The mechanism of degradation the wool and linen textiles by iron corrosion effect

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ABSTRACT:
When a textile comes into contact with metal surface such as iron, Metal starts to corrode very quickly in the presence of damp, oxygen and the increasing of acidity conditions. Corrosion products start to form on the metal surface around the textile fibres which contact with it. Through short time, a reaction between iron ions and textile will be happened, which cause deterioration in textile. The textile degrades due of the oxidation process, hydrolysis and acid accumulates, and its symptoms include loss of strength and brittleness. This study focus on the effect of iron corrosion on the linen and wool textiles. The methods of investigation were used, tensile strength and elongation of all samples. They were carried out to study the physical and mechanical properties of samples. Scanning Electron Microscopy equipped with EDAX (SEM–EDAX) was used for identifying the fibers deterioration. EDAX was also used to identify the types of corrosion presence and thus, for understanding deterioration. The degradation of the textile samples has been detected by infrared spectroscopy (IR).

1. Introduction:
Corrosion of metal is an electrochemical process with the surrounding environment. Corrosion is caused by moisture, pH levels and water. Base metals such as iron are more vulnerable to corrosion than other metals\(^1\). Corrosion is a reaction occurs when one metal contains positively charged ions and another contact surface contains negatively charged ions.

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\(^1\) Sangwoo Han, B.A. (1996): Museological Approaches to the General Preservation of Korean Archaeological Artifacts, a Thesis in Museum Science, Submitted to the faculty of Texas Tech University, p70.
When an electrical conductor is connected between them, the current will flow as in the discharge of a battery\(^2\). The anode in an electrochemical cell is the electrode that undergoes oxidation, and reduction occurs at the cathode. Thus, the corrosion process, as an electrochemical action, generates an excess of electrons at the anode and a lack of electrons at the cathode. Because of the voltage difference between anodes and cathodes, an electron flow in the metal substrate completes the electrical circuit, and corrosion proceeds. The ultimate corrosion product of iron, after the electrochemical cell is run down, is a corrosion product such as oxides, carbonate, and sulfates\(^3\). The mechanism of ion corrosion is described in:

\[
\begin{align*}
\text{Fe} & \rightarrow \text{Fe}^{2+} + 2e^- \quad \text{at the anode} \\
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- & \rightarrow 4\text{OH}^- \quad \text{at the cathode} \\
\text{Fe}^{2+} + 2\text{OH}^- & \rightarrow \text{Fe(OH)}_2 = \text{(Ferrous Hydroxide)} \\
4\text{Fe(OH)}_2 + \text{O}_2 + 2\text{H}_2\text{O} & \rightarrow 4\text{Fe(OH)}_3 = \text{(Ferric Hydroxide)} \\
2\text{Fe(OH)}_3 & \rightarrow 2\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O} \text{ (Rust)} + 4\text{H}_2\text{O}
\end{align*}
\]

As the ferric oxide becomes more hydrated, it swells and becomes more porous\(^4\). The process will continue until the iron dissolves at the anode, and each atom of iron releases two electrons\(^5\). These electrons flow through the metal to other non-metallic substances (Fig. 1) such as textile surface. The metal

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\(^2\) [sanctuaries.noaa.gov/alligator/.../corrosionpreservatio_lesson.pdf]

\(^3\) Graham R. D., (1976): Wood-Metal Corrosion, Forest Research Laboratory, School of Forestry Oregon State University, p5.


\(^5\) Graham R. D. Op Cit; p5.
atoms are removed from the cubic structure of the metal molecule and enter into cathodic (reduction) reactions\(^6\).

![Figure 1. Electrons flow through the metal to other non-metallic substances](image)

The catalytic effect of transition iron ions on the oxidation of natural polymers such as cellulose and keratin. The reaction could be cleared in two processes\(^7\):

- **production of organic radicals**:

  It's known that the organic materials can oxidize by transition the Fe\(^{2+}\) ions to Fe\(^{3+}\) ions in damp conditions to form inconstant compounds of metal ions with oxygen, as it shown in:

  \[
  \text{Fe}^{2+} + \text{O}_2 \rightleftharpoons \text{Fe}^{3+} + \text{O}_2^- \quad (1)
  \]

  The Fe\(^{3+}\) ions will react with organic radicals (R\(^-\)) to form perhydroxyl radicals (HOO\(^-\)), as it shown in:

  \[
  \text{Fe}^{3+} + \text{O}_2^- + \text{RH} \rightarrow \text{R}^- + \text{HOO}^- + \text{Fe}^{2+} \quad (2)
  \]

  The perhydroxyl radicals (HOO\(^-\)) (H point to natural polymers) and organic radicals (R\(^-\)) once formed, initiate further radical chain

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reaction in acidic condition to form radicals and carboxyl radicals, as it shown:

\[ R' + O_2 \rightarrow ROO' \]  \hspace{1cm} (3)
\[ ROO + RH \rightarrow ROOH + R' \]  \hspace{1cm} (4)

- **production of hydrogen peroxide:**

Hydrogen peroxide is formed during the reduction of molecular oxygen by iron (II) ions.

\[ Fe^{2+} + HOO^- + H^+ \rightarrow Fe^{3+} + H_2O_2 \]  \hspace{1cm} (5)

The hydrogen peroxide subsequently is decomposed by Fe\(^{2+}\) to form hydroxyl radicals and hydroxyl ions, as it shown:

\[ H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^- + OH^- \]  \hspace{1cm} (the Fenton reaction)  \hspace{1cm} (6)

The hydroxyl radical is very reactive and will react with organic polymers (cellulose and keratin) to form organic radicals, leading to depolymerization\(^{8,9,10}\).

**1.1 The cellulose degradation:**

Cellulose, a polysaccharide having a \((1-4)\)-linked glucopyranose units. These have an empirical formula, \(C_6H_{12}O_6\), and can be given a cyclic structure, sometimes designated as a beta-D-glucopyranose or anhydroglucose unit (AGU). This compound is made up of two anhydroglucose units having alternating orientation with respect to the bridge oxygen bond. Each AGU contains three hydroxyl (OH) groups. At carbon 6, there is a "primary" hydroxyl group; the OH there is attached to a carbon atom having at least two hydrogens.

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The hydroxyls on carbons 2 and 3 are classified as "secondary" hydroxyl groups\textsuperscript{11}.

When cellulose reacts with iron ions it produces cellulose–Fe coordination complexes. Transition metals will complex with de-protonated hydroxyl group of polysaccharides through oxo-bridges, the vicinal diol groups (2 and 3 hydroxyl groups) can be involved in the formation of diketone bonds in coordination with Fe\textsuperscript{2+}. However, the primary hydroxyl groups of cellulose at C6 have the potential to form complexes with adjacent cellulose chain through Fe bridges\textsuperscript{12}. After hydrogen leaves carboxylic group and Fe ions attaches instead, The above previous reactions in the equations (1-6) will take place to form organic radicals (R\textsuperscript{·}) and cellulose hydroperoxide (ROOH), Chain scission occurs when cellulose hydroperoxide reacts with present iron (II) ions, as it shown below\textsuperscript{13} \textsuperscript{14}.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{cellulose_structure.png}
\caption{The cellulose structure}
\end{figure}

The degradation isn’t caused only by oxidation catalyzed by free Fe ions, the acid hydrolysis due to acidic components will also happen. When hydrogen ions are liberated through oxidation, they will in combination with water, break the C1 - O bond. The broken bond leaves a cyclic carbonium ion, which can join with an available water molecule to form a new ionic bond with C1 by evolving a hydrogen ion from the water molecule. A second protonation site is possible at the C1 - O bond within the cyclic glucose ring. There, a hydrogen ion bonds with the ring O to form a hydroxyl group for the C5, opening up the ring and leaving, again, a positively charged carbonium ion. A water molecule can again evolve a hydrogen ion (acid) to stabilize the now-linear 6-carbon molecule. The three stages of hydrolysis is the hydrolysis of the bonds available in the amorphous regions of the cell wall. This stage is depicted by the rapid fall of the degree of polymerization of cellulosics until a leveling off point is reached. This is the point

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when nearly all glucosidic bonds in the amorphous regions of the cell wall have undergone acid hydrolysis.\textsuperscript{16}

1.2 The keratin degradation:

The fundamental structural units in keratins are long peptide chains derived from the condensation of amino acids. These are linked together in one plane by covalent cystine linkages, and by electrovalent salt linkages, between charged polar side chains, and in the other linkages by hydrogen bonding between suitably situated peptide groups and by less important Van der Waals forces. Fibres are not, however homogeneous and two regions (crystalline and amorphous) have been differentiated.\textsuperscript{17}

\begin{center}
\includegraphics[width=0.5\textwidth]{wool_structure.png}
\end{center}

The wool structure

Metals in an ionic form can catalyze the protein oxidation. The iron ions will attack the peptide chains as follows:\textsuperscript{18}


\textsuperscript{17} Whewell C. S., (1960): The Chemistry of Hair, Journal of the Society of Cosmetic Chemists, Department of textile industries, Leeds 2, Yorks, pp 208,212.

\textsuperscript{18} Whewell C. S. Op Cit; p212.
- The peptide links (-CO-NH-) of the main chains.
- The tyrosine and serine residues attached to the main chains.
- The -S-S- links and the salt links joining peptide chains.
- The hydrogen bonds between adjacent peptide chains.

The peptide links (-CO-NH-) of the main chains.

Structure of an Amino Acid

Fe ions attack the H in NH₂ group and H in COOH group

The fibre degradation is caused by the combination of acid-catalyzed hydrolysis and iron-catalyzed oxidation. The excess of iron(II) ion in the fibres reacts with atmospheric oxygen (O₂) and wool protein, producing organic radicals and keratin hydroperoxide (ROOH), producing hydrogen peroxide (H₂O₂), and finally the hydrogen peroxide reacts with iron (II) ions creating the hydroxyl radical (OH⁻), according to the above previous reactions in the equations (1-6). This hydroxyl radical is responsible for the textile oxidation degradation.¹⁹

On the other side of degradation the acid degradation. Mineral acids can degrade wool proteins to an extent that depends on pH, temperature and moisture. Sensitive sites in the wool proteins include the side chains of asparagine and glutamine, from which ammonia is released, and the peptide bonds formed by serine, threonine, cysteine, aspartic and glutamic acids, and tryptophan.²⁰ The liquors from acid-degraded wool contain ammonium salts, free amino acids, and peptides. The hydrolysis of peptide bonds leads to weight losses and the liberation of end groups in the wool proteins,

because a bond in an organic molecule (N-C) is broken, and an (O-H) bond in a water molecule also breaks. Then, from the water molecule, an OH group adds to one part from the organic molecule, and an H atom to the other. Peptide is converted into a carboxylic acid and peptidyl form. The carboxylic acid has a hydroxyl group derived from a water molecule and the peptidyl gains the hydrogen ion as it shown below: 21

![Diagram of peptide hydrolysis]

**Experimental part**

2. Materials and Methods

2-1 Materials

New wool and linen samples are prepared in size 3 × 15 cm, they contacted with iron metal surface and placed in conditions of air temperature 23º and humidity 65% and exposed to atmospheric oxygen through 25 days to form the iron corrosion products that their effect on the fabric can be studied (Fig, 2). Then, the testing and analyses were carried out on each of them.

2-2 Testing and Analysis:

2.2.1 Tensile Strength and Elongation:

The mechanical characterize of all samples were tested by tensile strength test and elongation before and after the corrosion effect using En ISO 13934-1:1999 Maximum Force & Elongation – strip Method under Load Range 100 N, Extension Range 20 mm, Gauge Length 100 mm, Speed 100 mm/min and Preload 2.0 N. Three samples were used for each test for the corrosion and standard wool and linen samples and statistical data were calculated.

2.2.2 PH Measurement:

The surface PH for linen and wool samples was 3-4 which means increasing of acidity.

2.2.3 SEM Investigation:

The scanning Electron Microscope (SEM) investigation was carried out for the corroded linen and wool samples, using SEM of Model (Jeol Jxa-840 A Electron Prob Microanalyzer Japan), for
identifying the fibers deterioration, attached with EDX Unit of Model (Inca X-sight Oxford England) with magnification 500X up to 2000X to identify the types of corroded presence. The samples were measured (SEM) investigation on small pieces after coated with gold. EDX analysis has been carried out on the corroded samples without any treatment.

2.2.4 FTIR Spectroscopy:
Crystallinity of wool and linen samples, before and after corroded, have been obtained by FTIR Spectroscopy shows a change in the chemistry of degraded samples by using Nicolet 380 spectrophotometer in the spectral rang 4000 – 400 cm\(^{-1}\), resolution of 4 cm\(^{-1}\) and a number of scans of 32. Sample preparation by dried it, ground and sieved to get fine powders. These fine powders (90 - 120 µm) were used for FTIR measurements after and before fabric corroded. FTIR analysis has been performed by transmission techniques, in which the infrared energy is passed directly through the compound being studied. The powder sample can be milled with potassium bromide (KBr) to form a very fine powder. This powder is then compressed into a thin pellet which can be analyzed. In this method the sample is diluted with KBr (IR grade) so that the concentration of the sample is 1%.

Fabrics were measured by (Smart Performer ATR) unit accessory with Zinc Selenide crystal. ATR accessories require minimal setup and are easy to clean. Samples are placed directly onto the crystal surface itself. Single - bounce crystal modules tend to be the most versatile, since most are supplied with a pressure device and are appropriate for a variety of organic liquids and powders.
3. Results and Discussion:
3.1 Tensile Strength and Elongation:

The results of the testing show that there is a decrease in the Tensile Strength and Elongation for the linen and wool samples that are affected with iron corrosion are illustrated in (fig, 3).

The data indicated in Table 1 confirm that there is a decrease in the tensile strength of wool samples that are affected by rust for the standard samples (after taking the average) by amount 85.8 N, and a decrease in the elongation by amount 10.6%.

The data indicated in Table 2 confirm that there is a decrease in the tensile strength of corroded linen samples for the standard samples by amount 104.3 N, and a decrease in the elongation by amount 17.51% (fig, 4).

This indicates that there is a decrease in the mechanical properties of the samples as a result of affected with iron corrosion.

<table>
<thead>
<tr>
<th>Warp Specimen</th>
<th>Elongation %</th>
<th>Maximum Force N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard – Warp 1</td>
<td>19.24</td>
<td>221.8</td>
</tr>
<tr>
<td>Warp 2</td>
<td>19.08</td>
<td>202.8</td>
</tr>
<tr>
<td>Warp 3</td>
<td>18.08</td>
<td>187.8</td>
</tr>
<tr>
<td>Mean</td>
<td>18.8</td>
<td>204.1</td>
</tr>
<tr>
<td>corroded – Warp 4</td>
<td>8.26</td>
<td>118.7</td>
</tr>
<tr>
<td>Warp 5</td>
<td>9.24</td>
<td>118.2</td>
</tr>
<tr>
<td>Warp 6</td>
<td>7.03</td>
<td>118.1</td>
</tr>
<tr>
<td>Mean</td>
<td>8.18</td>
<td>118.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Warp Specimen</th>
<th>Elongation %</th>
<th>Maximum Force N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard – Warp 1</td>
<td>29.0</td>
<td>450.0</td>
</tr>
<tr>
<td>Warp 2</td>
<td>25.12</td>
<td>423.5</td>
</tr>
<tr>
<td>Warp 3</td>
<td>26.0</td>
<td>400.1</td>
</tr>
</tbody>
</table>
3.2 SEM Investigation:

3.2.1 Surface morphology:

SEM micrographs of the surface morphology of the wool and linen samples show the presence of corrosion products on the surface of the wool (figs.5, A-B) and linen (figs.5, C-D) textiles fibres. The products resulted by the iron corrosion migration on the organic support when the iron pieces are in contact with textile fibres. Wool fibers appear severely damaged with the appearance of many cracks and were broken down into the cortical cells. The linen
surface is also much damaged with transverse cracking in the direction of the fibre axis and longitudinal splitting characterized by small scratches, large slits and holes cavities. The results show that the degree of the deterioration of the tested samples is indicating that these textiles had lost most of their strength and the other mechanical properties (figs.5, E-F). This is directly appearing in the damage of the surface morphology of fibers. All the obtained SEM photos noticed that the samples are degraded due to the iron corrosion effect.
3.2.2 EDX analysis:

The results of EDX scans for the corroded wool sample detected in table 3 the presence of Fe element by 25.20% with presence of O element and this is due to the presence of iron oxides as iron rust, such as hematite (Fe₂O₃, the red rust) and magnetite (Fe₃O₄, the black rust), but the high proportion of the O element which representing 50.22% is not for his presence in the iron oxide only, but for his participation with the C element which representing 20.85% in the formation of the carbonyl group C-O which involved in the chemical composition of wool, and may be the presence of the carbonyl group resulting from the oxidation of wool, also we show the S element which representing 3.24% as a distinctive element for sulfuric links in wool compound (fig, 6).

The results of EDX scans for the corroded linen sample detected in table 4 the presence of Fe element by 3.53% with presence of O element which representing 58.97% and that point to the presence of iron oxides (red hematite Fe₂O₃ and black magnetite Fe₃O₄), O element participation also with the C element which representing 37.50% in the formation of the carbonyl group C-O which involved in the chemical composition of cellulose, and may be the presence
of the carbonyl group resulting from the oxidation of cellulose (fig. 7).

Table 3. EDX analysis of corroded wool sample

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>20.85</td>
<td>31.91</td>
</tr>
<tr>
<td>O K</td>
<td>50.22</td>
<td>57.71</td>
</tr>
<tr>
<td>S K</td>
<td>3.24</td>
<td>1.86</td>
</tr>
<tr>
<td>Ca K</td>
<td>0.48</td>
<td>0.22</td>
</tr>
<tr>
<td>Fe K</td>
<td>25.20</td>
<td>8.30</td>
</tr>
<tr>
<td>Totals</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

Figure 6. EDX scans of the element present on a corroded wool sample

Table 4. EDX analysis of corroded linen sample

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>37.50</td>
<td>45.44</td>
</tr>
<tr>
<td>O K</td>
<td>58.97</td>
<td>53.64</td>
</tr>
<tr>
<td>Fe K</td>
<td>3.53</td>
<td>0.92</td>
</tr>
<tr>
<td>Totals</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>
3.3 FTIR Spectroscopy:

The IR Spectroscopy is very important for detecting the functional groups. The results were noticed from the chart in (Figure 8, A) for the corroded wool sample that could be recognized from the shoulder and widen the absorption band indication of oxidation at wavelength (1636.56 cm$^{-1}$, 1800 cm$^{-1}$) for that similar in the standard wool sample chart in (Figure 8, B), it is due to the appearance of a large density for the carbonyl CO group in this area.

These results indicate also that the most noticeable change in the infrared spectra during denaturation in the amide II band shift from 1511.78 cm$^{-1}$. This shift will correspond to an increase in the separation of the amide I and II bands$^{22}$ at 1640.19 and 1500.78 cm$^{-1}$ when subdivide amide I on amide II for the both samples standard and corroded as it shown below:

\[
\text{Standard sample} = \text{amide I} / \text{amide II} \\
= \text{CO stretching + OH bending} / \text{C-N stretching + N-H bending} \\
= 39.738 / 48.740 \quad = 0.81
\]

\[
\text{Corroded wool sample} = \text{amide I} / \text{amide II} \\
= 60.543 / 62.181 \quad = 0.97
\]

That was found with comparison the both subdivision result it's appear that there is divide between the two, that divide confirm that the hydrolysis process was happened.

That the overall deterioration of wool can be followed by the oxidation of disulfide bonds to sulfoxide groups, and the hydrolysis of main-chain peptide bonds that causes intermolecular bond cleavage resulting in strength loss. Wool as polyamide structures also can oxidize to form carbonyl and carboxyl groups\textsuperscript{23}.

The corroded linen fiber was identified by the interpretation of the absorption spectra from IR spectroscopy. The results noticed from the chart in (Fig, 9-A) that the C-O stretching of oxidized cellulose as a result of oxidation of some various hydroxyl groups of cellulose was found in the 1780 cm\textsuperscript{-1}, it's not found on the standard sample chart (Fig, 9-B).

The chart of corroded linen show that the intensities of C-O and OH bands increase as a result of hydrolysis the linen for the standard sample chart. This results show that linen sample who is in contact with iron corrosion is much deteriorated.

The overall deterioration of cellulosic materials can be followed by examining the effects of oxidation, hydrolysis and ensuing acidity and by analyzing for hydroxyl-to-carbonyl group conversion where the number of reducing carbonyl groups is indicative of main chain scission resulting in shorter molecules and reduced fiber strength\textsuperscript{24} [11].

\textsuperscript{24} Jeanette M. Cardamone, Op Cit; p.5.
Figure 8. FTIR spectra of wool fiber, A) corroded wool

Figure 8. FTIR spectra of wool fiber, B) standard wool
CONCLUSIONS:
1) A relative humidity accelerates iron corrosion.
2) Catalysis of cellulose oxidation and acid hydrolysis takes place by the presence of iron (II) ions.
3) The function groups can readily form complexes with iron ions.
4) Formation of brown stains at places of the contact between textile with iron metal, due to the presence of damp, oxygen and a high pH.

5) The textiles deterioration by iron ions happens with formation of hydroxyl radicals from hydrogen peroxide after reacted with iron (II) ions.

6) This study confirms that the deterioration by iron corrosion effect does not stop at only the deformation of textiles surface but it causes oxidation and hydrolysis of this textiles.

7) SEM, EDX and FTIR spectrophotometer are very useful tools to investigate the degradation fibers by iron corrosion.

8) The tensile strength and elongation test confirms that there is a decrease in the mechanical properties of the wool and linen tested samples.

9) The SEM investigation of the surface morphology of the tested samples confirms that the wool and linen samples appear severely damaged with the appearance of cracks.

10) The results of EDX scans for the textile samples detected the presence of iron oxides.

11) The FTIR spectroscopy confirms that the all samples were degraded with the iron corrosion effect that the oxidation and hydrolysis process was happened.

References:


3) Corrosion/Conservation/Preservation
sanctuaries.noaa.gov/alligator/.../corrosionpreservatio_lesson.pdf


