The process of pyrite oxidation with the resulting formation of sulfates in disturbed pyrite-rich mudstone is now recognised as a potential engineering hazard. Investigations of twenty-eight, approximately thirty-year old highway structures affected by the thaumasite form of sulfate attack (TSA) foundation structures on the M5 motorway enable the extent of pyrite oxidation in Lower Lias Clay in Gloucestershire to be established. Correlations with the extent of TSA and groundwater composition are sought.

Most of the structures have concrete spread footings founded on undisturbed and relatively unweathered Lower Lias Clay, and are surrounded by backfill of reworked Lower Lias Clay. Differences are identified in the sulfides, sulfates and total sulfur concentrations between unweathered and weathered Lower Lias Clay and the backfill. Overall, there has been a loss of about 70% of the pyrite present in the clay. In spite of a large increase of gypsum in the weathered clay, it only accounts for 36% of the available sulfur. The fill contains little gypsum and these changes are not apparently accompanied by changes in the amount of calcite present. Measurements of groundwater sulfate indicate an average increase in BRE sulfate value of one class. On average the ground water is alkaline.

The work was supported by laboratory pyrite oxidation trials on Lower Lias Clay samples stored in bags and sealed tubes. In these, a decline in the pyrite content occurred concurrently with an increase in gypsum. The changes were more rapid in the bagged samples.

In order to study the effects of environmental conditions on the changes in mineralogy and chemistry of the clay, samples of Lower Lias Clay were subjected to various temperature and humidity conditions. It was found warm and humid conditions gave rise to the most rapid changes, whereas dry and cool conditions had an inhibiting effect. Simulated UK climatic conditions also brought about significant changes. Although acid soluble sulfur increased within 14 days, there was little change in water soluble sulfur. The pH also remained constant, implying that acidity was being neutralised by reactions with calcite in the clay.

Further work on chipped clay samples showed similar results, with the rapid development of BRE class 3 conditions. Samples of water obtained by squeezing the clay and by withdrawing pore water via piezometer tubes gave similar results, but further work is required on the comparability of water extracts and pore waters obtained by squeezing or centrifuging samples and from piezometers.
Effects of Weathering on Pyritic Clay Aggressivity

Dr John Cripps
Clay studies

• Review of Halcrow (M5 bridge sites) data
• Laboratory weathering tests on Lower Lias Clay
• Storage tests on pyritic clays and mudrocks
• Foundation simulation
Halcow Investigation

- Thaumasite identified in concrete foundations [M5, Gloucestershire]
- Constructed during early 1970’s
- Concrete cast in situ against unweathered pyritic Lower Lias Clay with mixed clay backfill
- Extent of thaumasite sulfate attack (TSA) investigated
- Effects and rates of pyrite oxidation investigated
Damage associated with pyrite oxidation

Bridge foundation piers

TSA affected concrete
Sources of sulfur

Sulfide – pyrite
- Lias Clay
- Other clays and mudrocks
- Shales & mining waste
- Metamorphic rocks, slate
- Some alluvial deposits

Sulphates - gypsum
- Mercia Mudstone
- Weathered horizons
Weathering of pyrite

**Atmospheric conditions**

\[ 2 \text{FeS}_2 + 7 \text{O}_2 + n \text{H}_2 \text{O} \rightarrow 2 \text{FeSO}_4 \cdot n\text{H}_2\text{O} + \text{H}_2\text{SO}_4 \]

Pyrite \hspace{1.5cm} \text{Ferrous sulfate} \hspace{1.5cm} \text{Sulfuric acid}

**Free oxygen & higher Eh, ie saturated conditions**

\[ 2 \text{FeS}_2 + 2 \text{H}_2\text{O} + 7 \text{O}_2 \rightarrow 2 \text{Fe}^{2+} + 4\text{SO}_4^{2-} + 4\text{H}^+ \]

Pyrite \hspace{1.5cm} \text{Ferrous iron}

\[ 4\text{Fe}^{2+} + 4\text{H}^+ + \text{O}_2 \rightarrow \text{microbes} \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O} \]

Ferrous iron \hspace{1.5cm} \text{Ferric iron}

\[ \text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \]

Pyrite \hspace{1.5cm} \text{Ferric iron} \hspace{1.5cm} \text{Ferrous iron}

\[ \text{pH} \geq 4 \text{ ie flushing of system} \]

\[ 4\text{Fe}^{2+} + 10\text{H}_2\text{O} + \text{O}_2 \rightarrow 4\text{Fe(OH)}_3 + 8\text{H}^+ \]
Pyrite oxidation in Lower Lias Clay

Residual Fe-oxide/hydroxide (limonite) alteration pseudomorph from weathered Lower Lias Clay core

Pyrite poly-framboid from unweathered Lower Lias Clay core
Gypsum formation

\[
\text{CaCO}_3 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow \text{CaSO}_4.2\text{H}_2\text{O} + \text{CO}_2
\]

Calcite   Sulfuric acid   Gypsum

Authigenic euhedral gypsum crystals in Lias Clay
Partly dissolved pyrite frambooid
# Mineralogy of the Lower Lias Clay

## Published Data

<table>
<thead>
<tr>
<th></th>
<th>Qtz %</th>
<th>Calc %</th>
<th>Feld %</th>
<th>Pyrite %</th>
<th>Gyps %</th>
<th>Sid %</th>
<th>Dol %</th>
<th>Clay %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unweathered</strong></td>
<td>8-11</td>
<td>&lt;1-30</td>
<td>&lt;1-5</td>
<td>3-10</td>
<td>NA</td>
<td>1-6</td>
<td>NA</td>
<td>52-90</td>
</tr>
<tr>
<td><strong>Weathered</strong></td>
<td>2-11</td>
<td>&lt;1</td>
<td>NA</td>
<td>&lt;5</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>78-91</td>
</tr>
</tbody>
</table>

## Thaumasite Investigation

<table>
<thead>
<tr>
<th></th>
<th>Qtz %</th>
<th>Calc %</th>
<th>Feld %</th>
<th>Pyrite %</th>
<th>Gyps %</th>
<th>Sid %</th>
<th>Dol %</th>
<th>Clay %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unweathered</strong></td>
<td>8-11</td>
<td>10-38</td>
<td>1-7</td>
<td>0.7-2.5</td>
<td>0.3-0.9</td>
<td>NA</td>
<td>9-15</td>
<td>32-62</td>
</tr>
<tr>
<td><strong>Weathered</strong></td>
<td>5-13</td>
<td>16-32</td>
<td>3-5</td>
<td>0.2-0.8</td>
<td>0-17</td>
<td>NA</td>
<td>11-15</td>
<td>35-51</td>
</tr>
<tr>
<td><strong>Fill</strong></td>
<td>8-16</td>
<td>9-39</td>
<td>0-19</td>
<td>0.3-1.3</td>
<td>0-1.3</td>
<td>NA</td>
<td>7-13</td>
<td>33-57</td>
</tr>
</tbody>
</table>

Values for pyrite & clay minerals are relatively low & calcite is high in the study area.
Data from Thaumasite Report – Lower Lias Clay

<table>
<thead>
<tr>
<th></th>
<th>Qtz %</th>
<th>Cal %</th>
<th>Gyp %</th>
<th>Dol %</th>
<th>Pyr %</th>
<th>Clay %</th>
<th>Soil pH</th>
<th>WWS g/l</th>
<th>ASS %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unwthrd</td>
<td>9.4</td>
<td>24</td>
<td>0.6</td>
<td>12</td>
<td>1.6</td>
<td>47</td>
<td>8.3</td>
<td>1.0</td>
<td>0.71</td>
</tr>
<tr>
<td>Wthrd</td>
<td>8.6</td>
<td>24</td>
<td>7.9</td>
<td>13</td>
<td>0.5</td>
<td>43</td>
<td>8.1</td>
<td>1.1</td>
<td>2.05</td>
</tr>
<tr>
<td>Fill</td>
<td>11.0</td>
<td>24</td>
<td>0.6</td>
<td>10</td>
<td>0.6</td>
<td>45</td>
<td>8.2</td>
<td>1.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

- Amount of pyrite is similar to that found in current tests
- Amount of pyrite is reduced (~70%) in weathered clay and fill
- Large increase in gypsum in weathered clay but little in fill
- There has been about 36% loss of sulfur in weathered clay
- No apparent change to calcite
- Few values of pH below 7.5
- There is potential for further oxidation in weathered clay & fill
Pyrite loss, groundwater sulfate & degree of TSA

- Data available for 12 structures
- Pyrite losses vary between 9% & 90% (average 52%)
- Average groundwater sulfate increase by 1 BRE class, but no apparent correlation with pyrite loss
- Groundwater is not acidic
- No apparent correlation between pyrite loss & degree of thaumasite attack
- The amount of thaumasite is small compared with the sulfur available for reaction
Investigation of pyrite storage & oxidation rate

- Commonly encountered sample storage environments simulated: poorly sealed bagged core & well sealed, wrapped core in liner.
- Six Lower Lias core samples, 3 unweathered, 2 weathered & 1 fill sample
- Material was sub-sampled periodically and the acid soluble sulfate and pyrite determined
- Material was stored for 254 days (8 months)
Oxidation of pyrite during sample storage

- Loss of pyrite, gain in gypsum (8 months)
- Core samples undergo slower reaction than bagged samples
Clay weathering simulation tests

Samples:
Unweathered Lower Lias clay from M5 investigation and GCHQ
Refrigerated storage since December 2000

Environments:
1. Fridge - 5°C at 60%RH
2. Mist room - 20°C at 95%RH
3. Water tank- 40°C at 100%RH
4. Environmental chamber - UK day cycle
5. Freezer - Freezing/thawing at 50-65%RH

Times:
1, 2, 4, 14 and (28) days
Clay weathering simulation tests

Unweathered Lower Lias Clay
M5 Jnt 13  6/12/2000
Picture  23/07/2002

Unweathered Lower Lias Clay
GCHQ   7/12/2000
Picture  23/07/2002
Clay weathering simulation tests

Characterisation of clay

- Moisture content
- pH
- Water soluble sulfate
- Acid soluble sulfate
- Total sulfur
- Pyrite (Total sulfur - Acid soluble sulfur)
- (Carbonate)
- Whole rock XRD
Env 4: UK day cycle

- Calcite = C
- Dolomite = D
- Gypsum = G
- Illite = I
- Kaolinite = K
- Pyrite = P
- Qt = Q

Relative Intensity

°2θ

- Initial
- 1 day
- 3 days
- 7 days
- 14 days

UK day cycle climate
40°C at 100% RH constant

Initial

1 day

3 days

7 days

14 days

Env 3: 40°C at 100%RH

Calcite = C
Dolomite = D
Gypsum = G
Illite = I
Kaolinite = K
Pyrite = P

Initial

1 day

3 days

7 days

14 days

Relative intensity

°2θ

0 10 20 30 40 50 60 70
Acid soluble sulfur (gypsum)

- 40°C 100% RH
- Freeze-thaw
- UK cycle
- 5°C 60% RH
- 20°C 95% RH
Clay weathering simulation tests

- Chemical data indicate a small increase in acid soluble sulfate with time (up to 14 days)
- Small amount of pyrite (1 – 2%) present
- pH (2:1 extract remained near constant implying reaction with calcite)
- Water soluble sulfur near constant
  (~ 0.15%S  2.3g/l SO₄  Class 2)
- Most change for high temperature, humid conditions
- Surface changes masked by tests on whole sample
Controlled weathering
38°C, 100% R.H.

Unweathered, freshly cut Lower Lias clay from Northcot Brick Works, Glouc. Sealed and stored at 5°C (November 2002)

Samples prepared as 1-2 cm chips and 2cm³ cubes
XRD analysis

Counts vs. 2-Theta for different time periods:
- Original
- 7 days
- 28 days
- 60 days

Symbols:
- Ch = chlorite
- G = gypsum
- Q = quartz
- C = calcite
- A = aragonite
- K = kaolinite
- P = pyrite
- I = illite

Ch = chlorite, G = gypsum, Q = quartz, C = calcite, A= aragonite
K = kaolinite, P = pyrite, I = illite
Clay chips: 38°C, 100% R.H.

- pH falls (8.5 – 7.7)
- Rise in water soluble sulfur
- WSS = 0.08 - 0.18% S
  (1.2 – 2.7 g/l)
- Equivalent to Class 2 - 3 conditions
pH and water soluble sulfur (%)

1:1 water extract

- pH falls (8.5 – 7.7)
- Rise in water soluble sulfur
- WSS = 0.08 - 0.18%S (1.2 – 2.7 g/l)
- Equivalent to Class 2-3 conditions

Foundation simulation - pore water

Extracts 0-100mm (top) layer pH 7 – 8
- WSS ~ 0.05 – 0.12%S (0.75 – 1.8g/l Class 1 – 2)

Squeezed from 0-100mm (top) layer
- WSS ~ 0.03 %S (0.45g/l Class 2)

Piezometers @ 25mm from clay/PLC interface –
- all layers WWS ~ 0.03 – 0.04%S (0.45 – 0.6g/l Class 2)
- top layer WWS ~ 0.03%S (0.45g/l Class 2)
Clay Weathering

Conclusions

- Pyrite oxidation accounts for increase in water and acid soluble sulfate levels in clays
- Samples of clay should be sealed and refrigerated for short-term storage and dried and sealed for longer-term storage
- Amounts of pyrite are small, XRD is unreliable. Direct or indirect chemical testing for pyrite is required
- Oxidation process occurs most rapidly in hot, humid conditions in which measurable changes occur in about 14 days
- pH and WSS results are similar for extracts, piezometer and squeezed samples, but further work is required
- Values of pH and WSS are similar to those measured at M5 bridge sites
Effects of Weathering on Clay Aggressivity

Dr John Cripps

Thanks for listening!