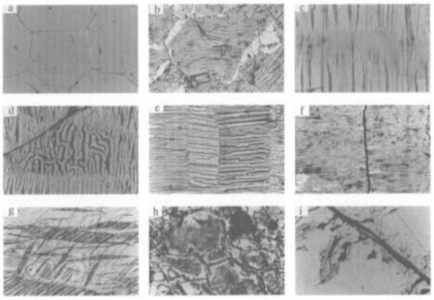
Fe_9S_{10} – 5C (monoclinic)

$Fe_{10}S_{11}$ – 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

Marcasite FeS_2:

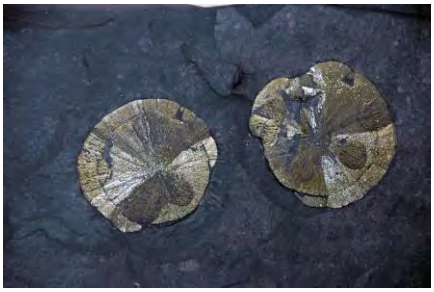
Marcasite is formed as a primary mineral under low-temperature highly acidic conditions (generally pH<5).

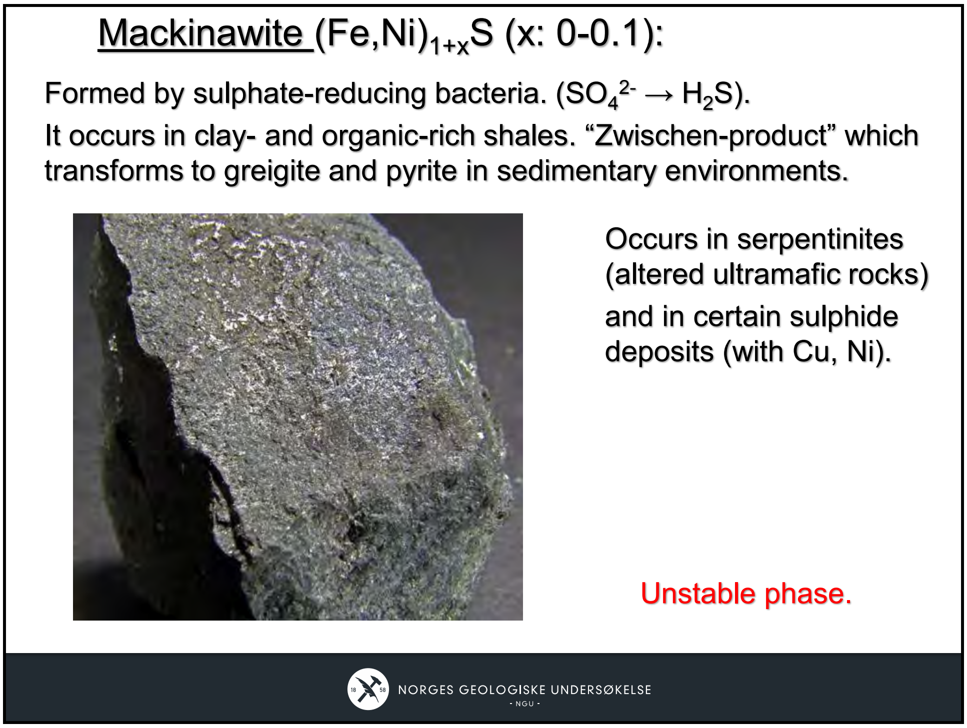
It occurs in sedimentary rocks (shales, limestones and low grade coals) as well as in low temperature hydrothermal veins.

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.





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

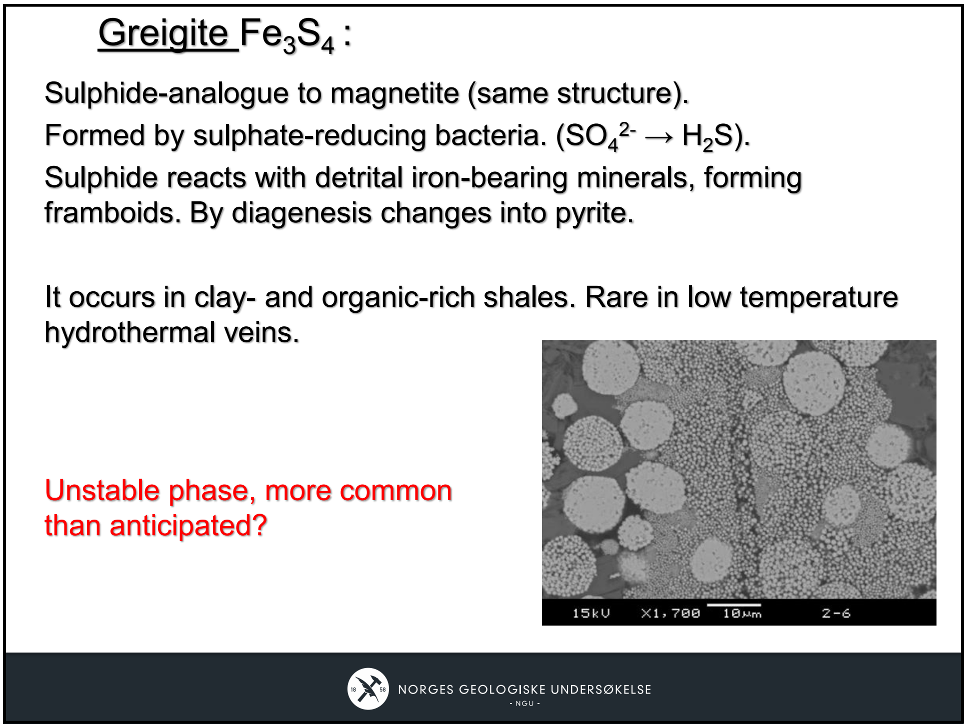
Formed by sulphate-reducing bacteria. ($SO_4^{2-} \rightarrow H_2S$).

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.



Greigite Fe_3S_4 :

Sulphide-analogue to magnetite (same structure).

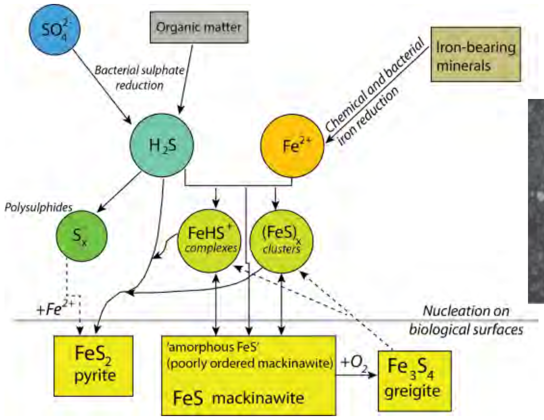
Formed by sulphate-reducing bacteria. ($SO_4^{2-} \rightarrow H_2S$).

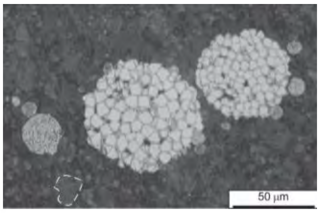
Sulphide reacts with detrital iron-bearing minerals, forming framboids. By diagenesis changes into pyrite.

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

Unstable phase, more common than anticipated?

Formation of mackinawite, greigite and pyrite in sedimentary environments:





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

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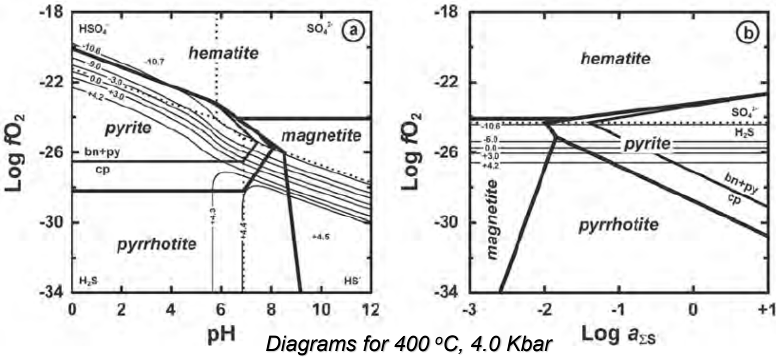
Pyrrhotite and pyrite stabilities:



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.

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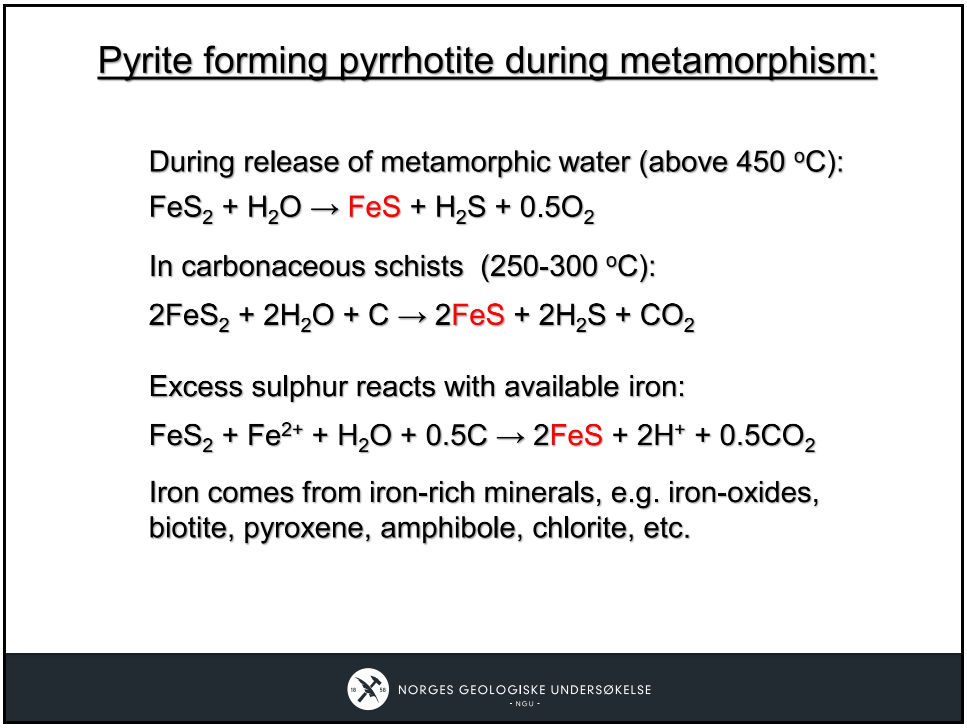


Pyrite forming pyrrhotite during metamorphism:

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

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

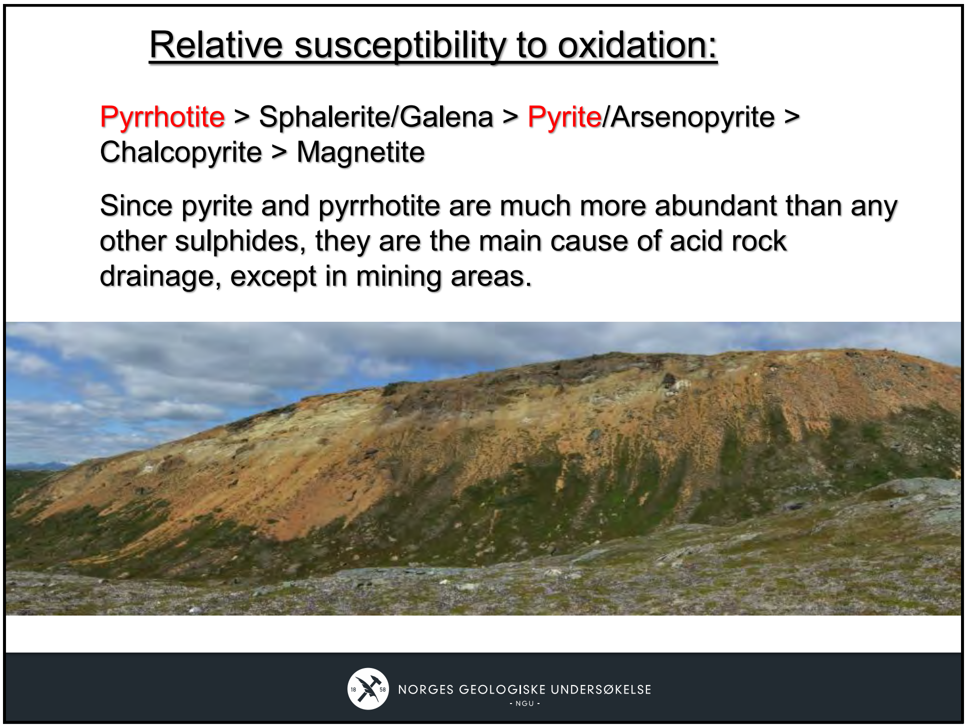
In carbonaceous schists (250-300 °C):

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

Excess sulphur reacts with available iron:

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

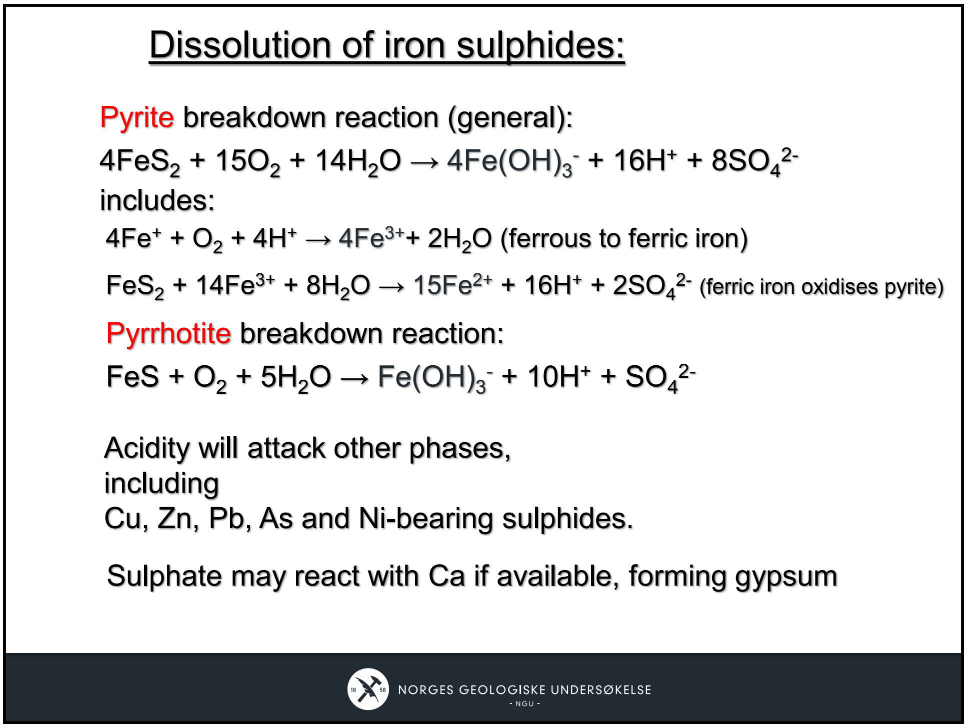
Iron comes from iron-rich minerals, e.g. iron-oxides, biotite, pyroxene, amphibole, chlorite, etc.



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.



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)

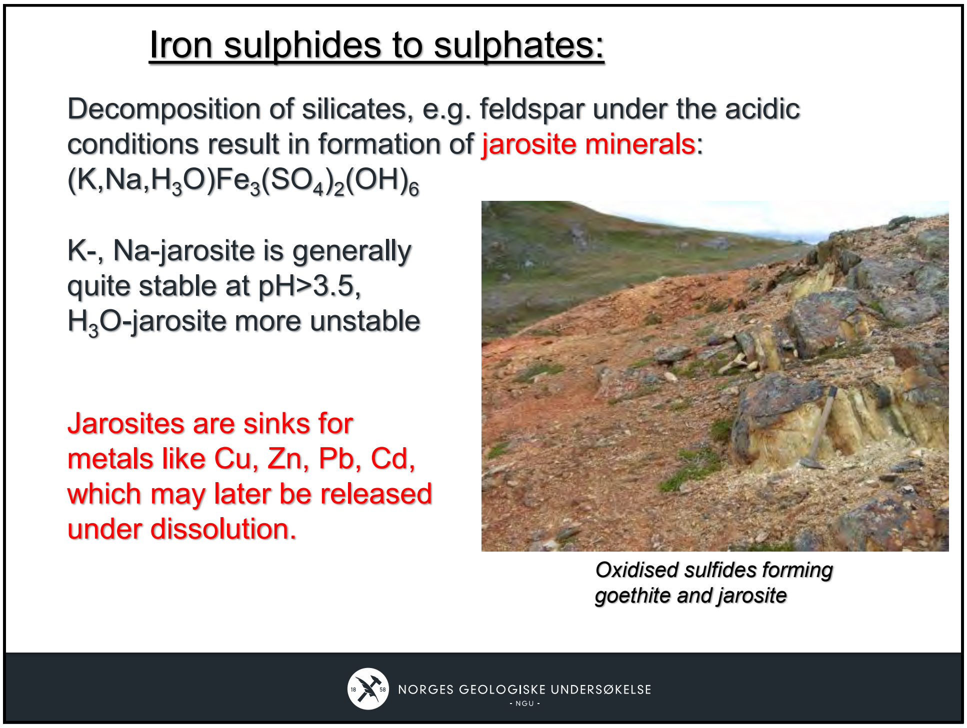
$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 16H^+ + 2SO_4^{2-}$ (ferric iron oxidises pyrite)

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



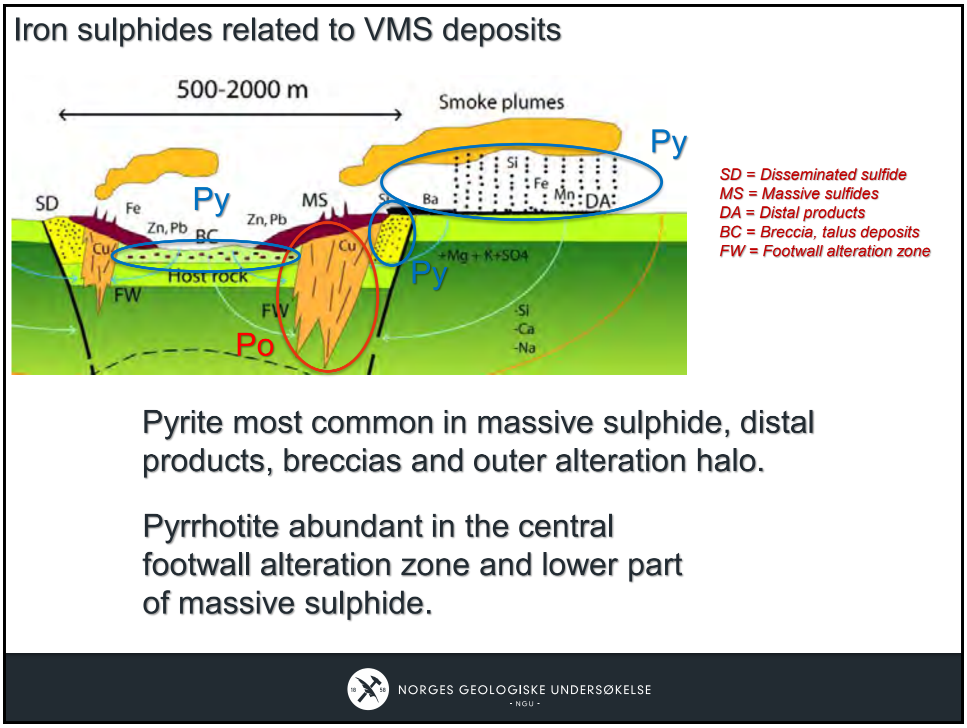
Iron sulphides to sulphates:

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

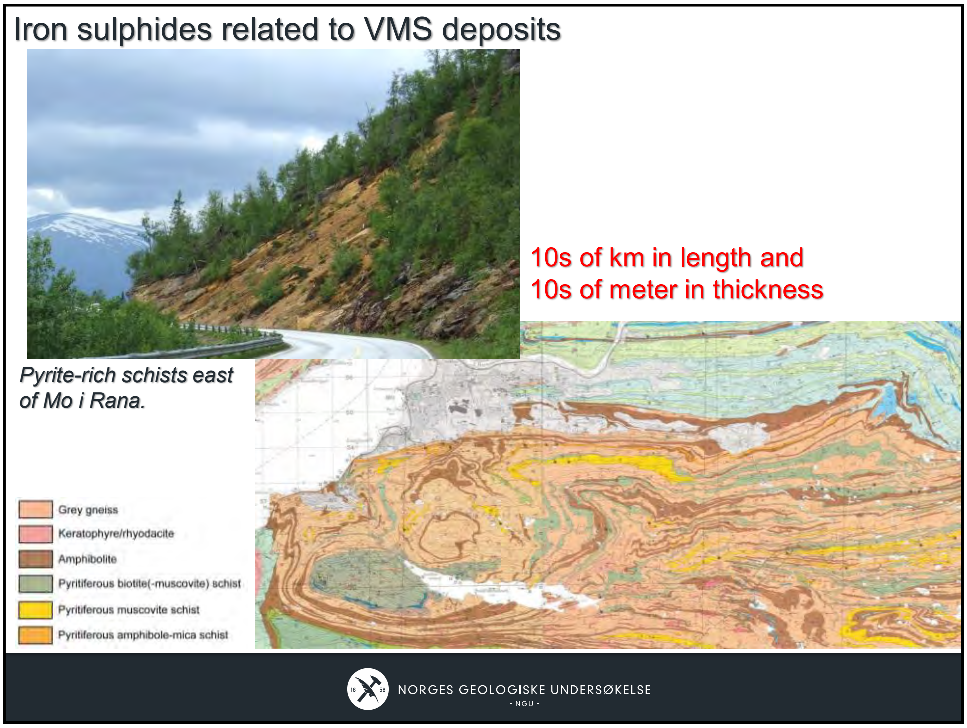


Iron sulphides related to VMS deposits

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.

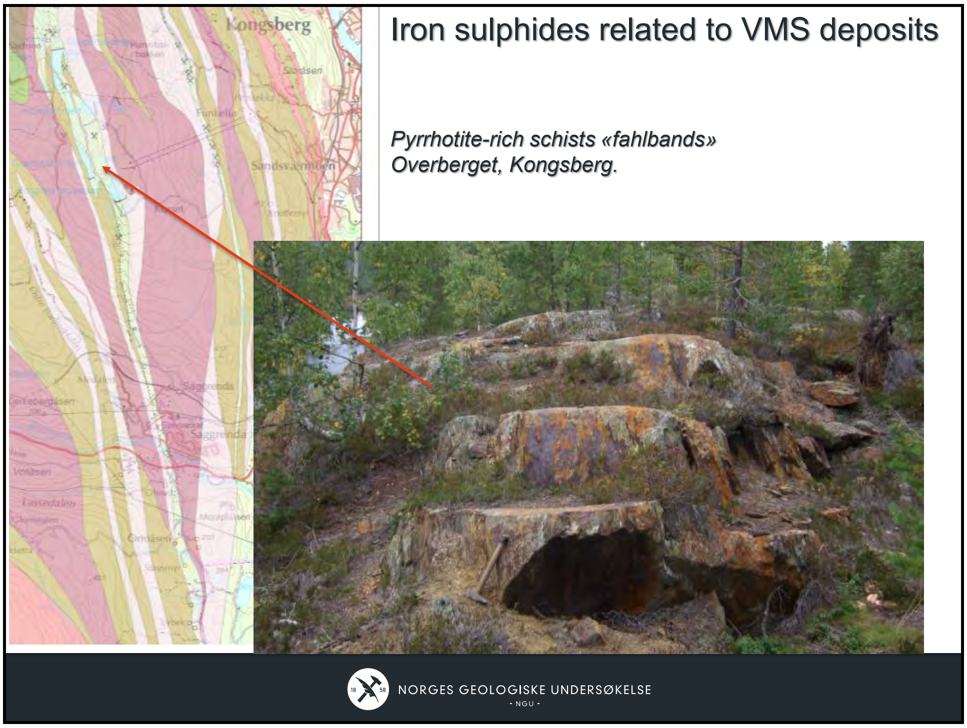
Pyrrhotite abundant in the central footwall alteration zone and lower part of massive sulphide.



Iron sulphides related to VMS deposits

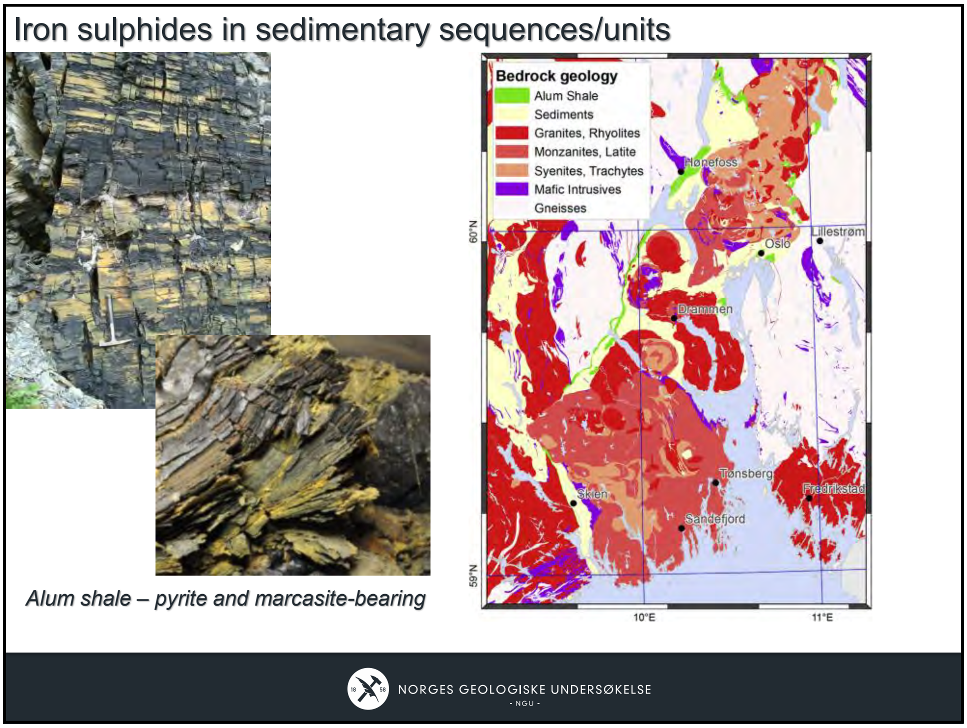
10s of km in length and
10s of meter in thickness

Pyrite-rich schists east of Mo i Rana.



Iron sulphides related to VMS deposits

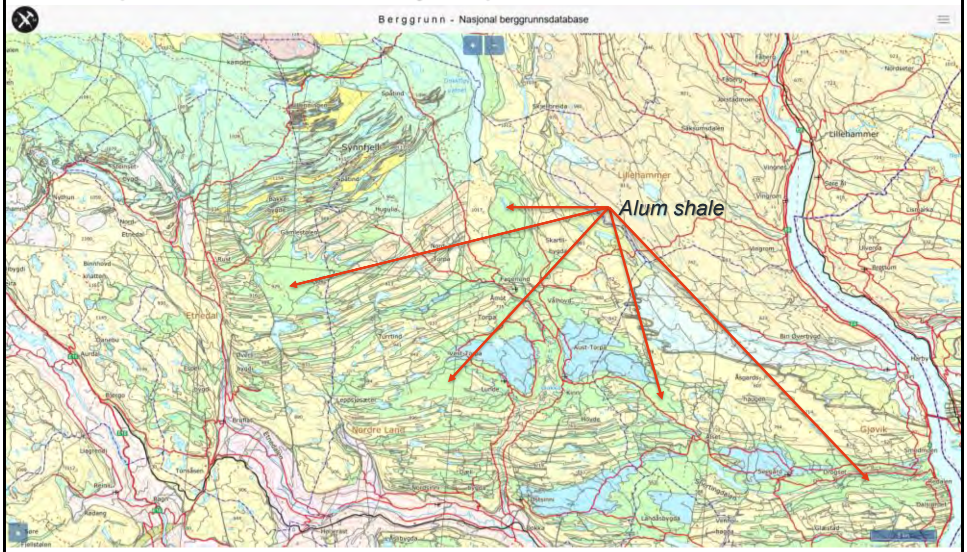
Pyrrhotite-rich schists «fahlbands»
Overberget, Kongsberg.



Iron sulphides in sedimentary sequences/units

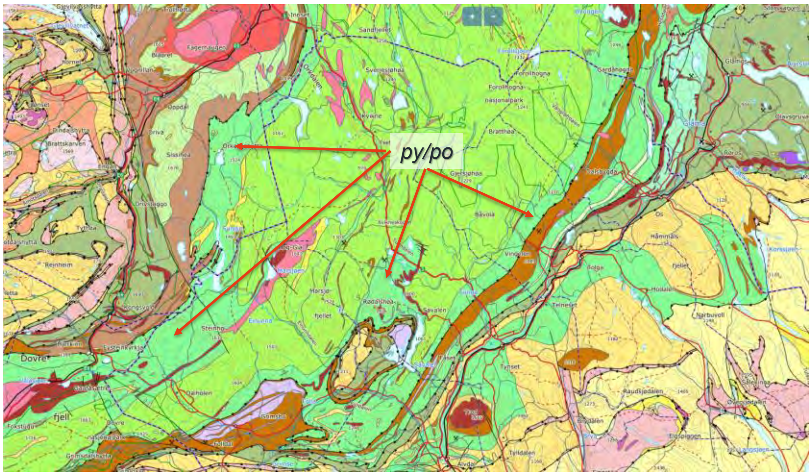
Alum shale – pyrite and marcasite-bearing

Iron sulphides in sedimentary sequences/units

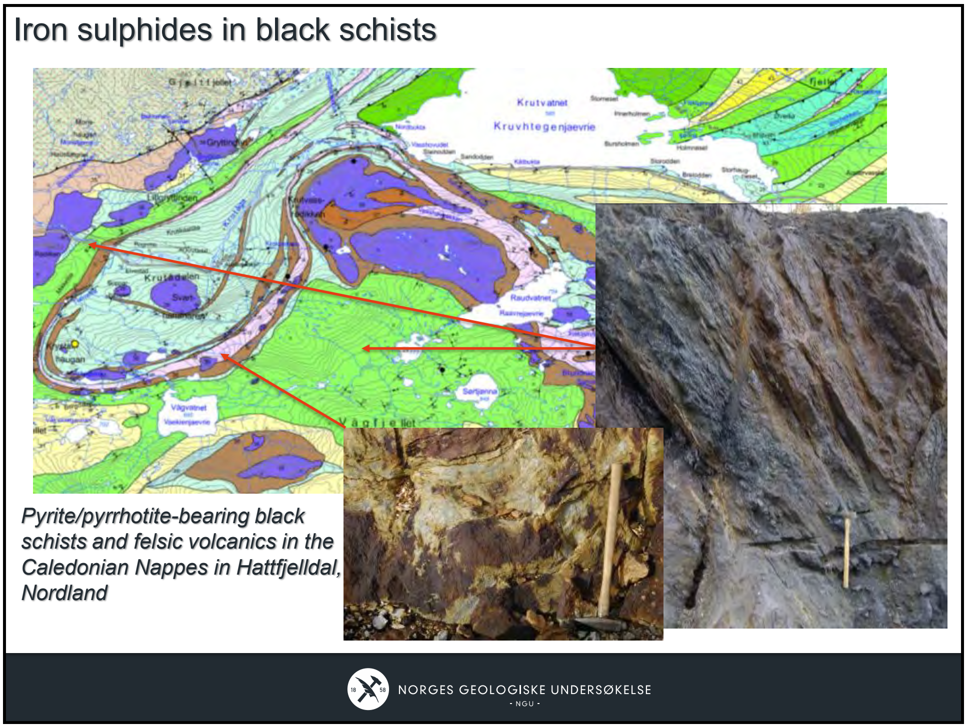


Pyritiferous schists in the parautochthonous below the Caledonian Nappes

Iron sulphides in black schists



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



Iron sulphides in black schists

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

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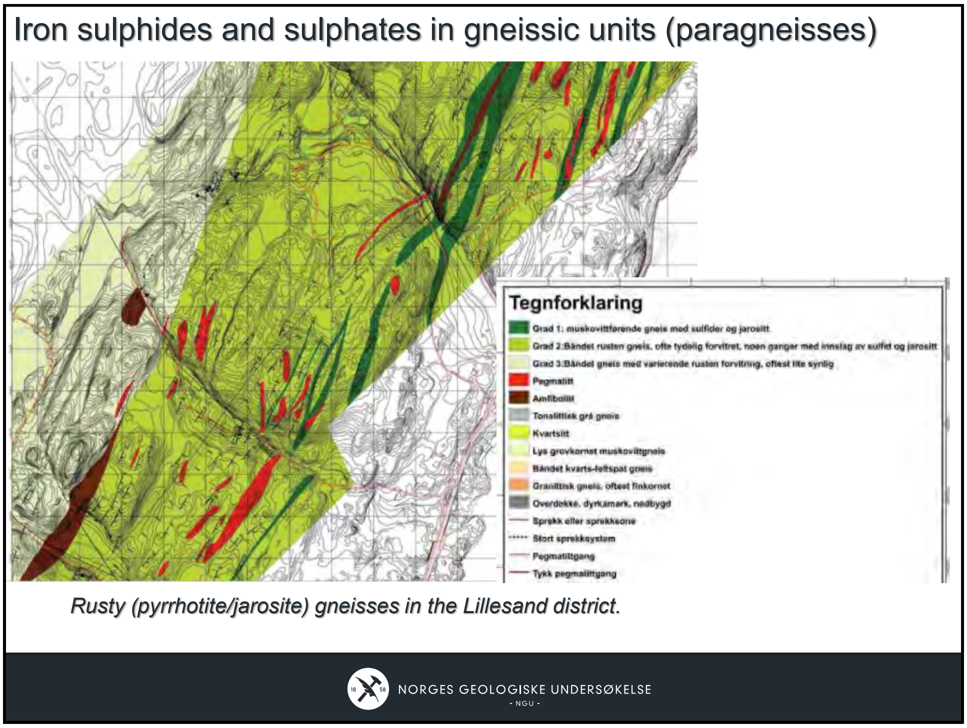

Iron sulphides and sulphates in gneissic units (paragneisses)

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

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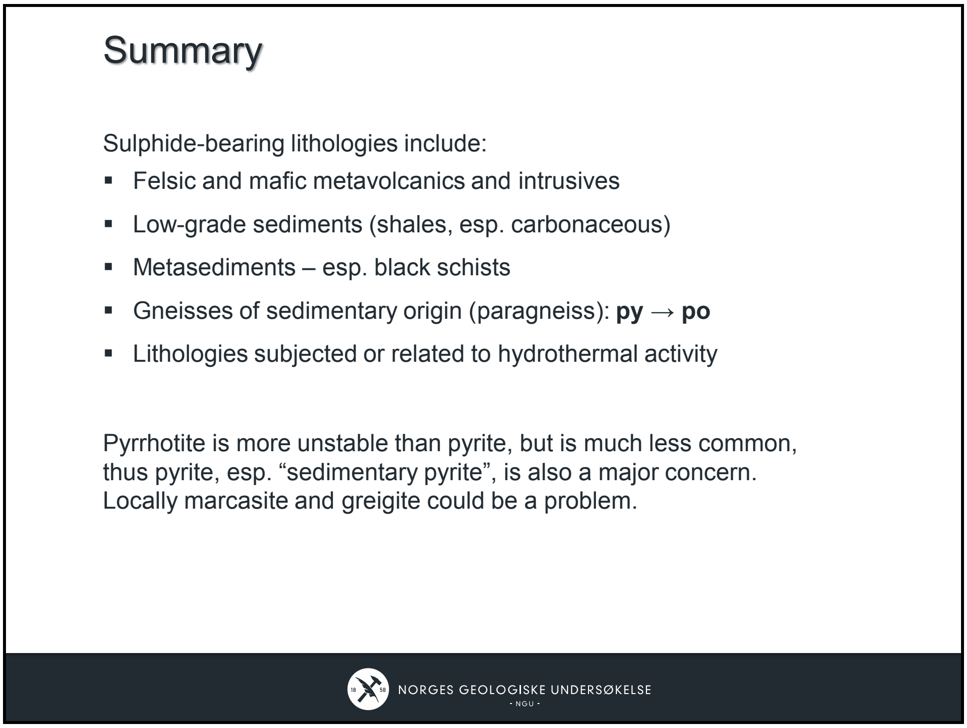


Summary

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.

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

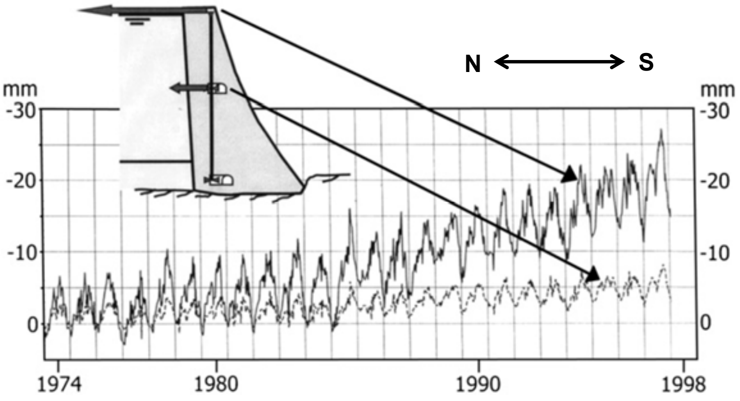
- Introduction
- Materials and methods
- Results
  - Optical microscopy
  - Scanning electron microscopy
- Summary

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

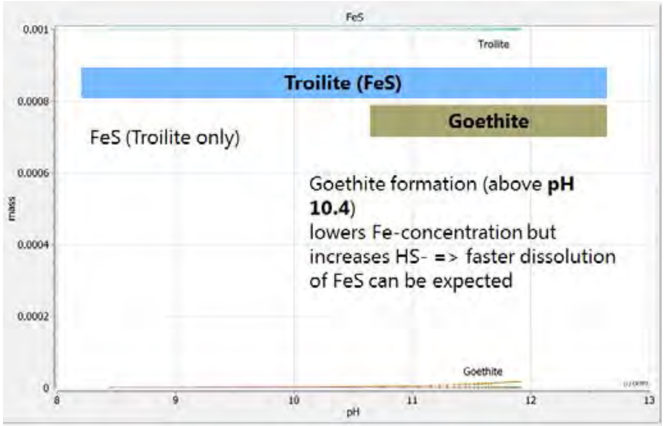
Pyrrhotite (troilite): $2FeS + 2H_2O + 4.5O_2 \rightarrow Fe_2O_3 + 2H_2SO_4$

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)



FeS (Troilite only)

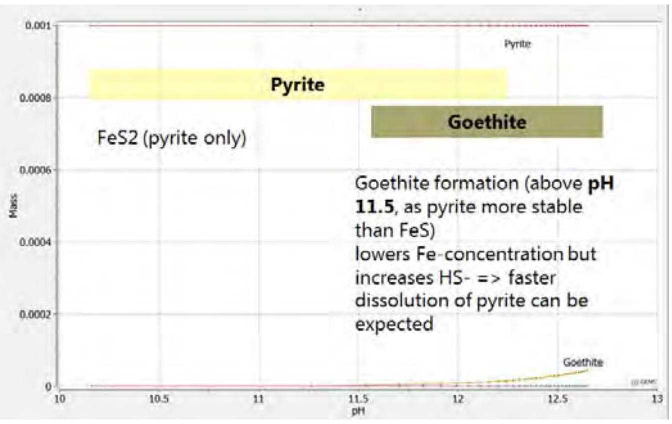
Goethite formation (above **pH 10.4**) lowers Fe-concentration but increases HS- => faster dissolution of FeS can be expected

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)



Goethite formation (above **pH 11.5**, as pyrite more stable than FeS) lowers Fe-concentration but increases HS- => faster dissolution of pyrite can be expected

B. Lothenbach

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

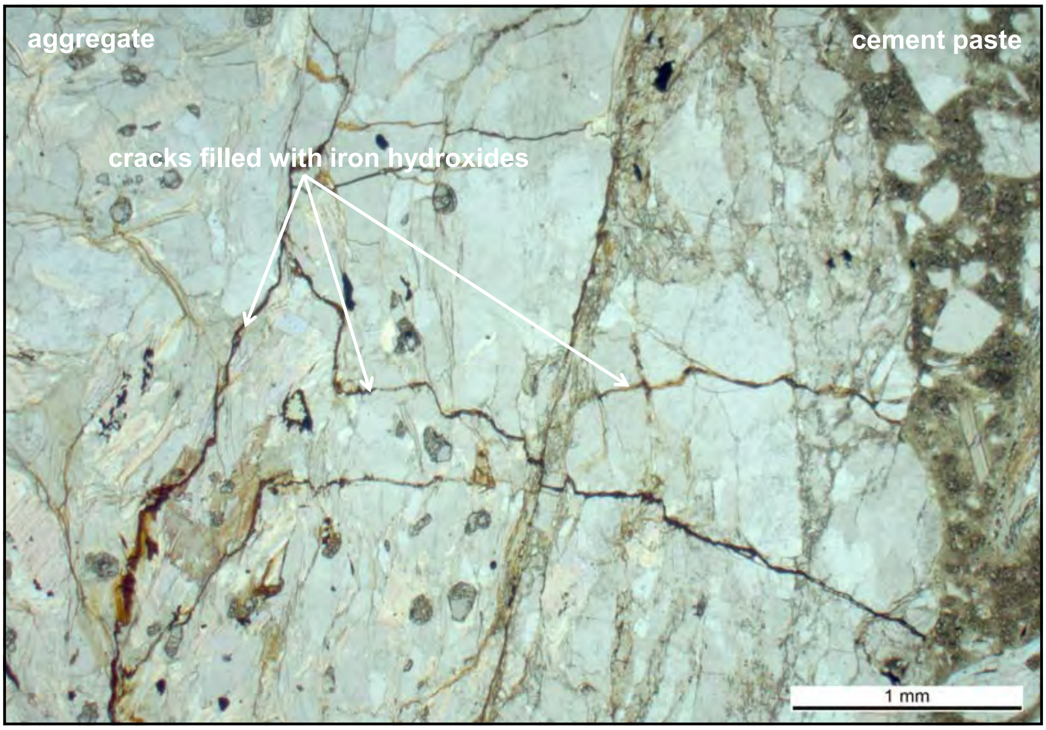
- Lab samples: storage in water at 60°C for five years
- Optical microscopy
- Scanning electron microscopy with energy-dispersive X-ray spectroscopy

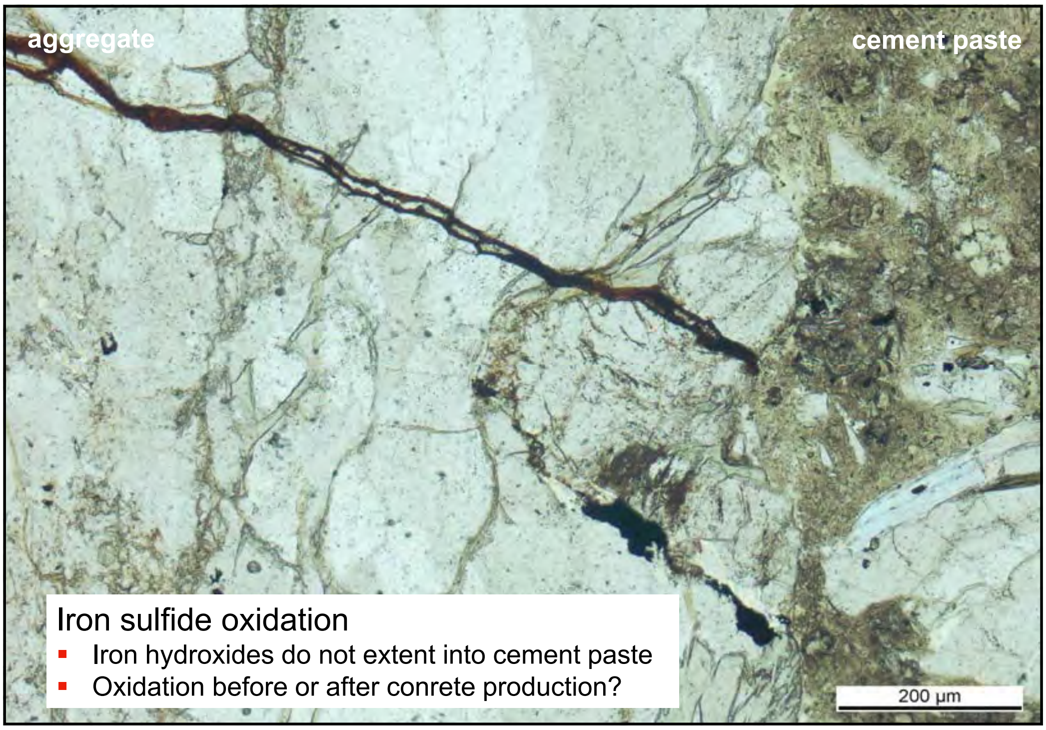
Simultaneous iron sulphide oxidation and alkali silica reaction in a Swiss dam

Aggregates

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

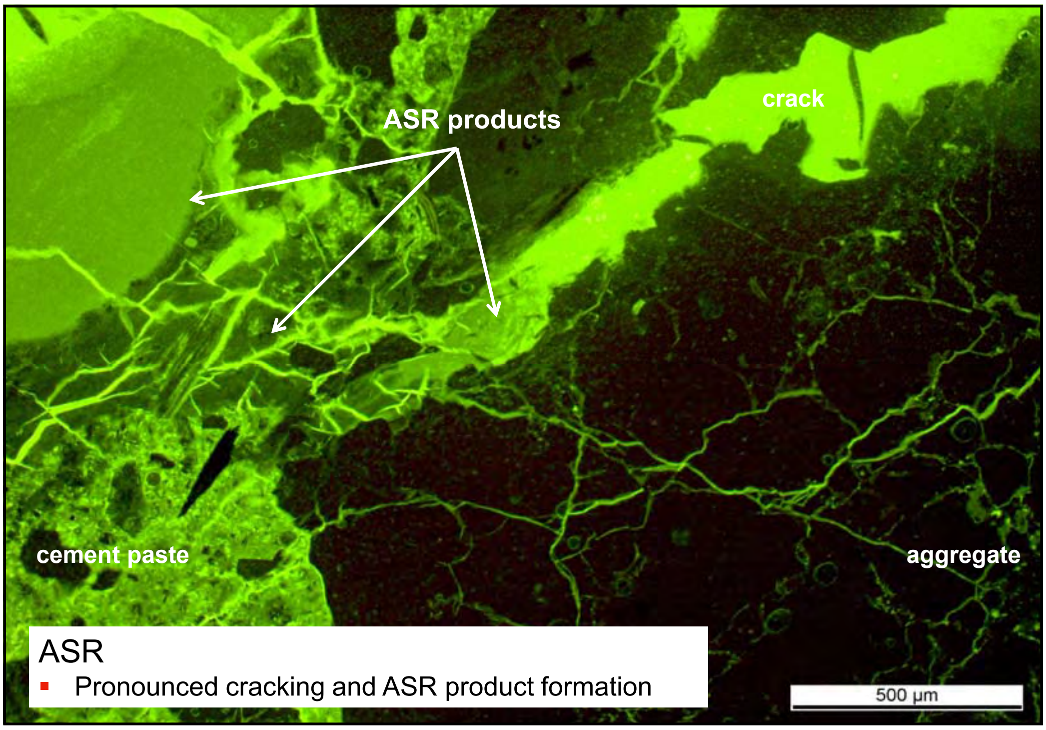
- total iron sulphide content: 0.3-0.4 volume-%





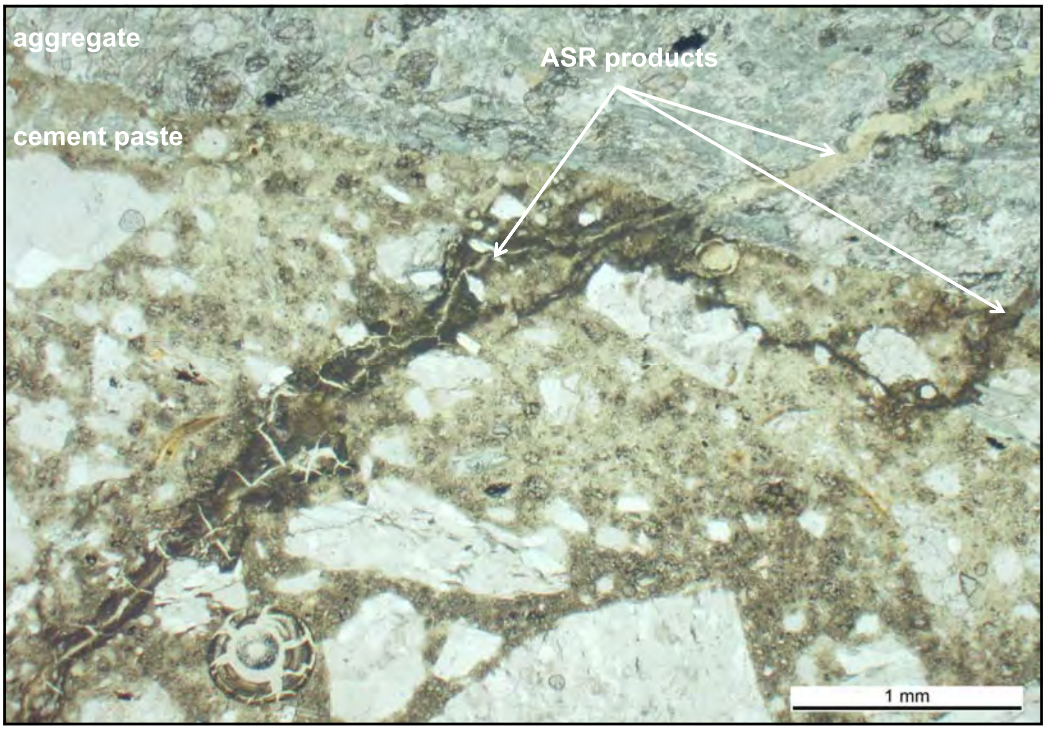
Iron sulfide oxidation

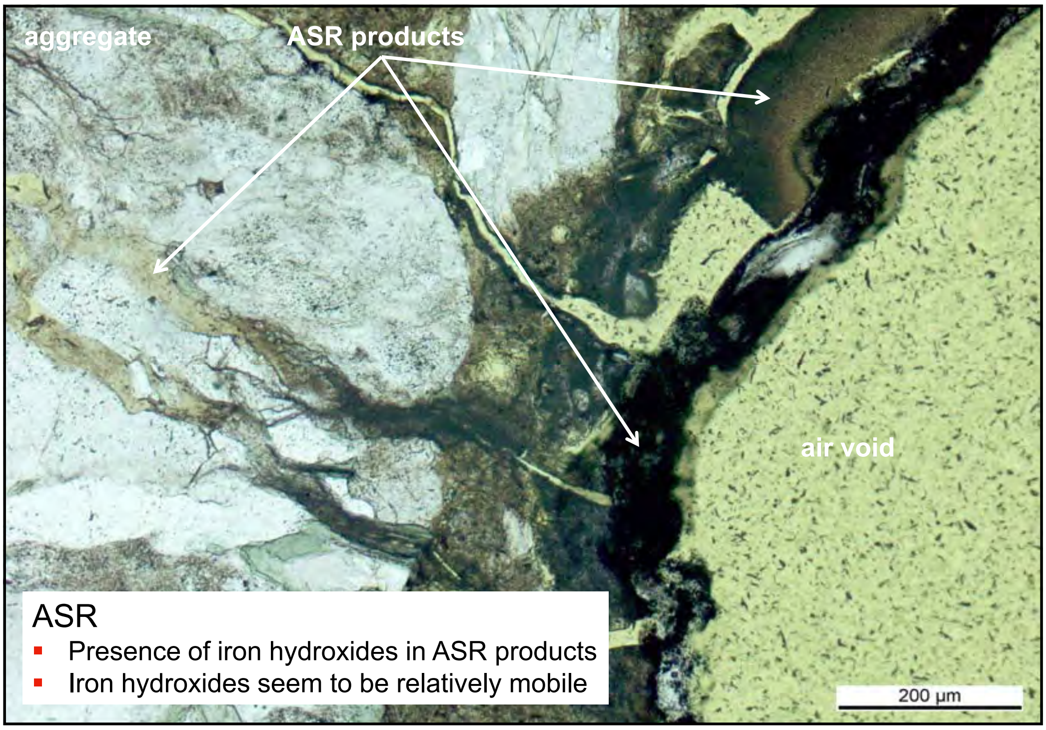
- Iron hydroxides do not extent into cement paste
- Oxidation before or after conrete production?



ASR

- Pronounced cracking and ASR product formation



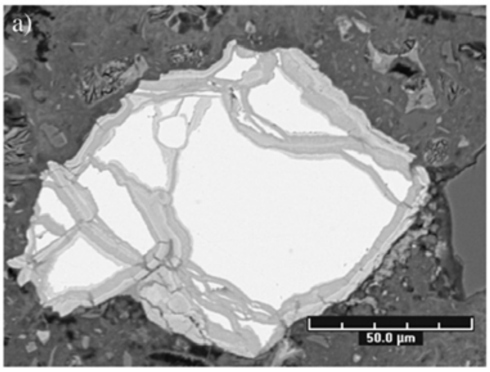


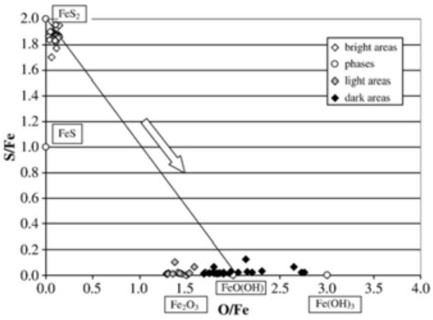
ASR

- 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

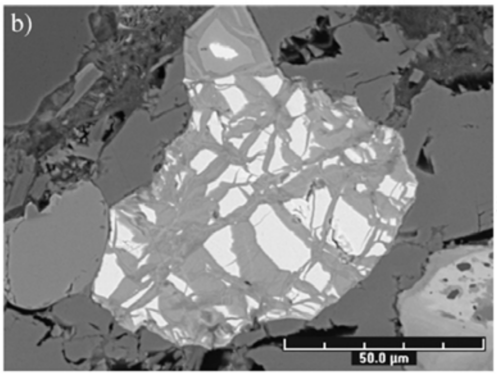


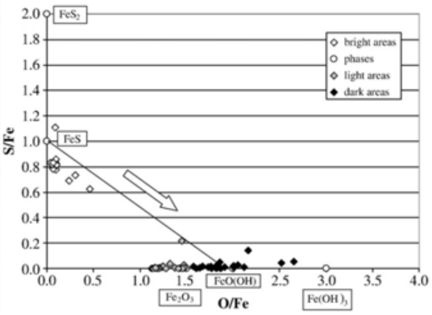


- Pyrite/marcasite (FeS_2) mostly with little oxidation products
- Oxidation still possible

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

Oxidating iron sulfides



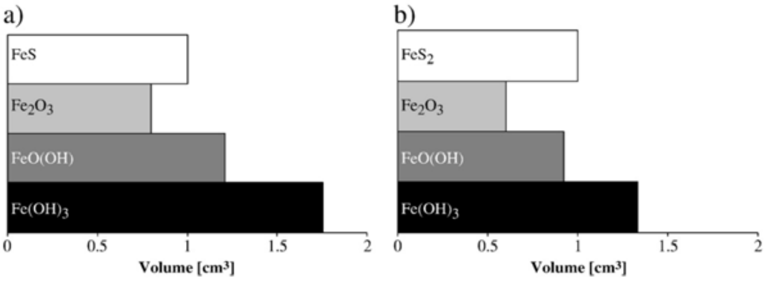


- Pyrrhotite (Fe(1-x)S often with oxidation products
- Less stable than pyrite

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

Oxidating iron sulfides

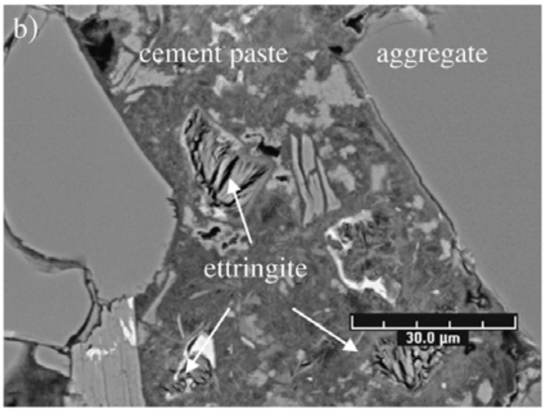
- Substantial (theoretical) volume increase due to oxidation



- 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

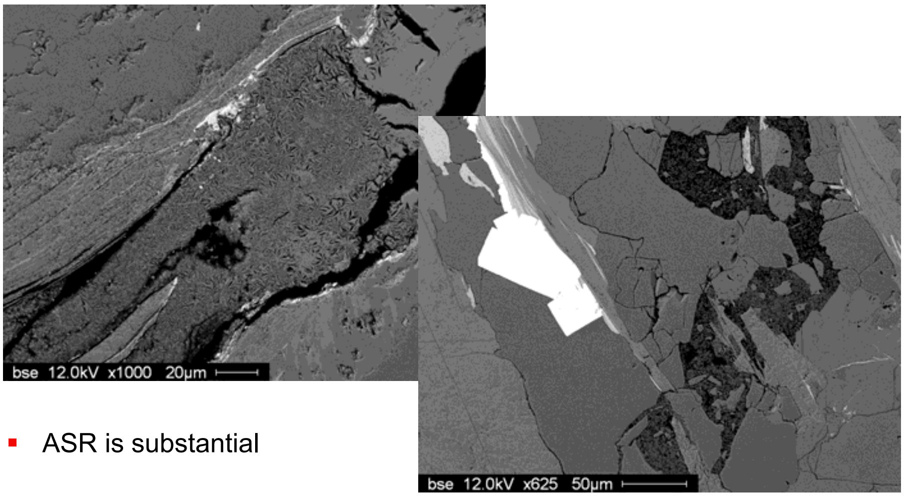
Oxidating iron sulfides



- 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

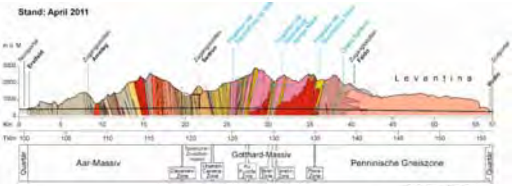
Roland WEISS
Hagerbach Testing Gallery Ltd.
Flums, Switzerland
Novembre 15th, 2018

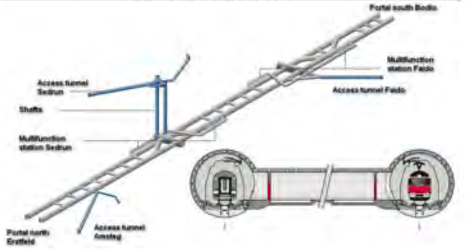
Topics

- Short Introduction
- AAR action plan
- recommendations

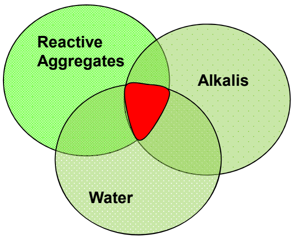
Introduction

Gotthard Base Tunnel (GBT)



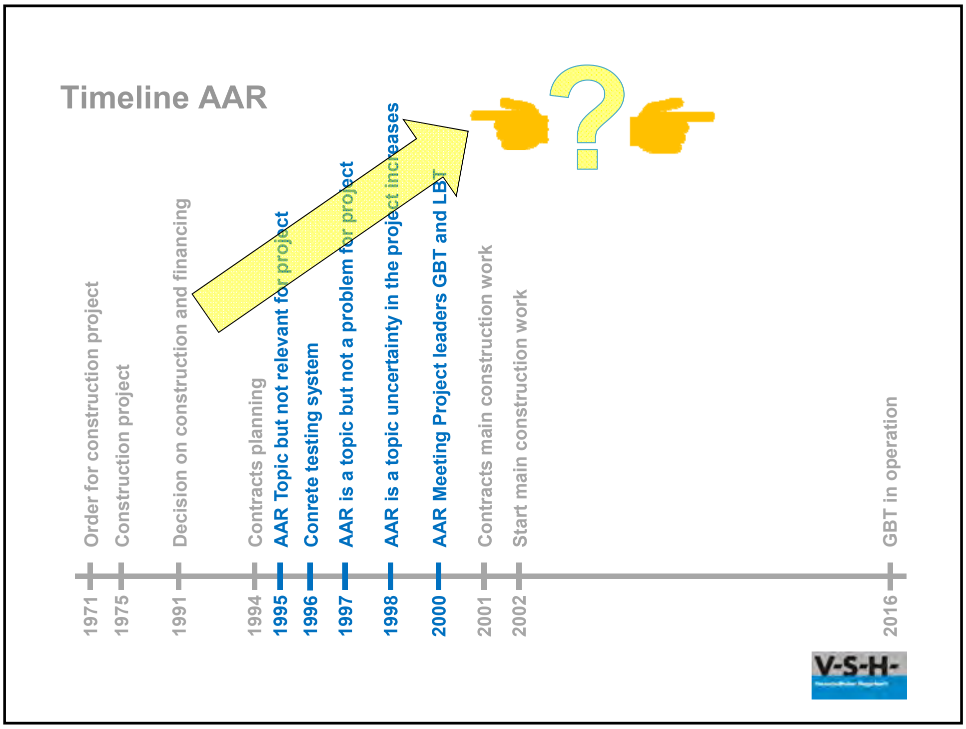


Alcali aggregate Reaction (AAR)



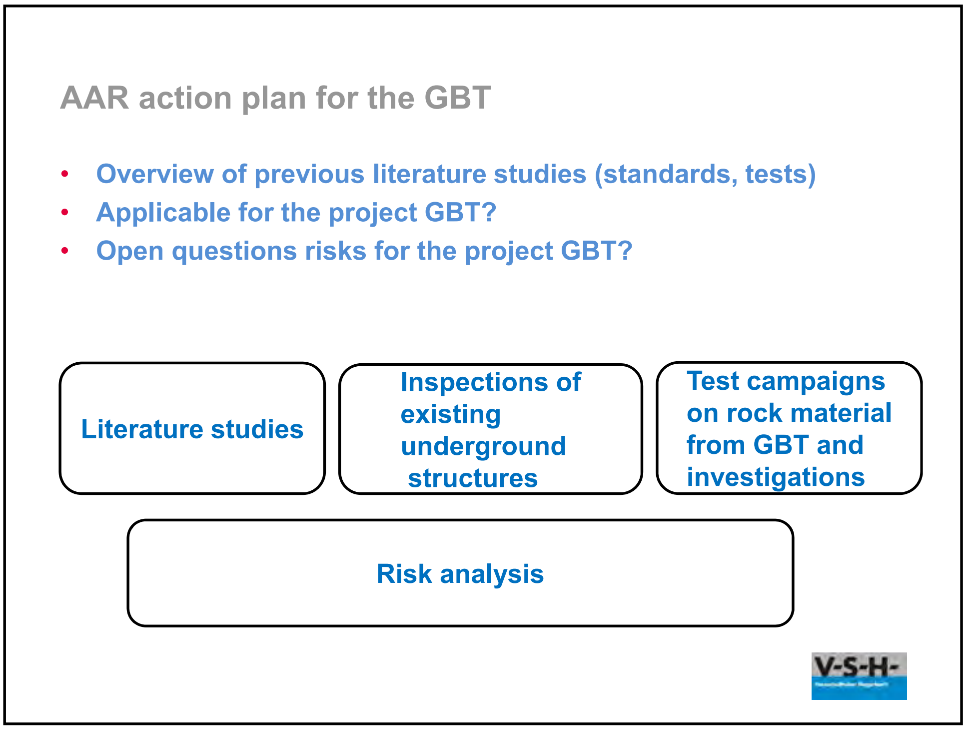
Timeline GBT

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

1971 Order for construction project
1975 Construction project
1991 Decision on construction and financing
1994 Contracts planning
1995 AAR Topic but not relevant for project
1996 Conrete testing system
1997 AAR is a topic but not a problem for project
1998 AAR is a topic uncertainty in the project increases
2000 AAR Meeting Project leaders GBT and LBT
2001 Contracts main construction work
2002 Start main construction work
2016 GBT in operation



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

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.

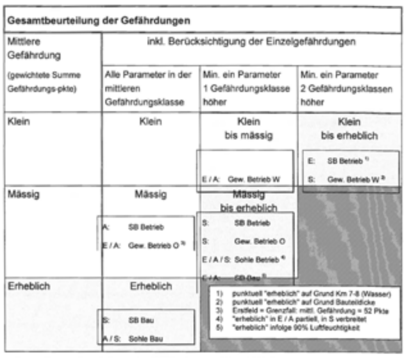
Gotthard-Strassentunnel, Spritzbeton (s. Kapitel 3.1.4.)

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)



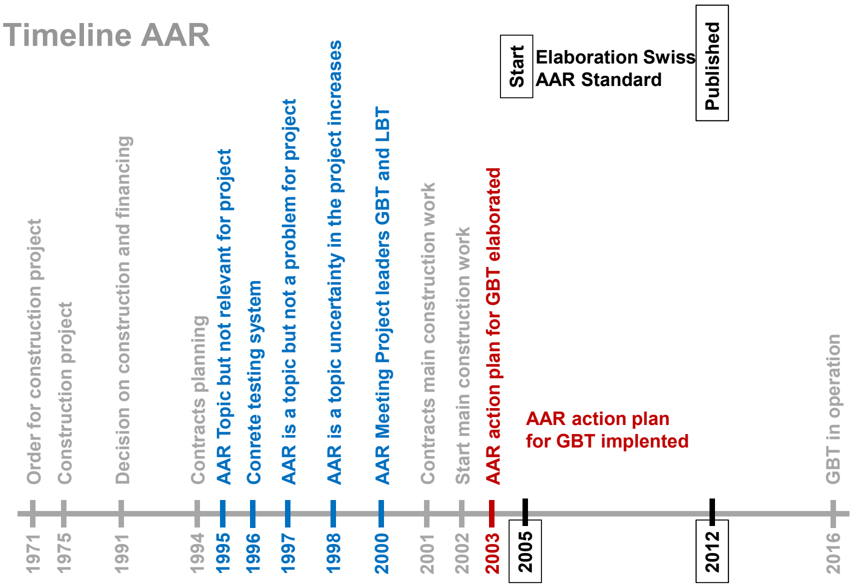
Gesamtbeurteilung der Gefährdungen			
Mittlere Gefährdung (gewichtete Summe Gefährdungs-pkte)	inkl. Berücksichtigung der Einzelgefährdungen		
	Alle Parameter in der mittleren Gefährdungsklasse	Min. ein Parameter 1 Gefährdungsklasse höher	Min. ein Parameter 2 Gefährdungsklassen höher
Klein	Klein	Klein 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

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

Timeline AAR



1971 Order for construction project
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1997 AAR is a topic but not a problem for project
1998 AAR is a topic uncertainty in the project increases
2000 AAR Meeting Project leaders GBT and LBT
2001 Contracts main construction work
2002 Start main construction work
2003 AAR action plan for GBT elaborated
2005 Start Elaboration Swiss AAR Standard
AAR action plan for GBT implented
2012 Published
2016 GBT in operation

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

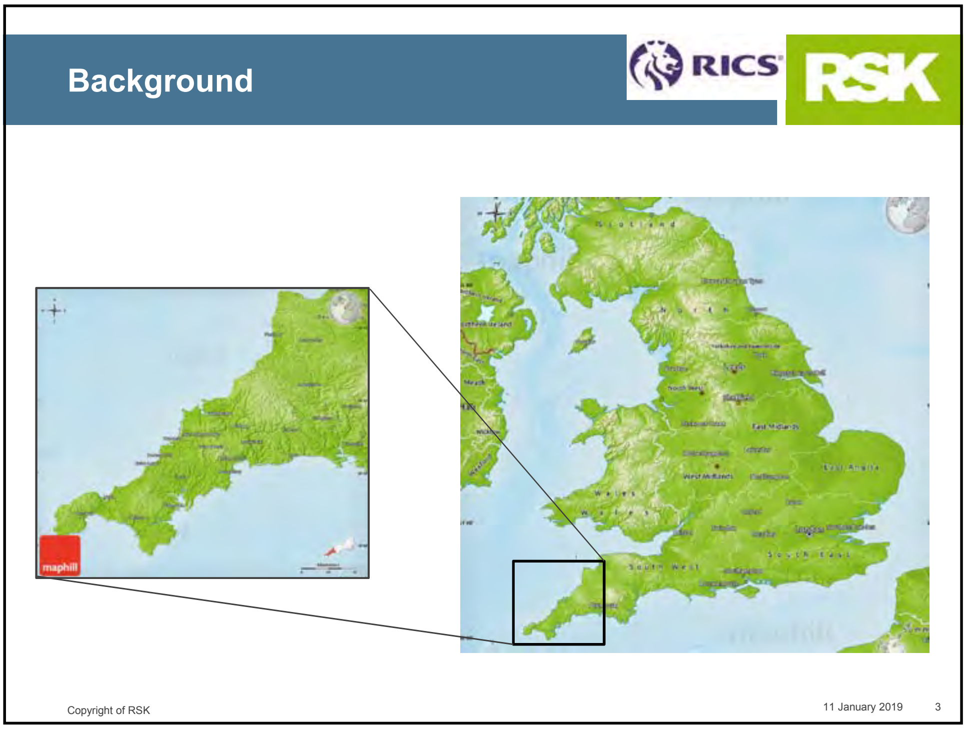
Oslo, Norway – 15 & 16 November, 2018

11 January 2019 1

Managing the 'Mundic' Problem in South-West England

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

11 January 2019 2



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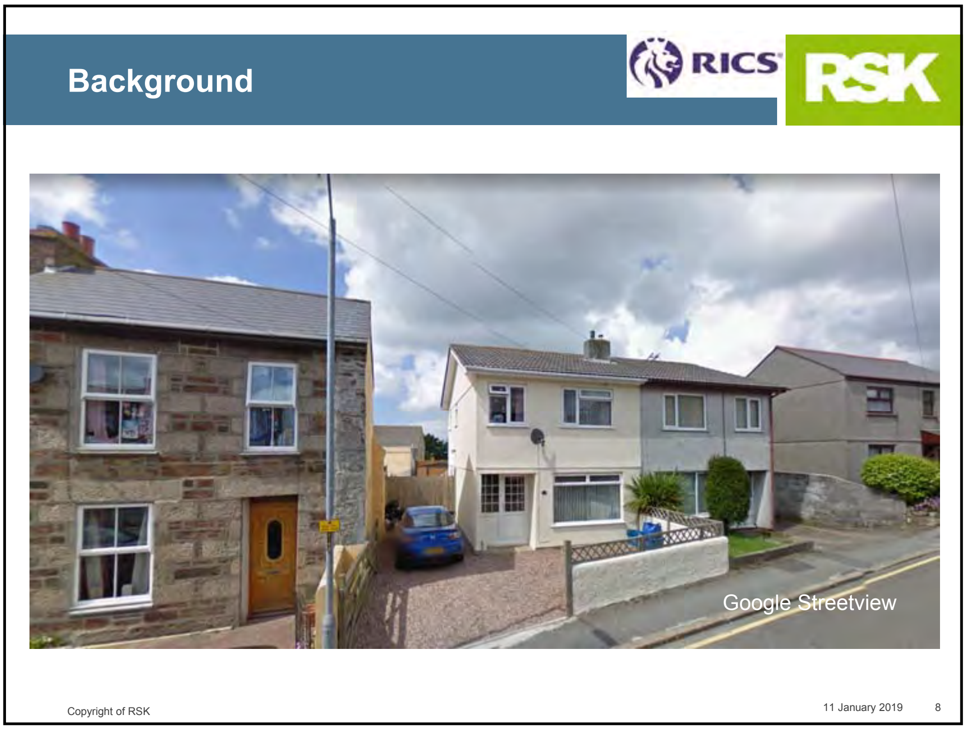

Background

Google Streetview

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

RICS guidance note

RICS

RICS Professional Guidance, UK

The mundic problem

3rd edition

rics.org/guidance

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

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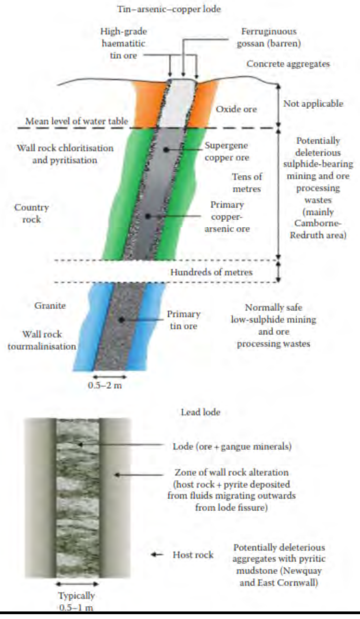
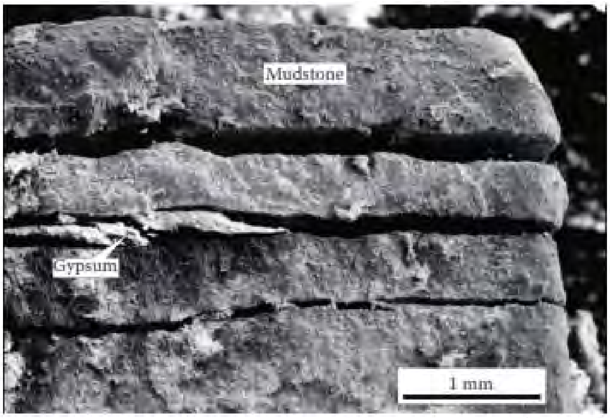
Geological Source of the Sulfides



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

Courtesy of the late Dr Alan Bromley

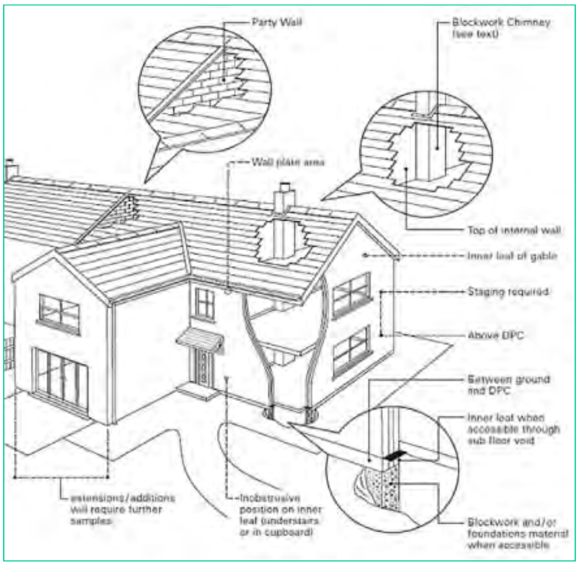
Gypsum-induced expansion of mudstone

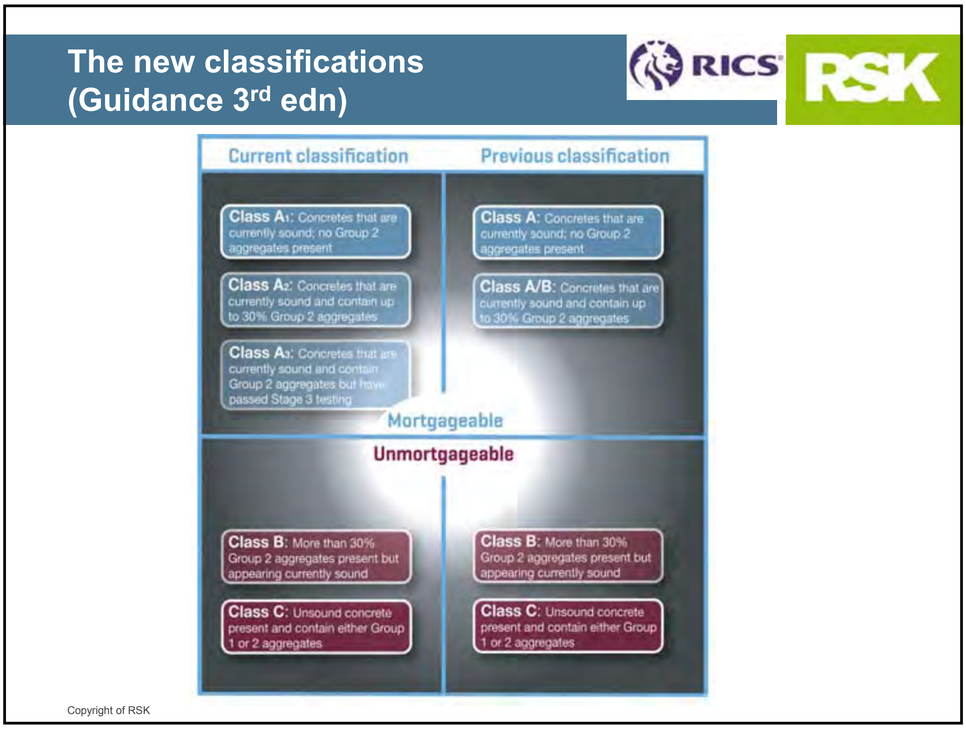


Scanning electron microscope image (secondary electron image), showing spalling and expansion of a small mudstone aggregate fragment following growth of secondary gypsum in lenses along cleavage planes. Concrete block from a house in Liskeard, East Cornwall, UK. *Image courtesy of Alan Bromley.*

Representative Sampling by Surveyor

Third Edition Diagram: Typical Sampling Locations





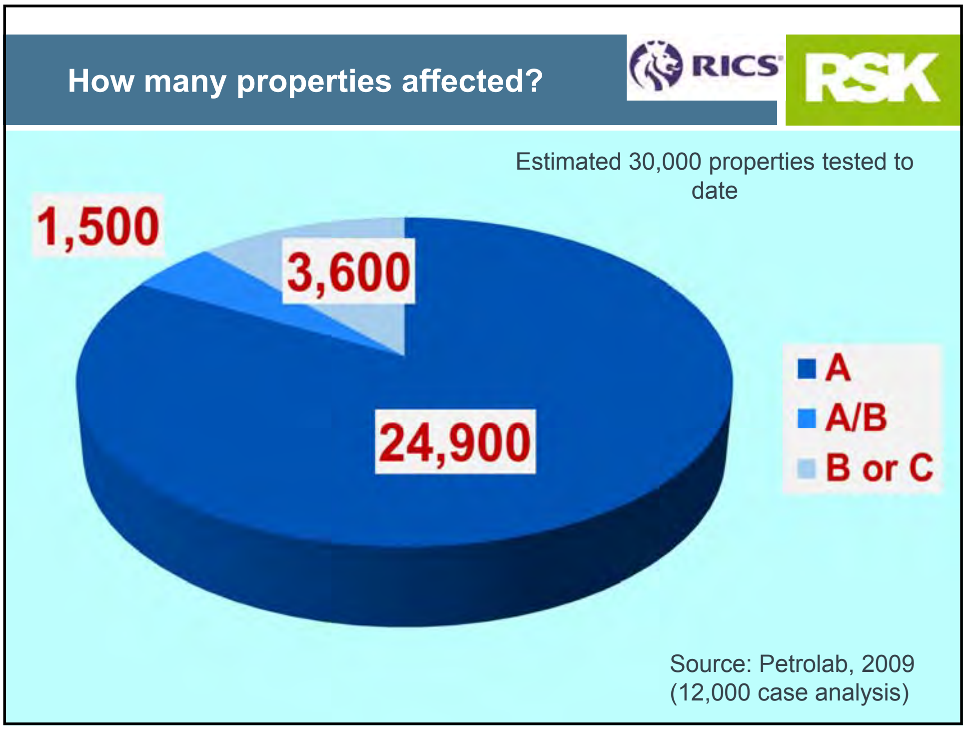
The new classifications (Guidance 3rd edn)

Current classification	Previous classification
Class A_1: Concretes that are currently sound; no Group 2 aggregates present	**Class A:** Concretes that are currently sound; no Group 2 aggregates present
Class A_2: Concretes that are currently sound and contain up to 30% Group 2 aggregates	**Class A/B:** Concretes that are currently sound and contain up to 30% Group 2 aggregates
Class A_3: Concretes that are currently sound and contain Group 2 aggregates but have passed Stage 3 testing	

Mortgageable

Unmortgageable

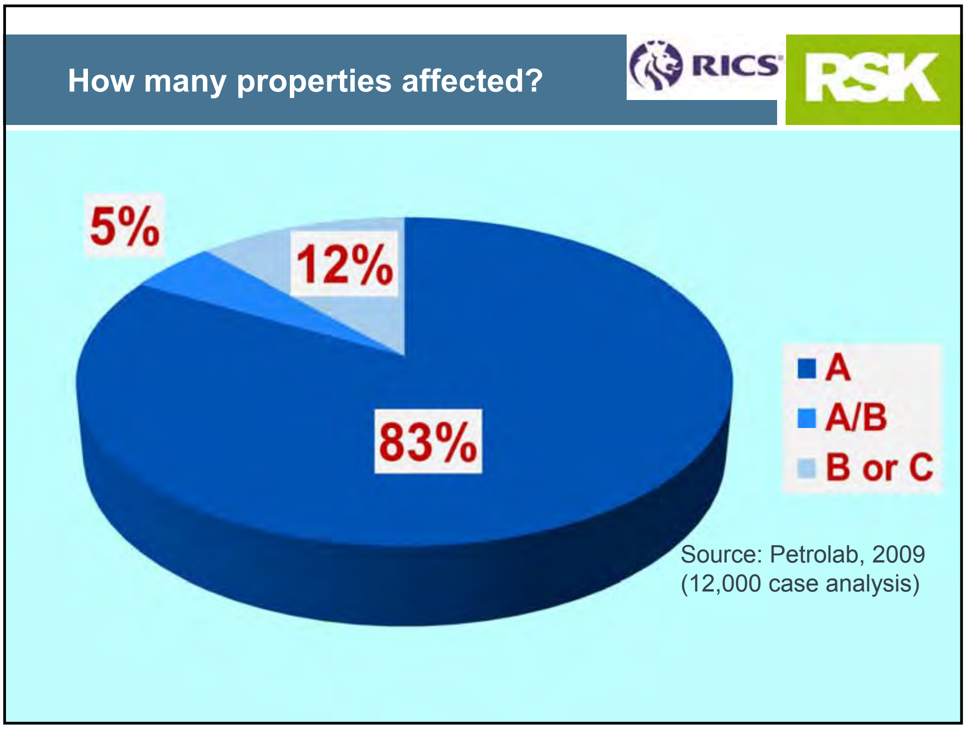
Current classification	Previous classification
Class B: More than 30% Group 2 aggregates present but appearing currently sound	**Class B:** More than 30% Group 2 aggregates present but appearing currently sound
Class C: Unsound concrete present and contain either Group 1 or 2 aggregates	**Class C:** Unsound concrete present and contain either Group 1 or 2 aggregates



How many properties affected?

Estimated 30,000 properties tested to date

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



How many properties affected?

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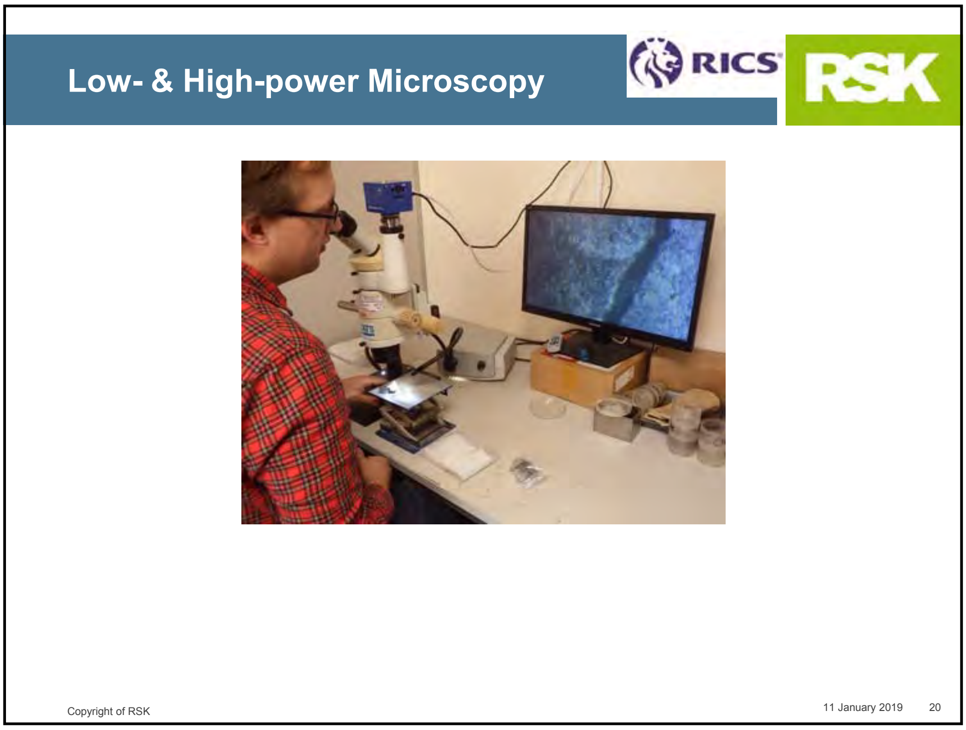


Low- & High-power Microscopy

Low- & High-power Microscopy

Classification Flow Chart

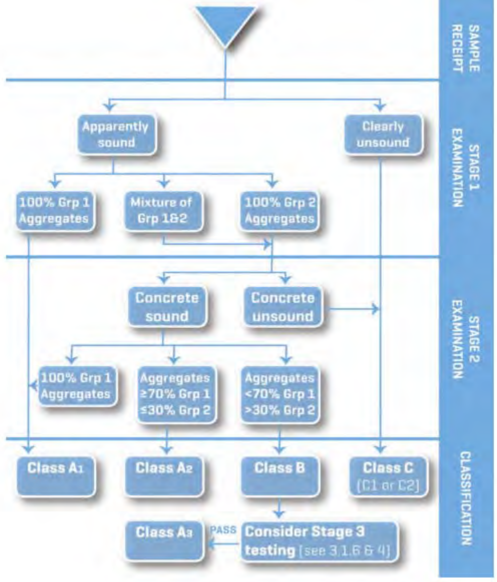


Figure 4: Examination and classification procedure

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: **Considered potentially deleterious**	2–1	Crushed sedimentary or meta-sedimentary rocks ('killas') [2, 4, 5]
	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

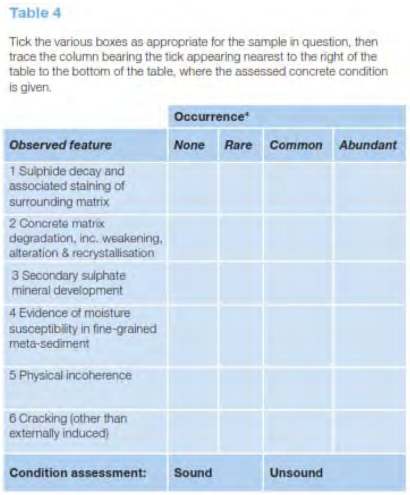


Table 4

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

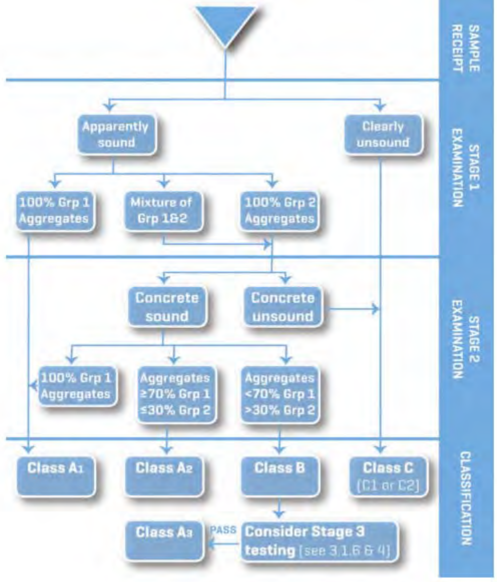


Figure 4: Examination and classification procedure

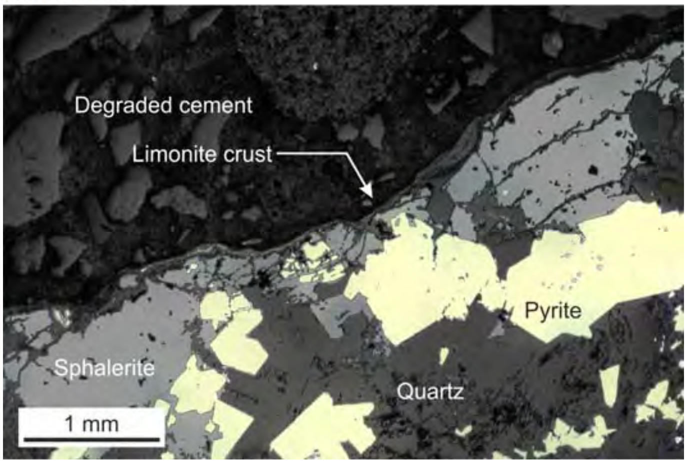
Note: The flow chart is simplified and reference should be made to the full text.

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

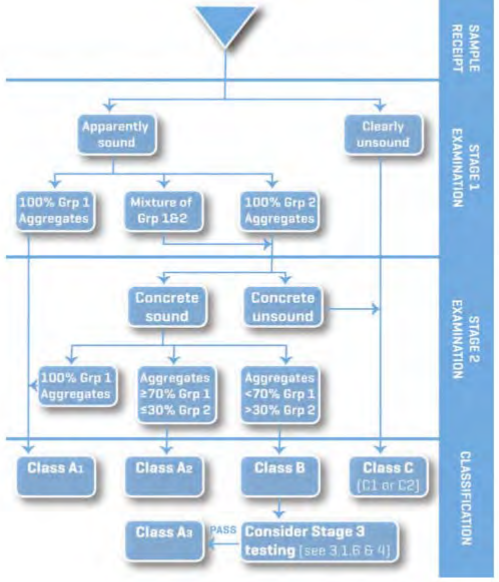
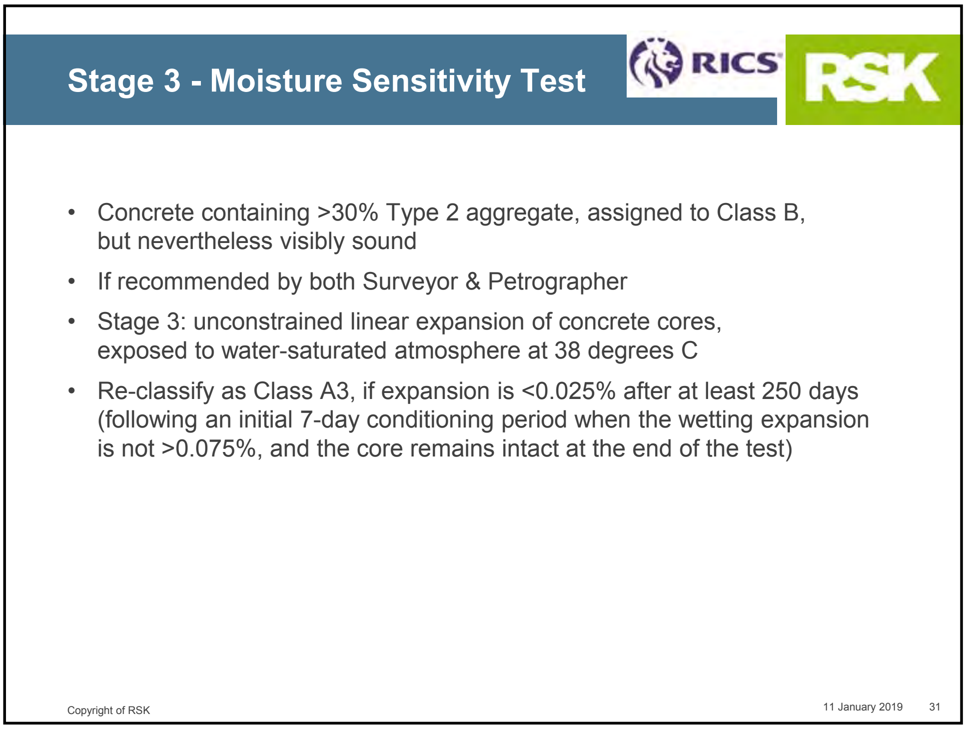


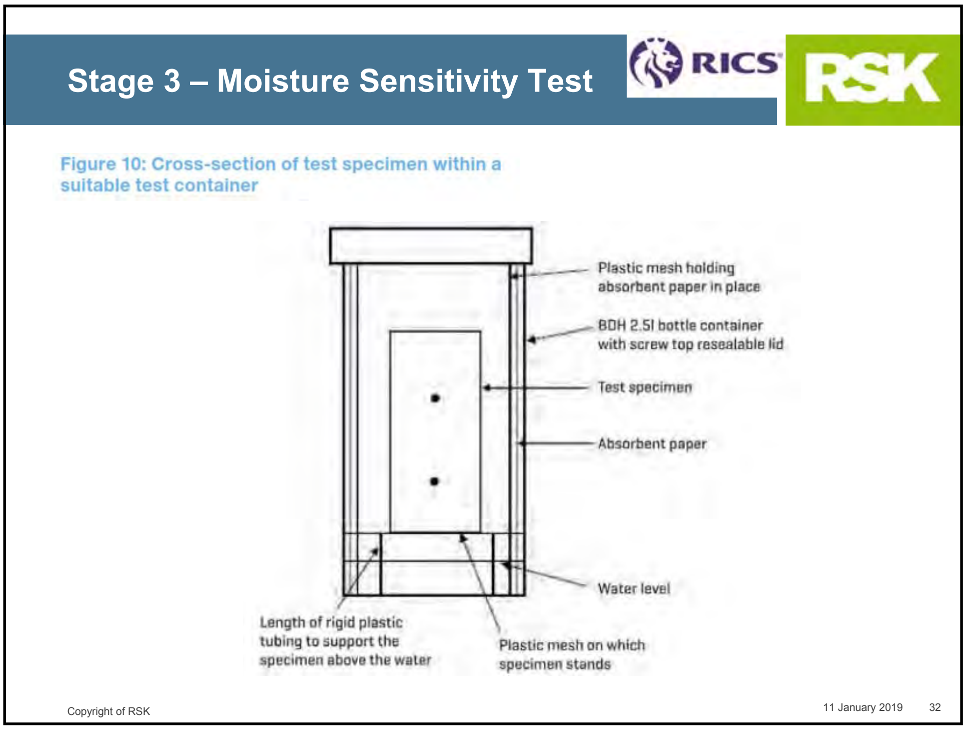
Figure 4: Examination and classification procedure

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



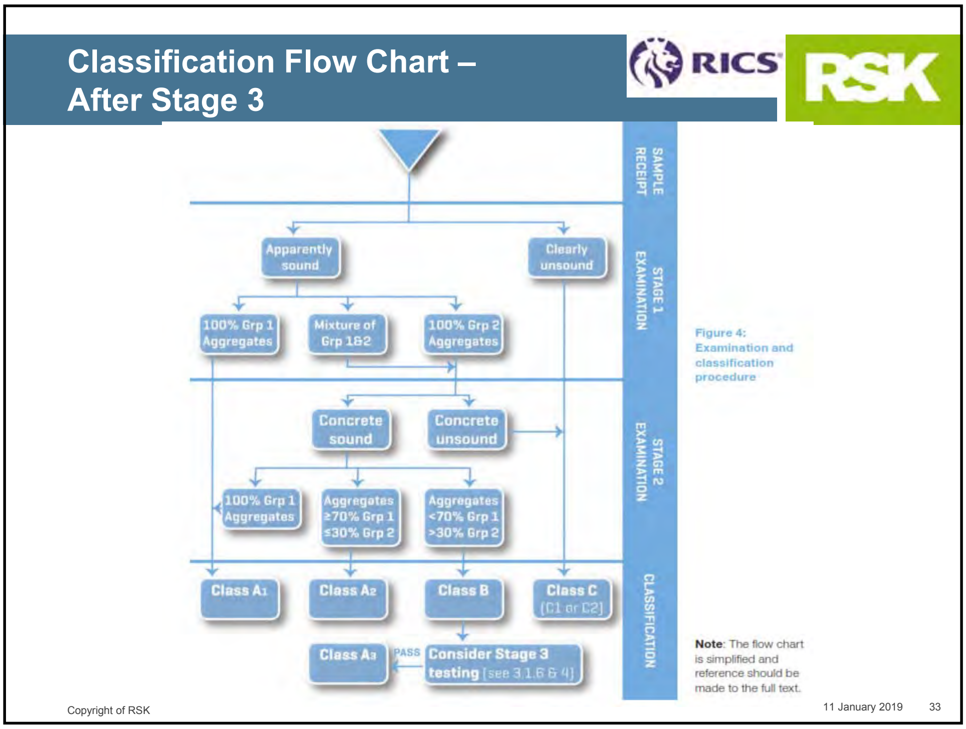
Stage 3 - Moisture Sensitivity Test

- 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

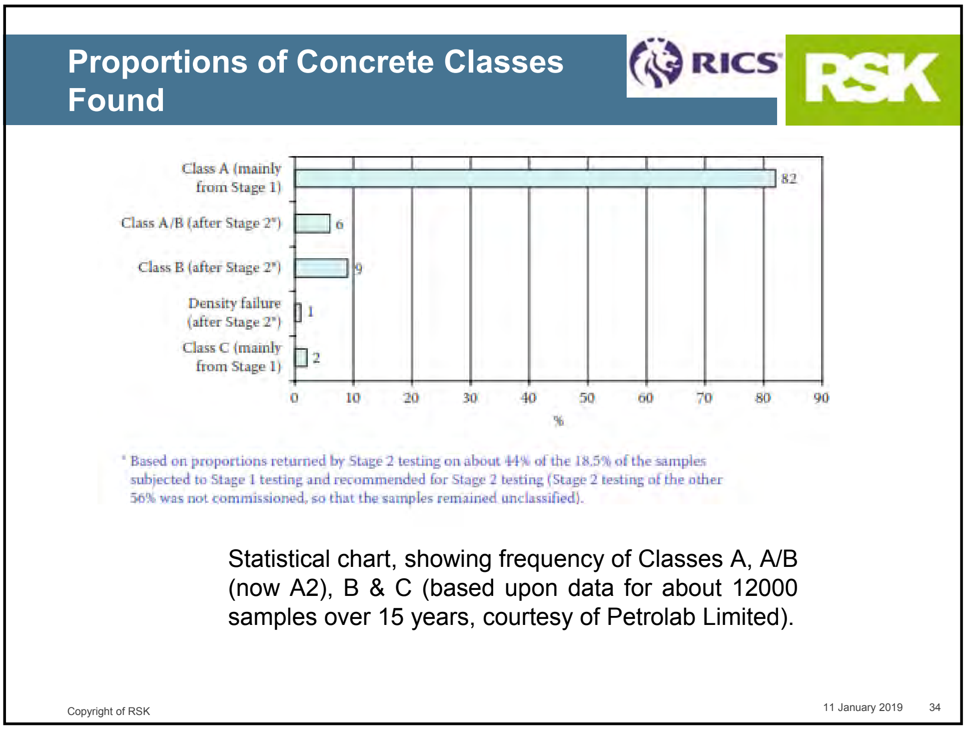
Figure 10: Cross-section of test specimen within a suitable test container



Classification Flow Chart – After Stage 3

Figure 4: Examination and classification procedure

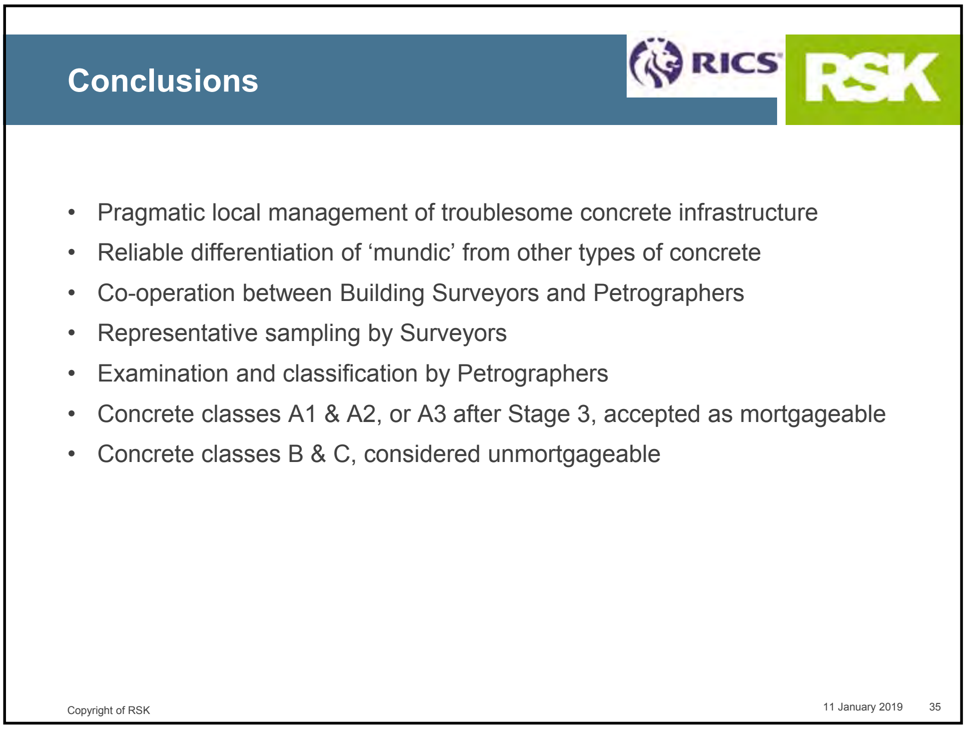
Note: The flow chart is simplified and reference should be made to the full text.



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.

Centre de recherche sur les infrastructures en béton

Montréal • Québec • Sherbrooke

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

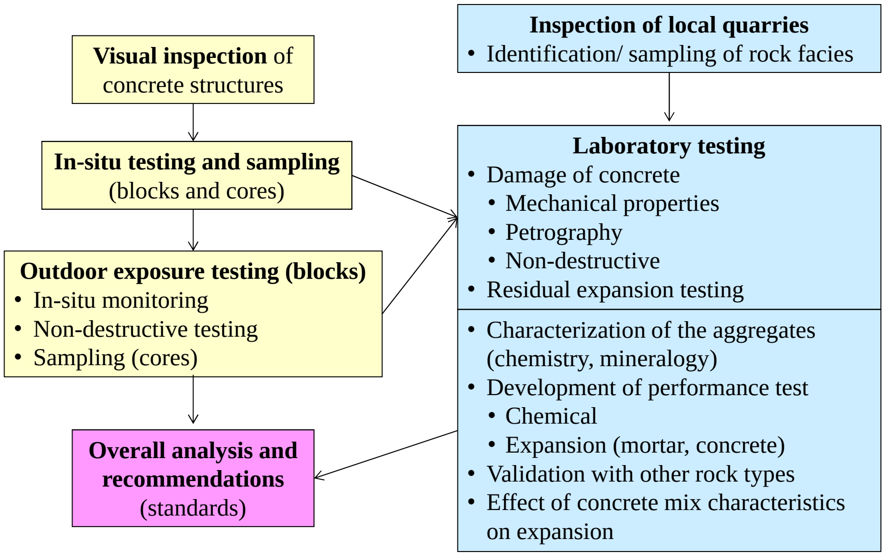
Partnership: University – Industry - Gouvernment

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**

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

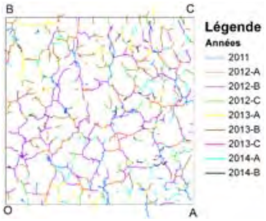
- Characterization of the aggregates (chemistry, mineralogy)
- Development of performance test
  - Chemical
  - Expansion (mortar, concrete)
- Validation with other rock types
- Effect of concrete mix characteristics on expansion

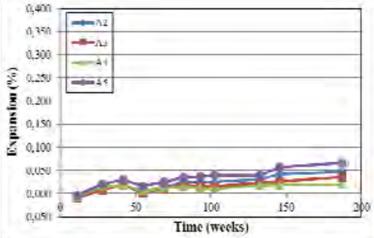
Outdoor exposure testing

5 blocks per house foundation

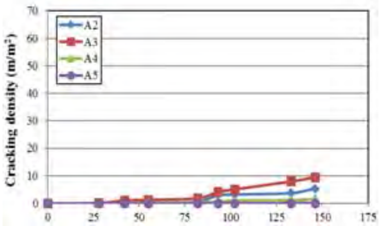
- **Non destructive testing (Sh. U,)**
- **Expansion (Nov. 2011-Aug. 2014)**
- **Monitoring of cracking**
- **Sampling of blocks**

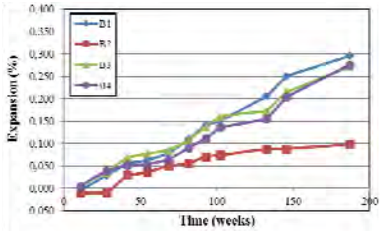
Francoeur (2016)



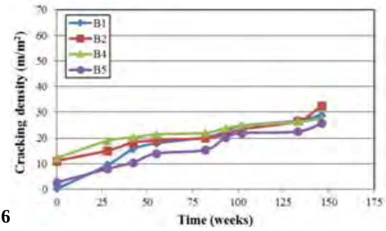


**Set A
(rating 0)**





**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)

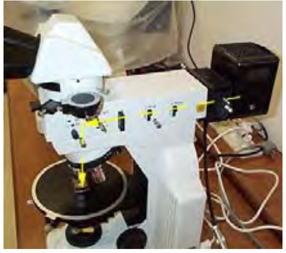
- « Reactive aggregate » & various concrete mix designs
- Monitoring of cracking and expansion development

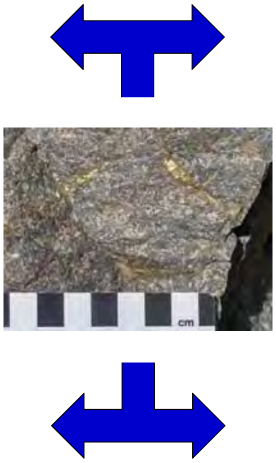
(Durand 2013)

Laboratory testing program

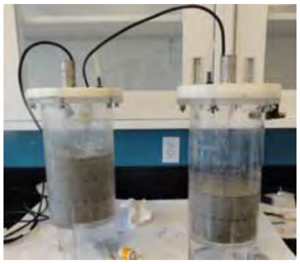
S_T determination

Mineralogy





O_2 consumption



Expansion

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

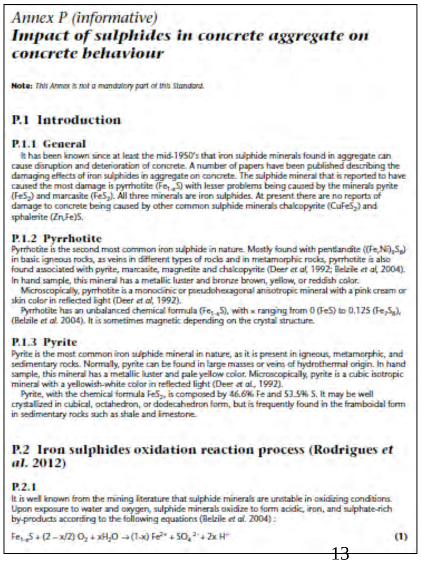
P.1 Introduction
- **General**
- **Pyrrhotite → Fe (1-x) S**
- **Pyrite → FeS_2**

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) :

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

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

(<u>conducive to final accceptance by CSA A23 committee members</u>)

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

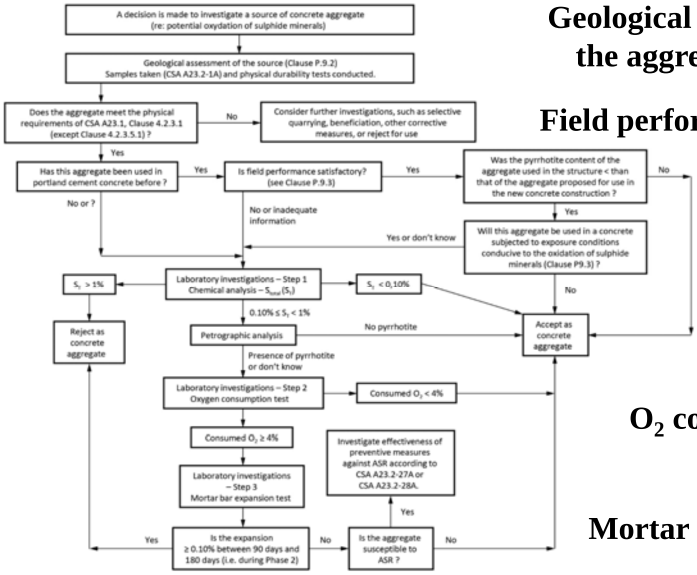
P.12 Accelerated mortar bar expansion test

New test methods

P.13 Discussion, summary and interpretation of PEP

P.14 Conclusion

Protocol for testing sulphide-bearing aggregates



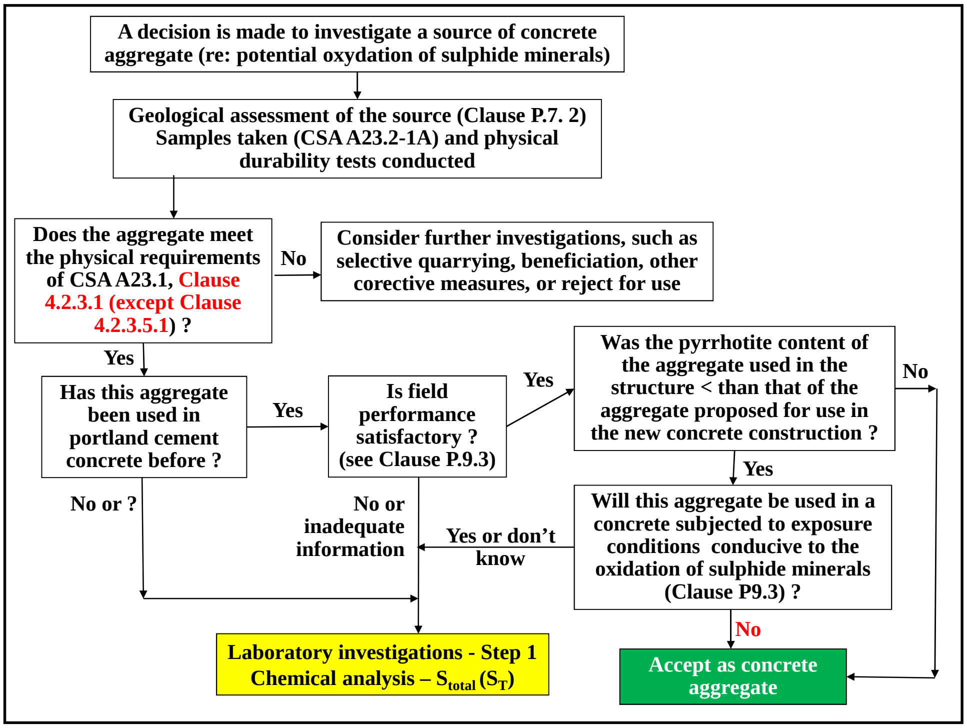
Geological assessment of the aggregate source

Field performance survey

Chemical analysis Ss

O_2 consumption

Mortar bar expansion



A decision is made to investigate a source of concrete aggregate (re: potential oxydation of sulphide minerals)

Geological assessment of the source (Clause P.7. 2) Samples taken (CSA A23.2-1A) and physical durability tests conducted

Does the aggregate meet the physical requirements of CSA A23.1, Clause 4.2.3.1 (except Clause 4.2.3.5.1) ?

No

Consider further investigations, such as selective quarrying, beneficiation, other corective measures, or reject for use

Yes

Has this aggregate been used in portland cement concrete before ?

Yes

Is field performance satisfactory ? (see Clause P.9.3)

Yes

Was the pyrrhotite content of the aggregate used in the structure < than that of the aggregate proposed for use in the new concrete construction ?

No

Yes

Will this aggregate be used in a concrete subjected to exposure conditions conducive to the oxidation of sulphide minerals (Clause P9.3) ?

No or ?

No or inadequate information

Yes or don't know

No

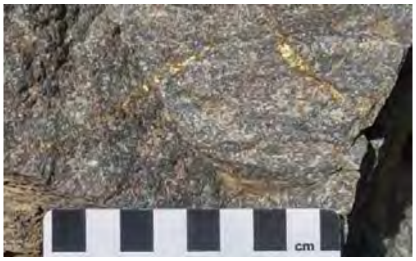
Laboratory investigations - Step 1
Chemical analysis – S_{total} (S_T)

Accept as concrete aggregate

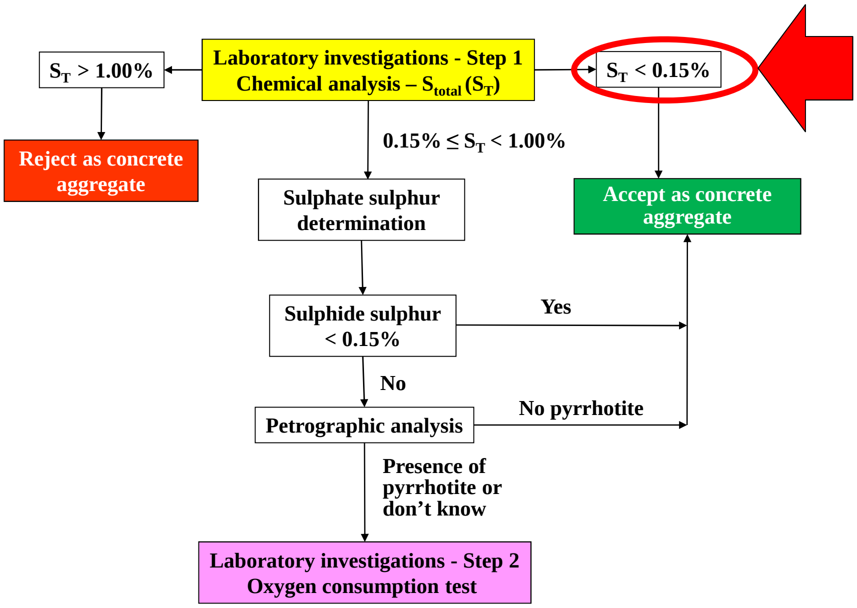
Performance testing program – Step 1

Screening tests

- Chemistry → Sulphur content
- Petrography → pyrrhotite



Protocol for testing sulphide-bearing aggregates



Laboratory investigations - Step 1
Chemical analysis – S_{total} (S_T)

S_T > 1.00%

Reject as concrete aggregate

S_T < 0.15%

Accept as concrete aggregate

0.15% ≤ S_T < 1.00%

Sulphate sulphur determination

Sulphide sulphur < 0.15%

Yes

No

Petrographic analysis

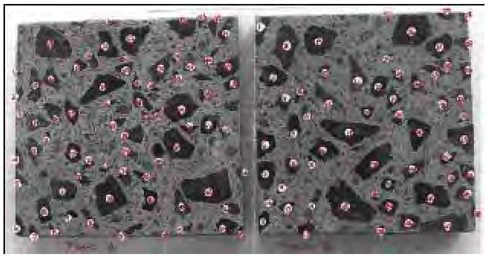
No pyrrhotite

Presence of pyrrhotite or don't know

Laboratory investigations - Step 2
Oxygen consumption test

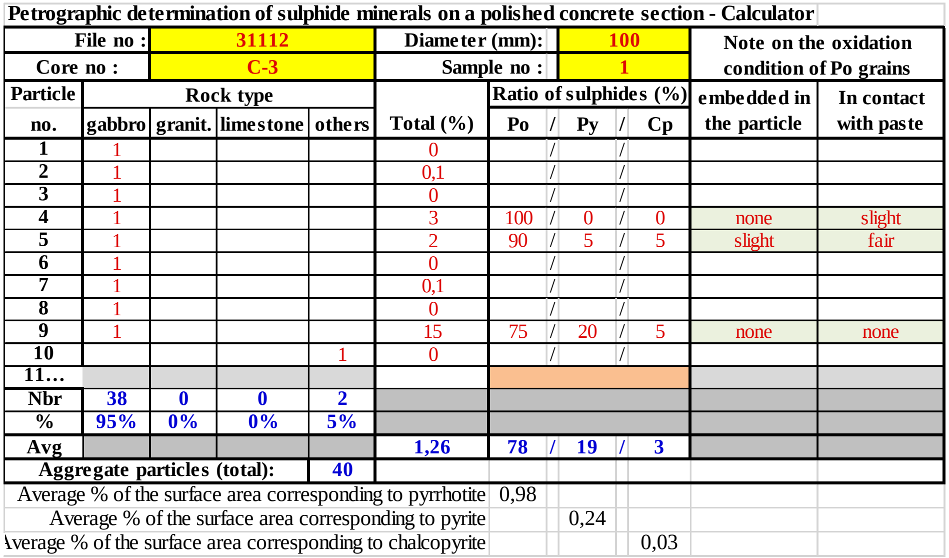
Defense experts in TR case (as per April 2018)

- 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)

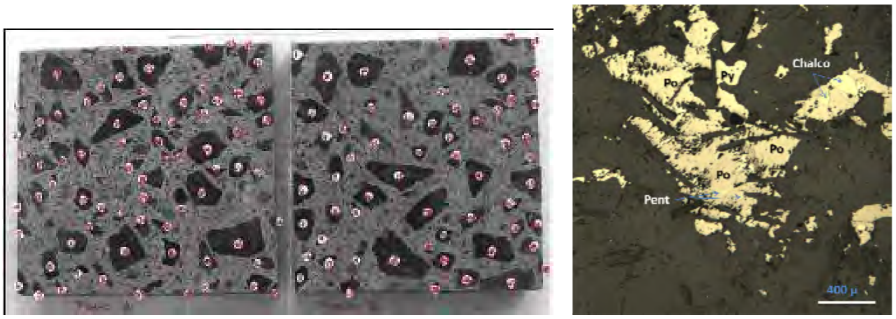


Petrographic determination of sulphide minerals on a polished concrete section - Calculator

File no :	31112				Diameter (mm):		100				Note on the oxidation condition of Po grains	
Core no :	C-3				Sample no :		1					
Particle	Rock type					Ratio of sulphides (%)					embedded in	In contact
no.	gabbro	granit.	limestone	others	Total (%)	Po	/	Py	/	Cp	the particle	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								
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

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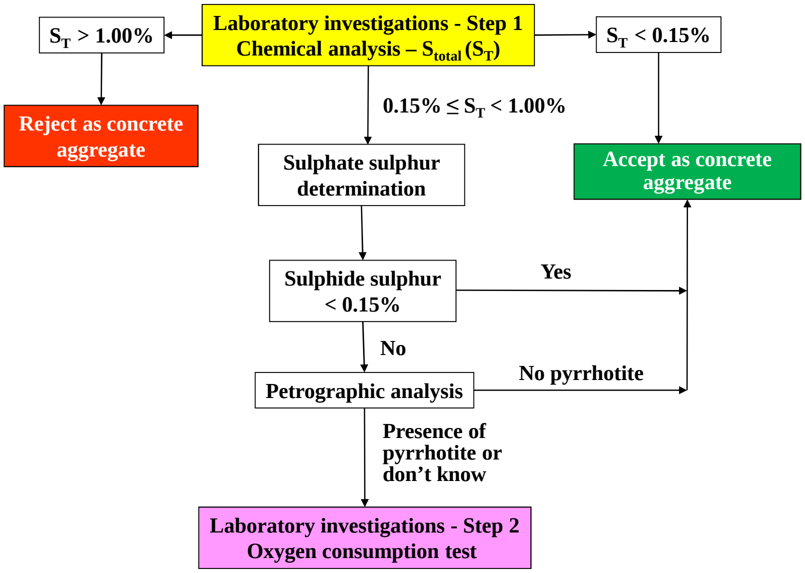
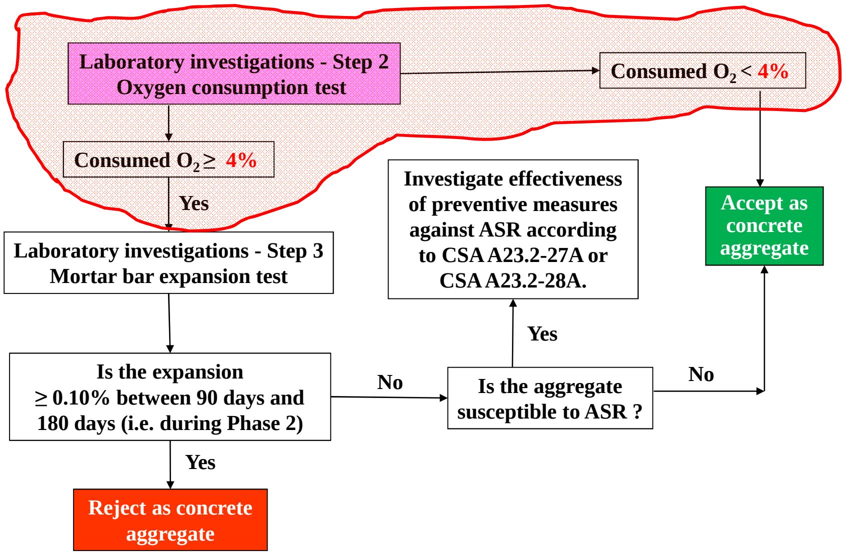
Protocol for testing sulphide-bearing aggregates



Protocol for testing sulphide-bearing aggregates



Laboratory investigations - Step 2
Oxygen consumption test

Consumed $O_2 < 4\%$

Consumed $O_2 \geq 4\%$

Yes

Laboratory investigations - Step 3
Mortar bar expansion test

Is the expansion
$\geq 0.10\%$ between 90 days and
180 days (i.e. during Phase 2)

Yes

Reject as concrete aggregate

No

Is the aggregate susceptible to ASR ?

Yes

Investigate effectiveness of preventive measures against ASR according to CSA A23.2-27A or CSA A23.2-28A.

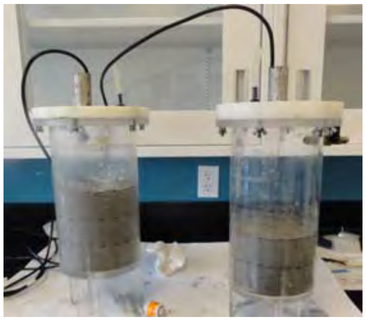
No

Accept as concrete aggregate

O_2 consumption Test

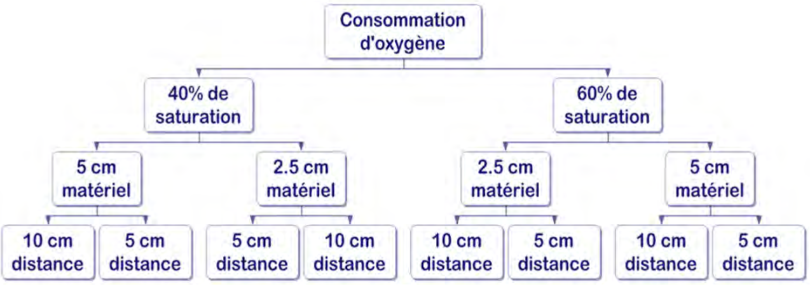
$$Fe_{1-x}S + \boxed{(2-x/2)O_2} + xH_2O \rightarrow (1-x)Fe^{2+} + SO_4^{2-} + 2x\ H^+$$

- 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

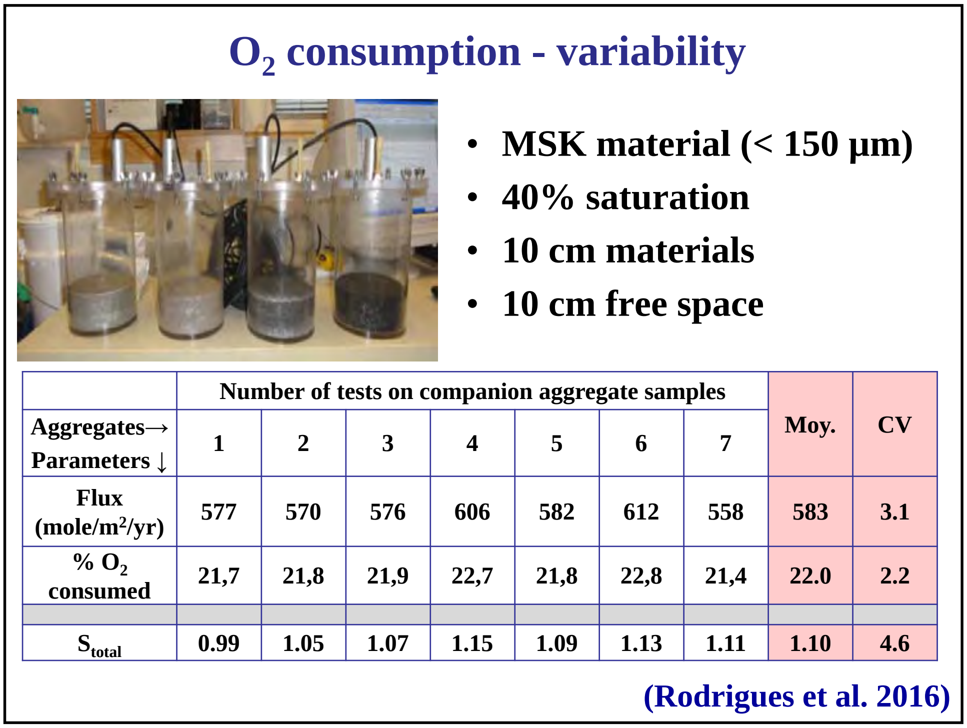


O_2 consumption Test

- 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)

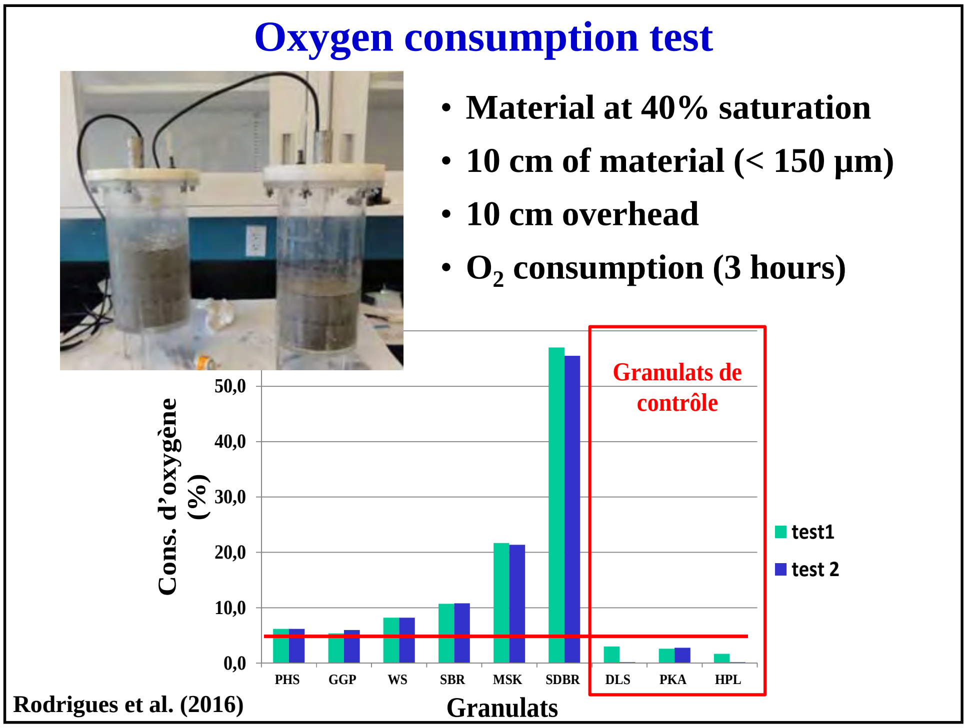


O_2 consumption - variability

- 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/m^2/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)

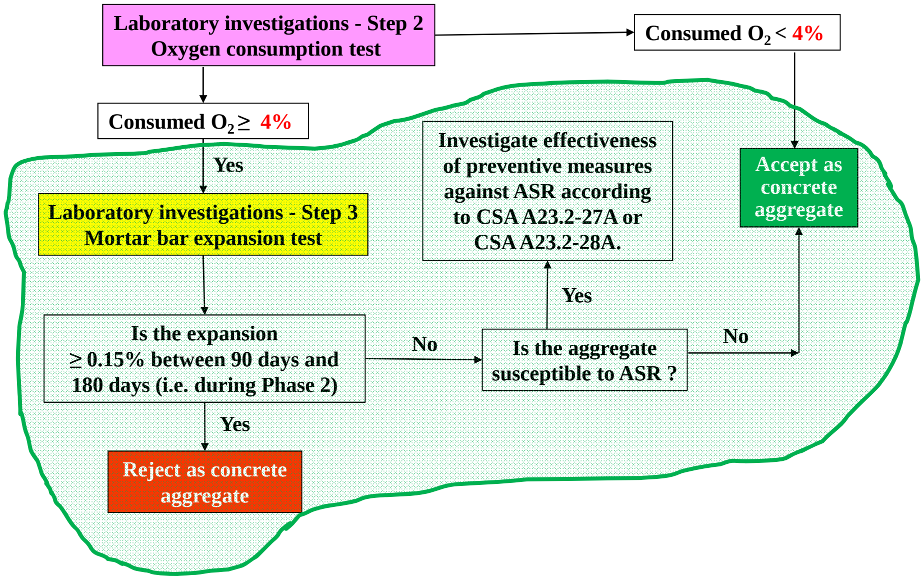


Oxygen consumption test

- 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



Laboratory investigations - Step 2
Oxygen consumption test

Consumed O_2 < 4%

Consumed $O_2 \geq$ 4%

Yes

Laboratory investigations - Step 3
Mortar bar expansion test

Investigate effectiveness of preventive measures against ASR according to CSA A23.2-27A or CSA A23.2-28A.

Accept as concrete aggregate

Yes

Is the expansion $\geq$ 0.15% between 90 days and 180 days (i.e. during Phase 2)

No

Is the aggregate susceptible to ASR ?

No

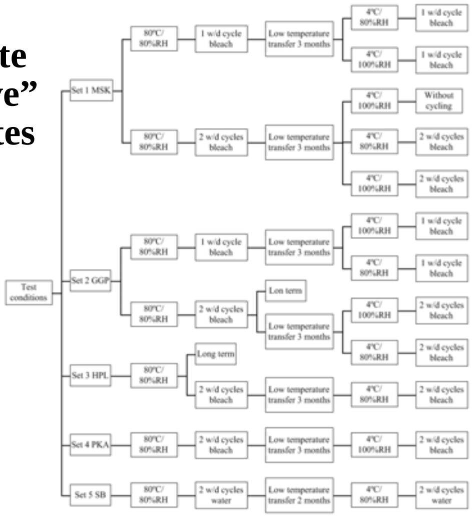
Yes

Reject as concrete aggregate

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)

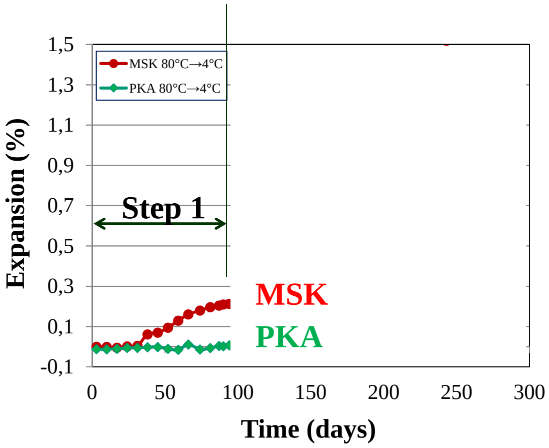
E/C: 0.65

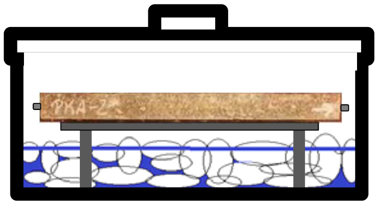
(Rodrigues et al. 2015)

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)



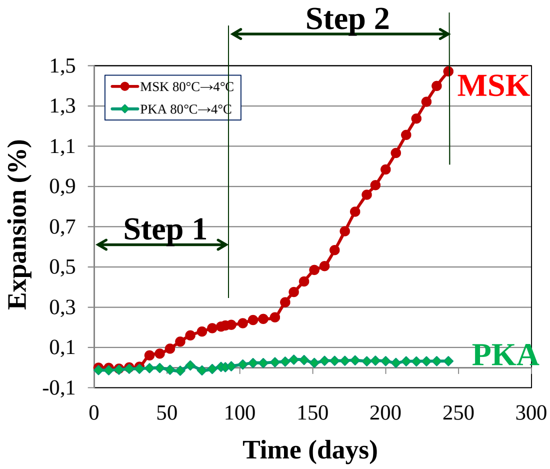


Bars above oversaturated solution of sodium chloride (NaCl)

Mortar bar test (Rodrigues et al. 2015)

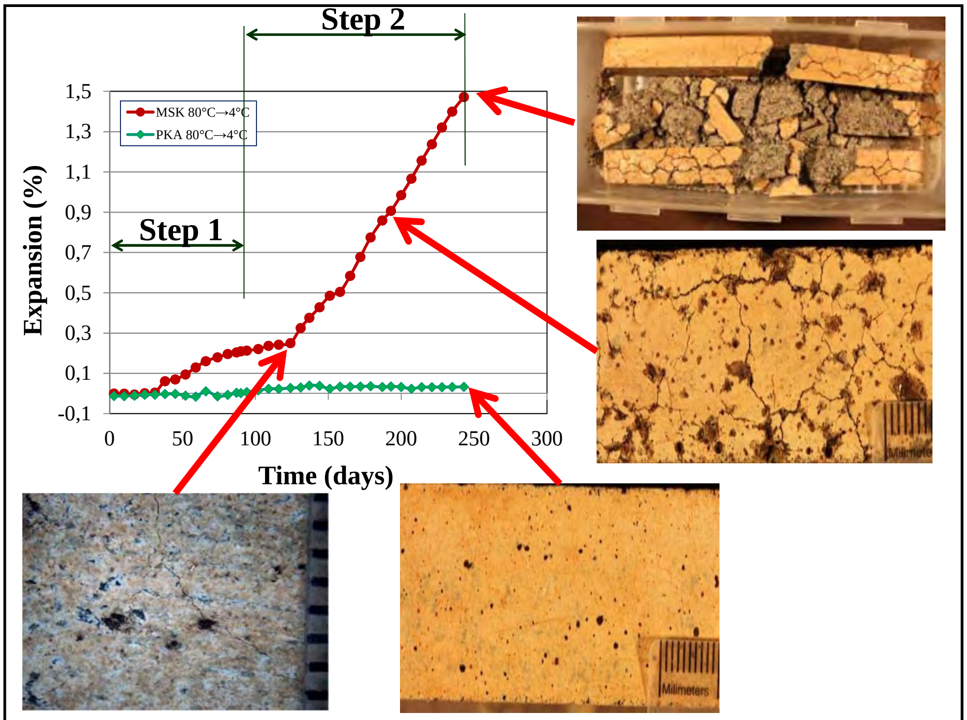
Step 1: Oxydation of sulphides and internal sulfate attack

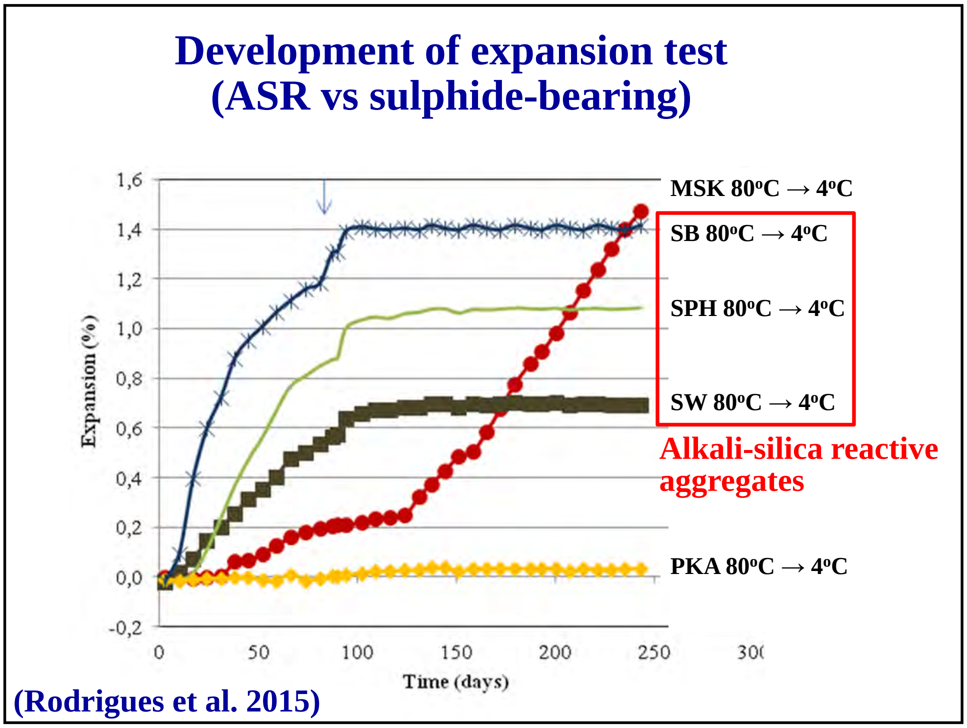
- 80°C, 80% R.H. + wetting in bleach (NaClO) 6% (2 x 3 hrs / week)
- Expansion and mass measurements (1x / week)



Step 2: Thaumasite Formation

- 4°C, 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)

MSK 80°C → 4°C

SB 80°C → 4°C

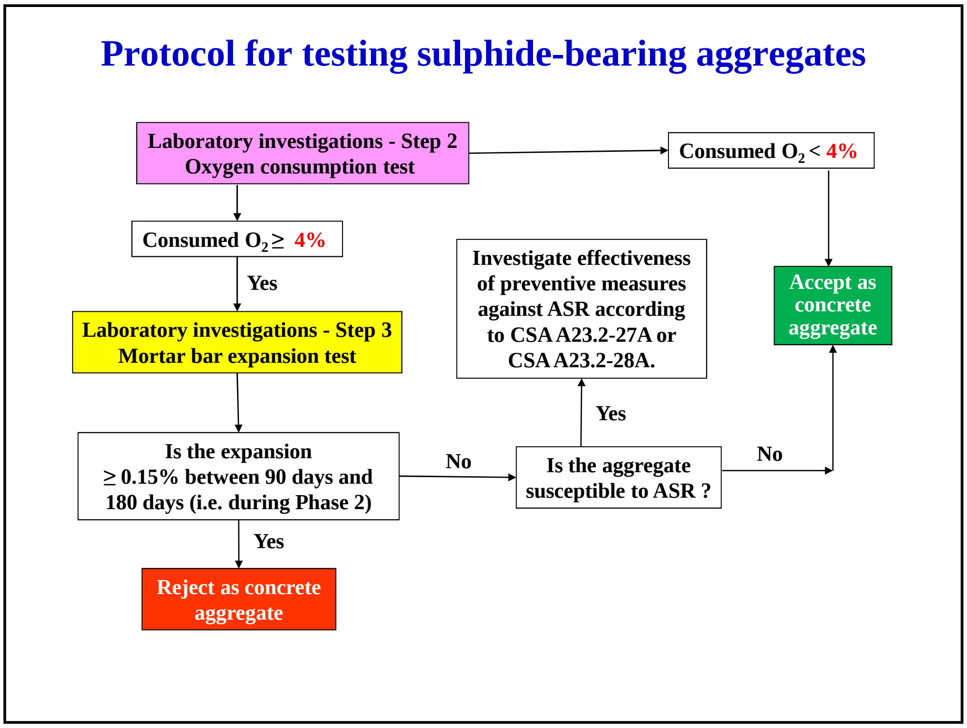
SPH 80°C → 4°C

SW 80°C → 4°C

Alkali-silica reactive aggregates

PKA 80°C → 4°C

(Rodrigues et al. 2015)



Protocol for testing sulphide-bearing aggregates

Laboratory investigations - Step 2
Oxygen consumption test

Consumed $O_2 < 4\%$

Accept as concrete aggregate

Consumed $O_2 \geq 4\%$

Yes

Laboratory investigations - Step 3
Mortar bar expansion test

Is the expansion ≥ 0.15% between 90 days and 180 days (i.e. during Phase 2)

Yes

Reject as concrete aggregate

No

Is the aggregate susceptible to ASR ?

Yes

Investigate effectiveness of preventive measures against ASR according to CSA A23.2-27A or CSA A23.2-28A.

No

NRC·CNRC

NRC - U. Laval Pyrrhotite project

Colloque sur la pyrrhotite – 24-25 Sept. 2018

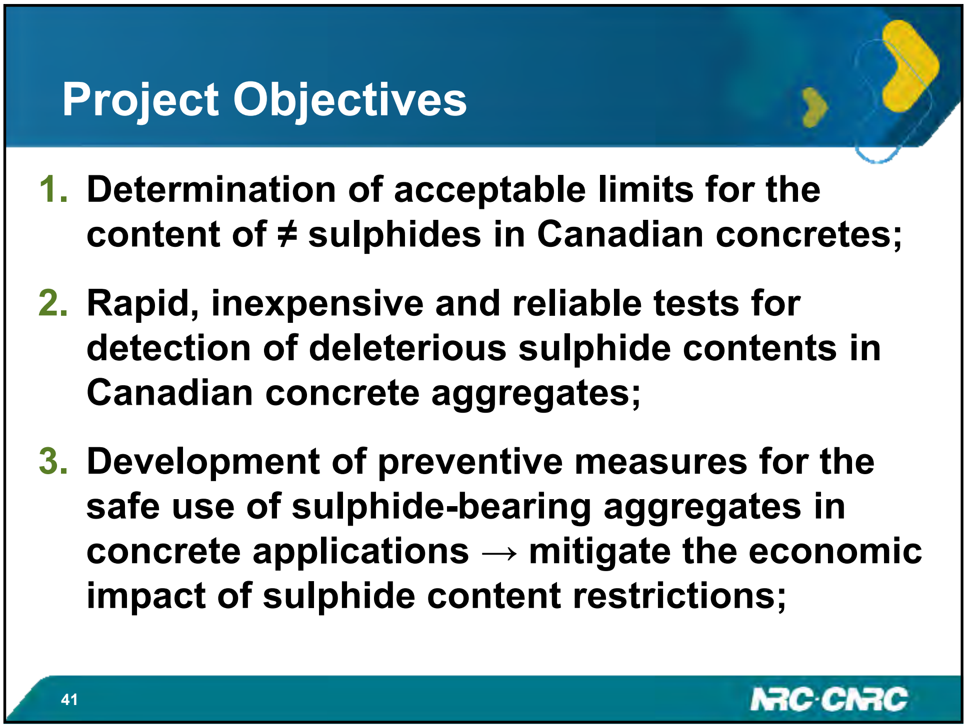
Jon Makar, Ph.D., P. Eng.

National Research Council Canada
Conseil national de recherches Canada

Canada

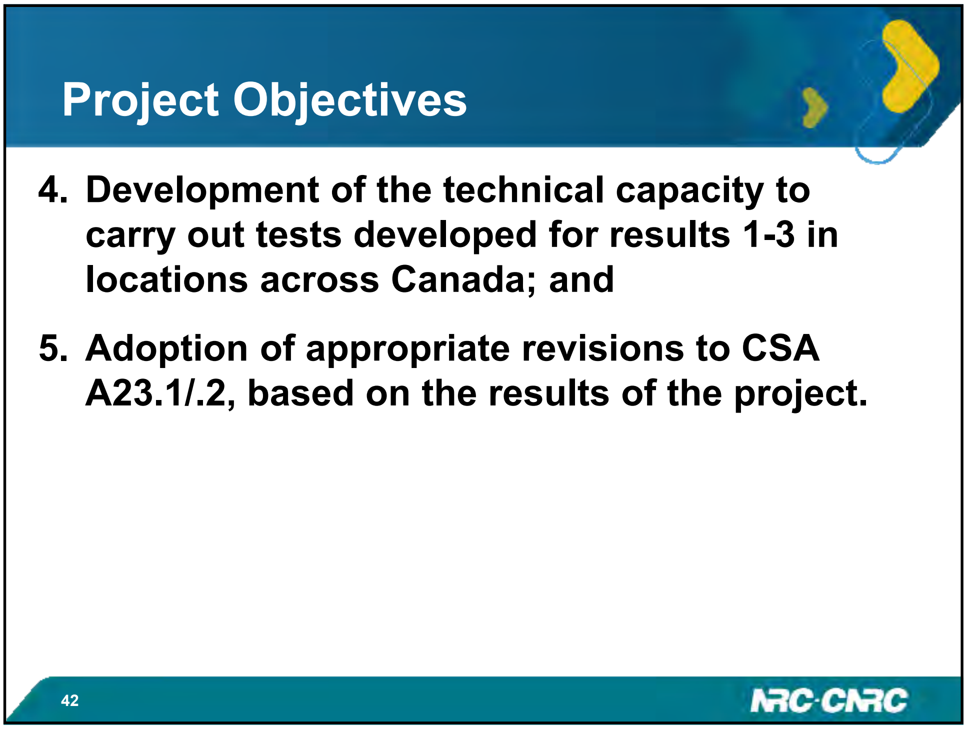
Project Partners

- 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;

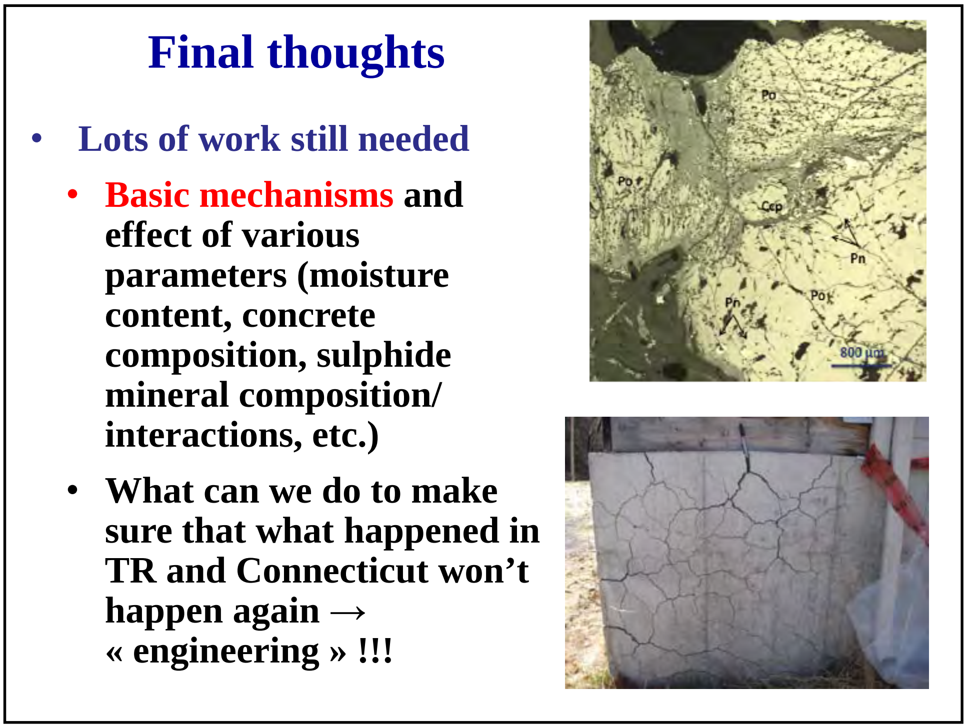


Project Objectives

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



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 » !!!

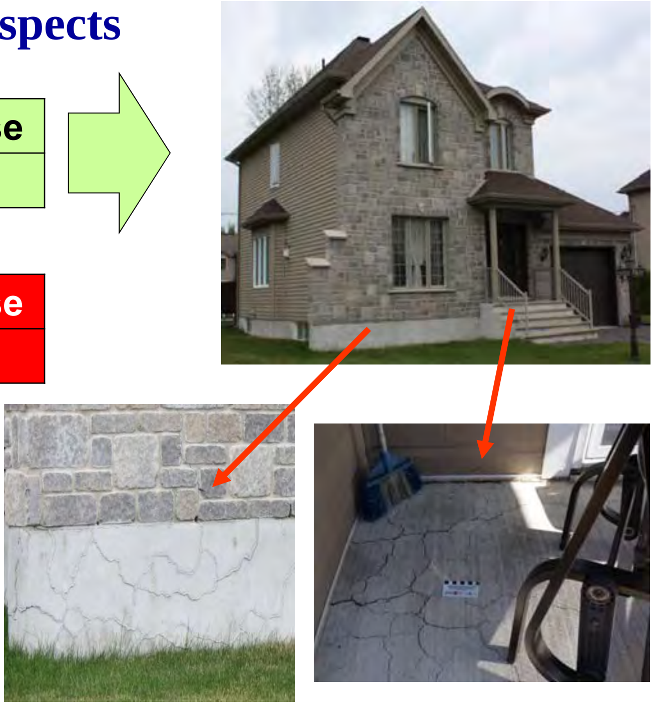
People’s aspects

Value of house

$ 500,000

Value of house

$ 0 !!!!



September 24th & 25th 2018 (TR)

PYRRHOTITE SYMPOSIUM

The situation in Mauricie and Connecticut

CAVP Coalition d’aide aux victimes de la pyrrhotite

crumbling BASEMENTS

Connecticut Coalition Against Crumbling Basements

Québec

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)
(1) Department of Geoscience and Petroleum, Faculty of Engineering, NTNU, Norway
(2) Department of Structural Engineering, Faculty of Engineering, NTNU, Norway

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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NS-EN 1744-1:2009+A1:2012: Tests for chemical properties of aggregates - Part 1: Chemical analysis

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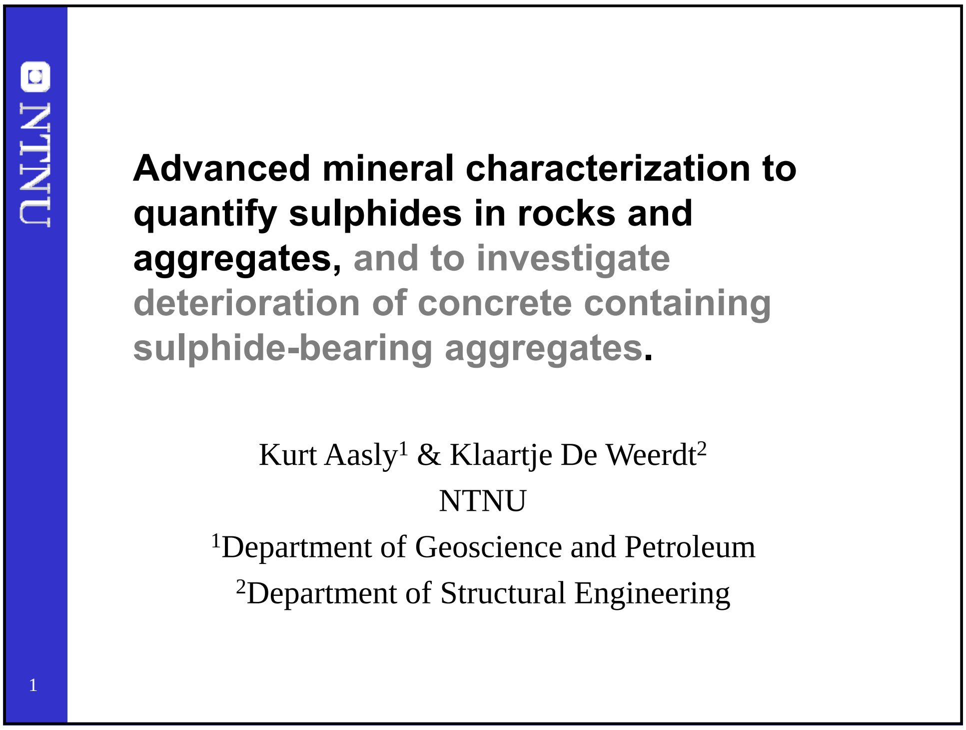

Advanced mineral characterization to quantify sulphides in rocks and aggregates, and to investigate deterioration of concrete containing sulphide-bearing aggregates.

Kurt Aasly[1] & Klaartje De Weerdt[2]
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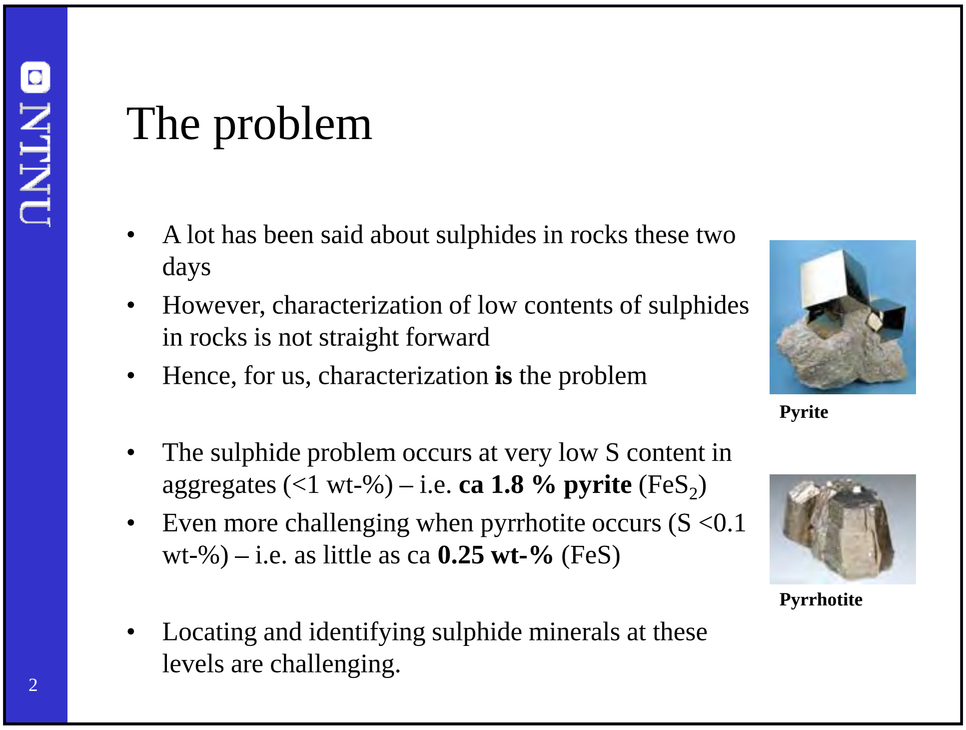
[1]Department of Geoscience and Petroleum
[2]Department of Structural Engineering



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

- 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)

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

Pyrite

Pyrrhotite

Standard test methods

Chemical analyses:

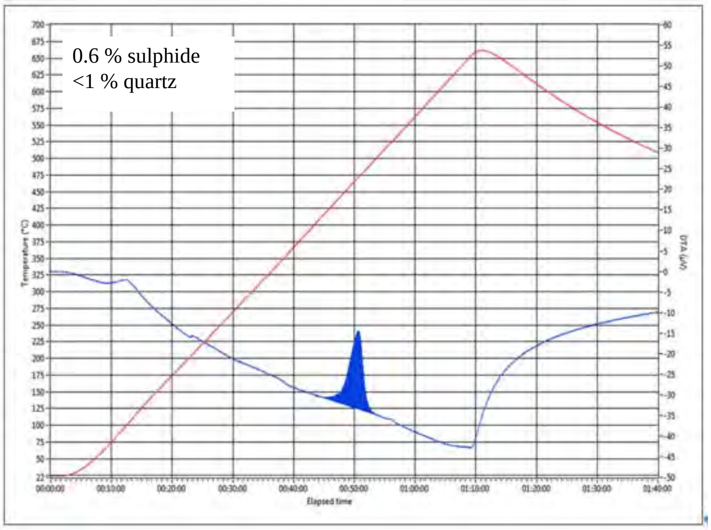
- X-ray fluorescence (XRF):
  - Quantitative analyses
  - down to ppm level
  - Short lead time sample prep
  - Not suited for S
- Combustion method for S
  - e.g. Leco
  - Sub %
  - Short lead time sample prep
- Acid solubility/gravimetric
  - Sub % (?)
  - Short lead time sample prep

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

DTA analyses

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



Pers. com.: Filip Dahl, SINTEF

DTA analyses

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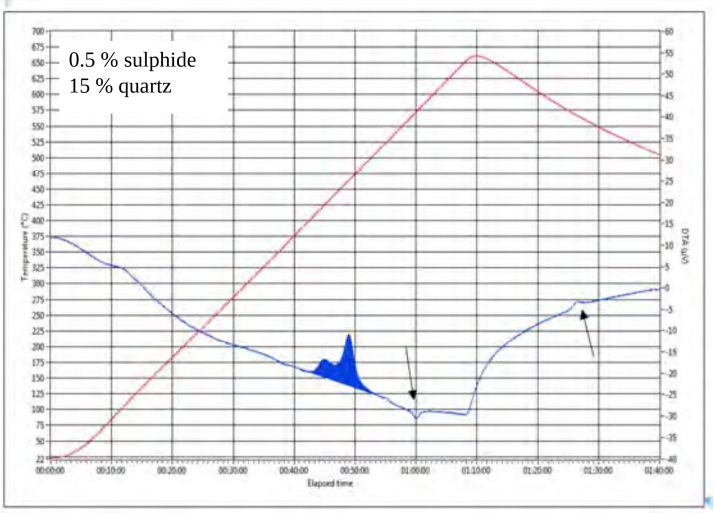
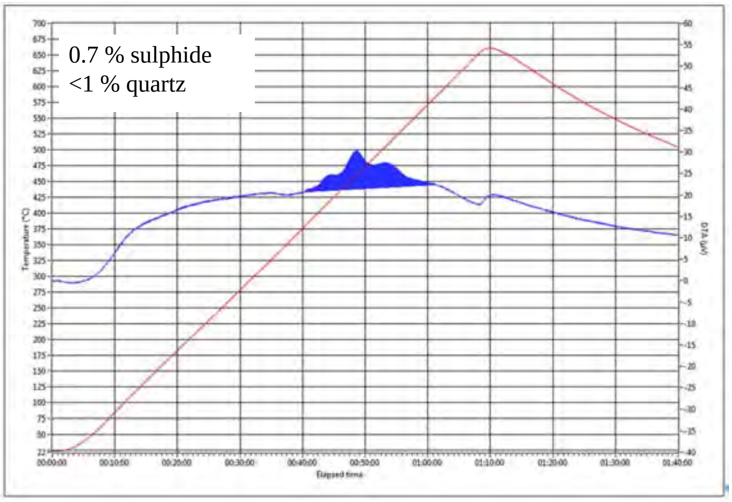

0.5 % sulphide
15 % quartz

Pers. com.: Filip Dahl, SINTEF

DTA analyses

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


0.7 % sulphide
<1 % quartz

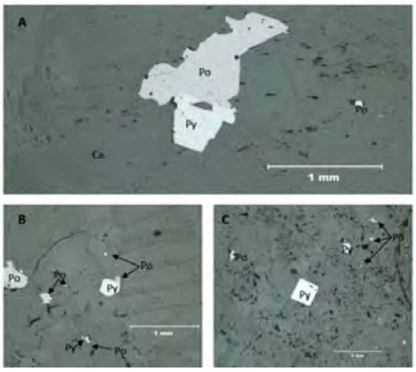
Pers. com.: Filip Dahl, SINTEF

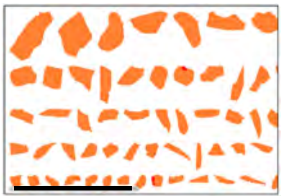
Relevant research

- 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

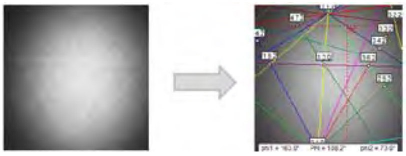
Photo: Omya Hustadmarmor

Photo: Brønnøy Kalk, 2012





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



KA2

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

Bunkholt (2015)

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

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:

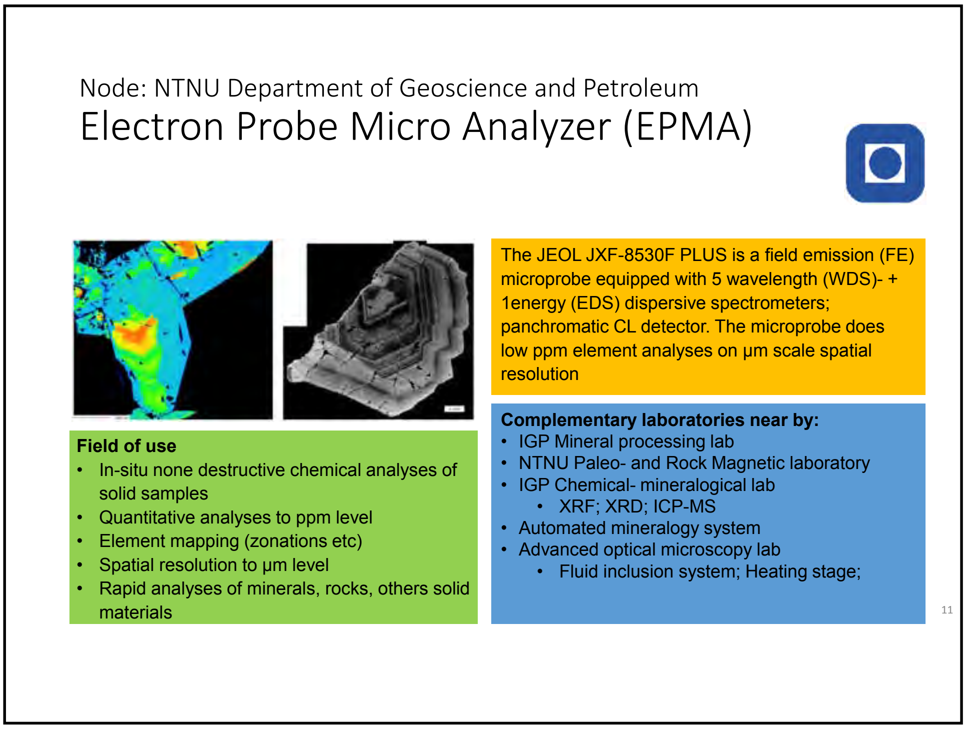
- 3D Atom probe
- EPMA
- AMS
- LA-SS-MC/QqQ-ICP-MS
- LA-QqQ-ICP-MS

GEOLOGICAL SURVEY OF NORWAY
- NGU -

SINTEF

NTNU

Forskningsrådet



Node: NTNU Department of Geoscience and Petroleum

Electron Probe Micro Analyzer (EPMA)

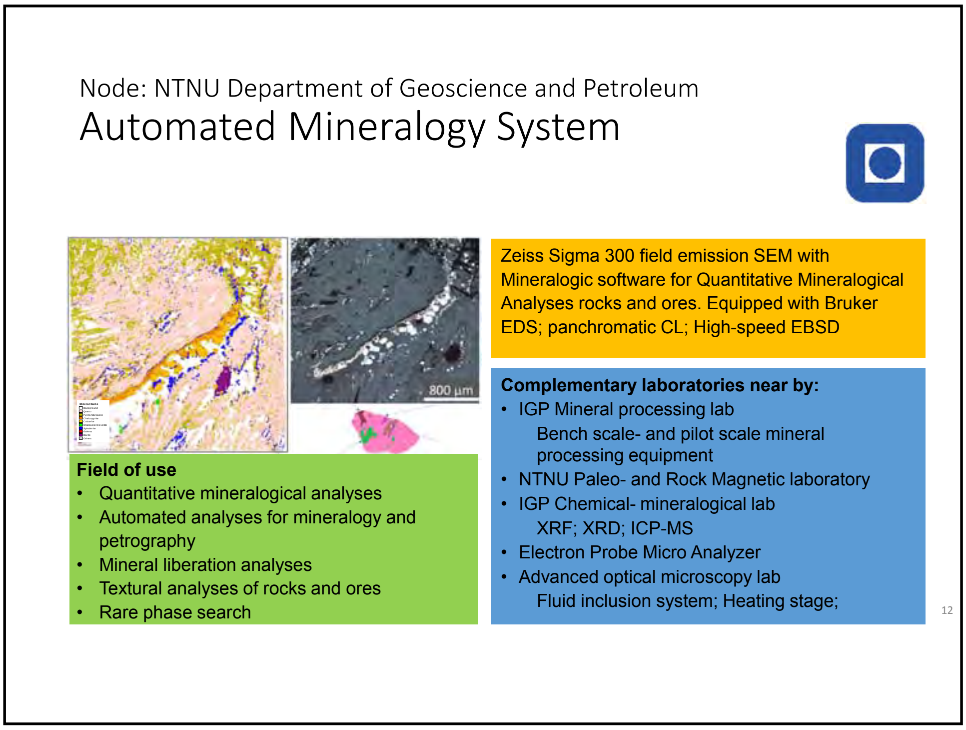
The JEOL JXF-8530F PLUS is a field emission (FE) microprobe equipped with 5 wavelength (WDS)- + 1energy (EDS) dispersive spectrometers; panchromatic CL detector. The microprobe does low ppm element analyses on µm scale spatial resolution

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;

Lab facilities – IGP/NTNU

Existing labs

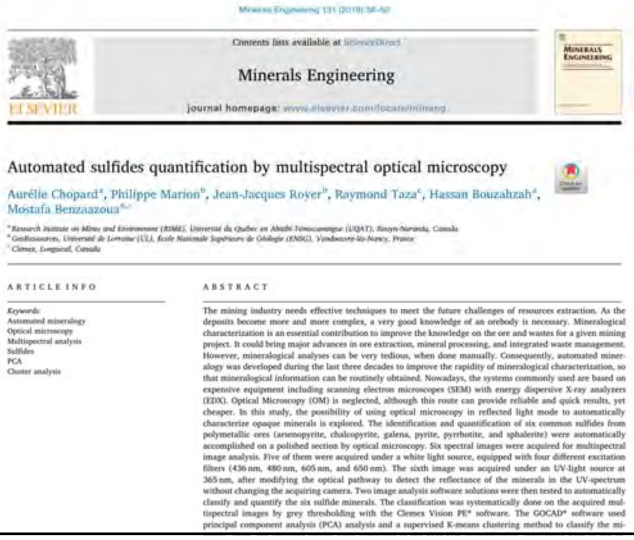
- XRD
- XRF
- DTA (co-op with SINTEF)
- SEM and EPMA
- Petrographic microscopes

- + 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

Fresh from the press



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Automated sulfides quantification by multispectral optical microscopy

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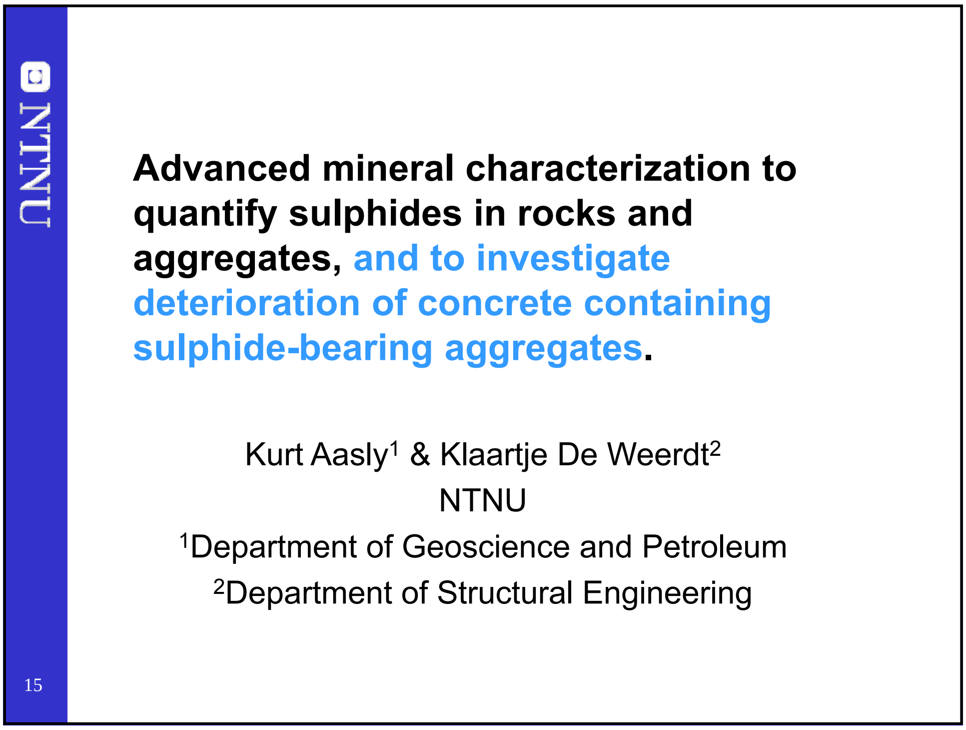
ABSTRACT

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-



Advanced mineral characterization to quantify sulphides in rocks and aggregates, and to investigate deterioration of concrete containing sulphide-bearing aggregates.

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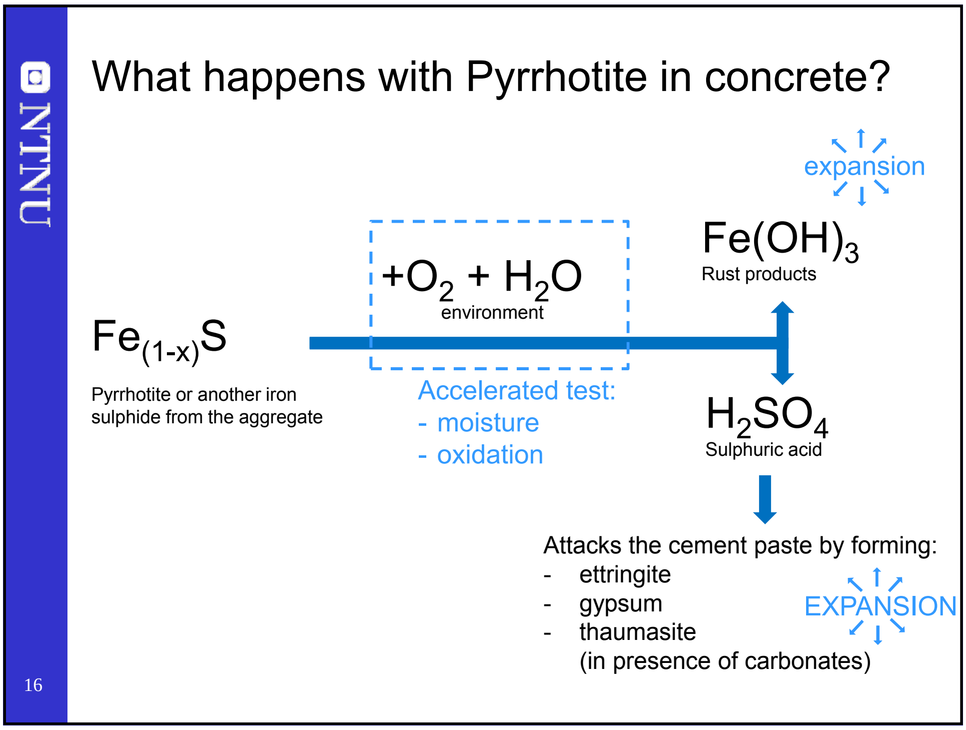
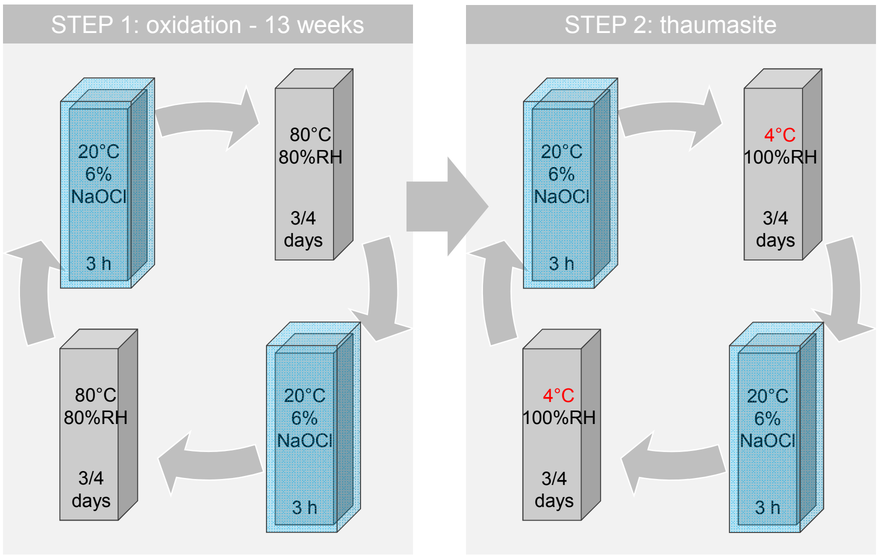


What happens with Pyrrhotite in concrete?

Attacks the cement paste by forming:
- ettringite
- gypsum
- thaumasite (in presence of carbonates)

Accelerated test for iron-sulphide minerals



STEP 1: oxidation - 13 weeks

20°C
6%
NaOCl
3 h

80°C
80%RH
3/4
days

20°C
6%
NaOCl
3 h

80°C
80%RH
3/4
days

STEP 2: thaumasite

20°C
6%
NaOCl
3 h

4°C
100%RH
3/4
days

20°C
6%
NaOCl
3 h

4°C
100%RH
3/4
days

Rodrigues Duchesne Fournier (2015) CCR

Accelerated test for iron-sulphide minerals

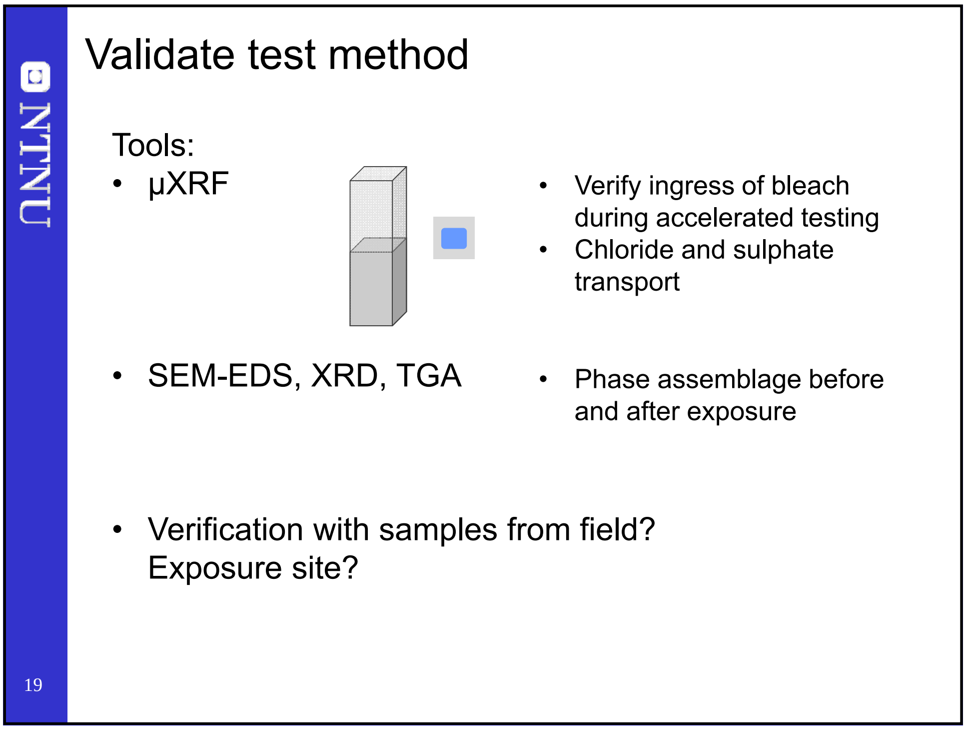
The accelerated test method can potentially be used to assess the impact of:

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

Remaining questions:

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

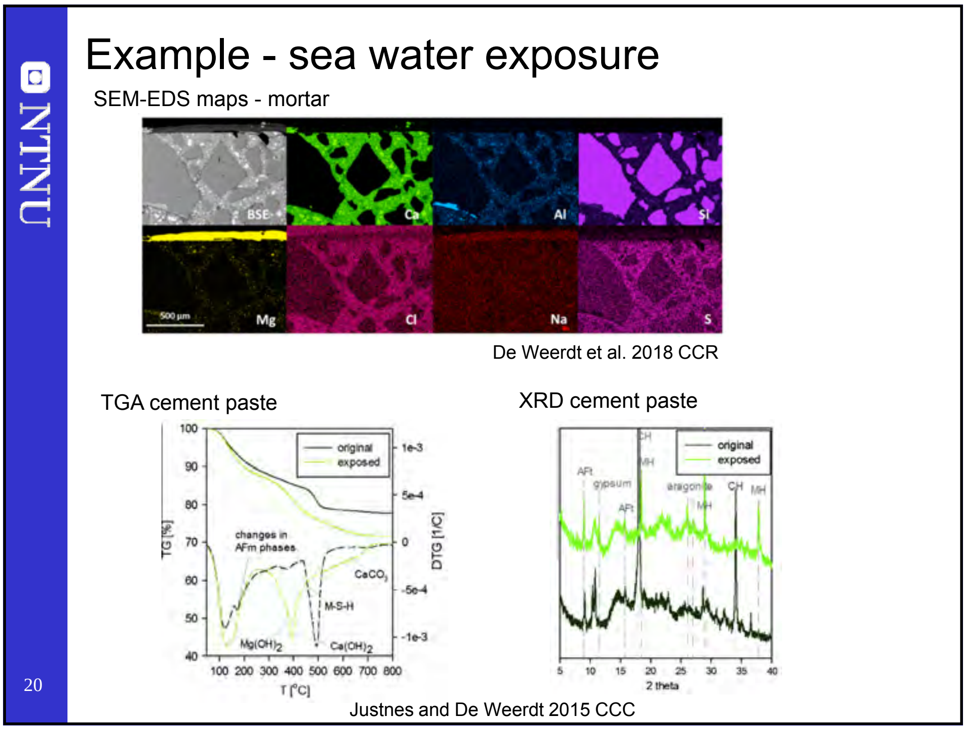
- Correlation laboratory expansion – field?
- Do we test the same mechanisms?
- Do we get the same reaction products?
- Is the test applicable on all kinds of concretes?



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?



Example - sea water exposure

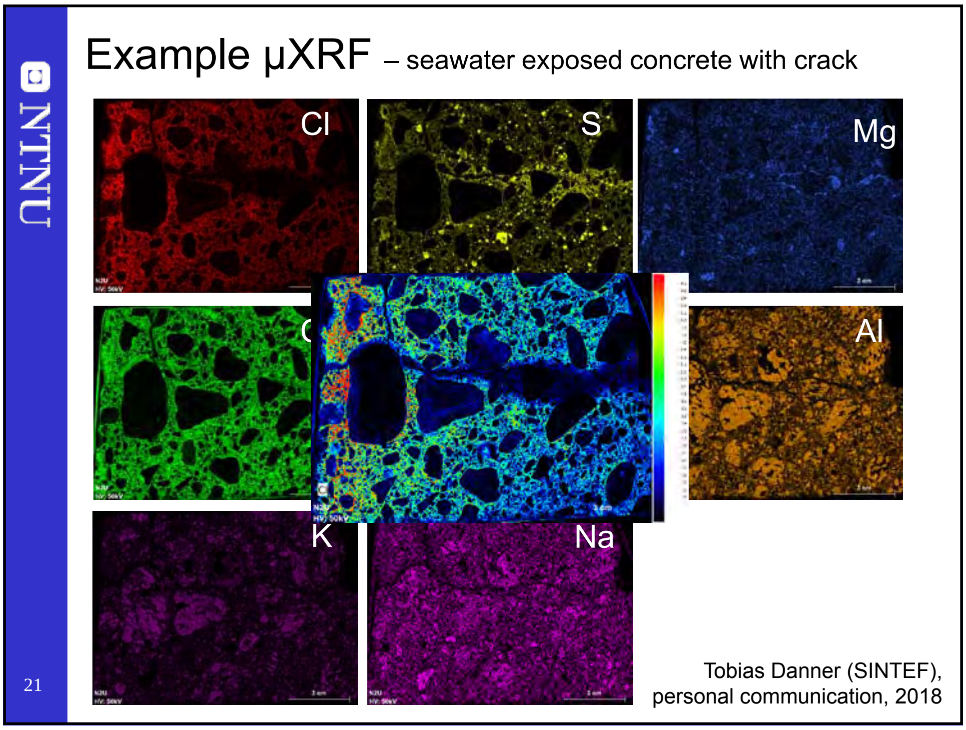
SEM-EDS maps - mortar

De Weerdt et al. 2018 CCR

TGA cement paste

XRD cement paste

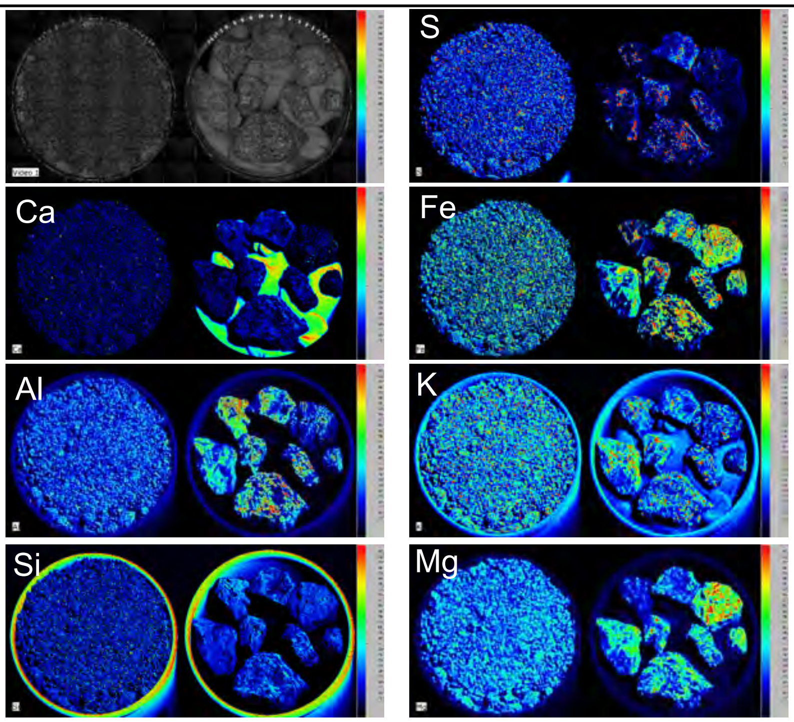
Justnes and De Weerdt 2015 CCC



Example µXRF – seawater exposed concrete with crack

Tobias Danner (SINTEF),
personal communication, 2018

Example µXRF



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.

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

rosjekt:	Pyrrhotite in concrete aggregates - Magnetkis i betongtilslag
ato: 14.11.2018	**Forslagsstiller/seksjon:**

- 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.

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

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