Evaluation of the Effect of the Deep Ocean Environment on the Physical and Chemical Characteristics of Linen Fabric

A thesis

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by

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This work is dedicated to my parents and my brother
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iii
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# TABLE OF CONTENTS

DEDICATION.......................................................... ii

ACKNOWLEDGEMENT................................................... iii

VITA............................................................................. v

LIST OF TABLES........................................................ viii

LIST OF FIGURES...................................................... ix

CHAPTER  PAGES

I.  Introduction ...................................................... 1

II. The Review of Literature........................................ 10
    Studies on Marine Textiles.................................... 10
    Techniques of Textile Fiber Analysis....................... 12
        Light Microscopy........................................... 12
        Scanning Electron Microscopy.......................... 14
        Infrared Spectroscopy................................... 15
    Historic Background of the S.S. Central America........ 18
    Underwater Environment....................................... 20
    Summary.................................................................. 22

III. Methodology....................................................... 23
    Sample.................................................................... 23
    Immersion Treatment............................................ 24
    Testing and Evaluation Procedures........................ 26
        Optical Microscopy Examination....................... 27
        SEM Examination............................................ 28
        Fabric Yarn Count......................................... 29
        Fabric Thickness.......................................... 29
        Evaluation of Color Changes............................. 29
        Infrared Spectroscopy.................................... 30
    Statistical Analysis............................................ 34

IV. Results and Discussion......................................... 36
    Fiber Morphology Examination.............................. 37
        Microscopy Examination Checklist...................... 37
        Fibers From Group D....................................... 41
        Fibers From Group E....................................... 47
        Fibers From Group F....................................... 53
    Summary.................................................................. 57
    Physical Properties............................................. 58
<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>PAGES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test Results</td>
<td>58</td>
</tr>
<tr>
<td>Statistical Analysis Results</td>
<td>60</td>
</tr>
<tr>
<td>Fiber Diameter</td>
<td>60</td>
</tr>
<tr>
<td>Fabric Yarn Count</td>
<td>64</td>
</tr>
<tr>
<td>Fabric Thickness</td>
<td>64</td>
</tr>
<tr>
<td>Fabric Color Changes</td>
<td>65</td>
</tr>
<tr>
<td>Summary</td>
<td>70</td>
</tr>
<tr>
<td>Chemical-Physical Molecular Structure Changes</td>
<td>70</td>
</tr>
<tr>
<td>FT-IR Spectra</td>
<td>70</td>
</tr>
<tr>
<td>Crystallinity Measurement</td>
<td>72</td>
</tr>
<tr>
<td>Results of Statistical Analysis</td>
<td>76</td>
</tr>
<tr>
<td>Summary</td>
<td>78</td>
</tr>
<tr>
<td>V. Conclusion and Summary</td>
<td>79</td>
</tr>
<tr>
<td>Suggestion for Future Study</td>
<td>84</td>
</tr>
<tr>
<td>Bibliography</td>
<td>86</td>
</tr>
<tr>
<td>Appendix A Sign Interval Boxplot</td>
<td>93</td>
</tr>
<tr>
<td>Appendix B Infrared Spectra of Flax Samples</td>
<td>98</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>PAGES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Test Methods, Apparatus, and Number and Size of Specimen</td>
<td>28</td>
</tr>
<tr>
<td>2. Microscopy Examination Checklist</td>
<td>38</td>
</tr>
<tr>
<td>3. Mean Values and Standard Deviation of Fiber Diameter, Yarn Count and Fabric Thickness Measurement</td>
<td>59</td>
</tr>
<tr>
<td>4. Mean Values and Standard Deviation of Fabric Color Coordinates</td>
<td>60</td>
</tr>
<tr>
<td>5. Summary of Sign Interval Statistical Analysis on Fiber Diameter, Fabric yarn Count and Fabric Thickness</td>
<td>61</td>
</tr>
<tr>
<td>7. Mean Values and Standard Deviation of Changes in Fabric Color Coordinates</td>
<td>68</td>
</tr>
<tr>
<td>8. Mean Values and Standard Deviation of Crystallinity Ratio of Samples from Each Treatment</td>
<td>75</td>
</tr>
<tr>
<td>9. Summary of Sign Interval Statistical Analysis on the Crystallinity Ratio of Samples from Each Treatment</td>
<td>75</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Immersion Jars on the Ocean Floor</td>
<td>26</td>
</tr>
<tr>
<td>2. Calculation of FT-IR Crystallinity Ratio</td>
<td>33</td>
</tr>
<tr>
<td>3. Boxplot from Minitab</td>
<td>35</td>
</tr>
<tr>
<td>4. Flax Fibers From Group D: SEM</td>
<td>42</td>
</tr>
<tr>
<td>5. Flax Fibers From Group D: SEM</td>
<td>42</td>
</tr>
<tr>
<td>6. Bending of a Fiber</td>
<td>43</td>
</tr>
<tr>
<td>7. Bending Break of a Fiber</td>
<td>43</td>
</tr>
<tr>
<td>8. Flax Fiber From Group D: DIC</td>
<td>44</td>
</tr>
<tr>
<td>9. Flax Fibers From Group D: SEM</td>
<td>45</td>
</tr>
<tr>
<td>10. Flax Fibers From Group D: DIC</td>
<td>46</td>
</tr>
<tr>
<td>11. Flax Fibers From Group D: Pol</td>
<td>46</td>
</tr>
<tr>
<td>12. Flax Fiber From Group E: BF</td>
<td>47</td>
</tr>
<tr>
<td>13. Flax Fibers From Group E: Pol</td>
<td>48</td>
</tr>
<tr>
<td>14. Flax Fibers From Group E: SEM</td>
<td>48</td>
</tr>
<tr>
<td>15. Flax Fibers From Group E: SEM</td>
<td>49</td>
</tr>
<tr>
<td>16. Flax Fibers From Control Group: SEM</td>
<td>51</td>
</tr>
<tr>
<td>17. Flax Fiber From Group E: SEM</td>
<td>51</td>
</tr>
<tr>
<td>18. Flax Fiber From Group E: Pol</td>
<td>52</td>
</tr>
<tr>
<td>19. Flax Fiber From Group E: DIC</td>
<td>52</td>
</tr>
</tbody>
</table>
FIGURE

20. Flax Fibers From Group E: SEM..........................54
21. Flax Fibers From Group F: SEM..........................54
22. Flax Fibers From Group F: DIC..........................55
23. Flax Fibers From Group F: DIC..........................56
24. Flax Fibers From Group F: SEM..........................56
25. Fringed Fibrillar Internal Structure of Cellulose Fiber..........................73
26. Sequence of Structures with Increasing Order............74
27. Boxplot of Fabric Yarn Count: Fill..........................94
29. Boxplot of Flax Fiber Diameter..........................95
30. Boxplot of Fabric Thickness..........................95
31. Boxplot of Fabric Color Coordinates L*..........................96
32. Boxplot of Fabric Color Coordinates a*..........................96
33. Boxplot of Fabric Color Coordinates b*..........................97
34. Linen Fabric IR Crystallinity Ratio..........................97
32. IR Spectrum of Standard flax Fiber..........................99
33. IR Spectrum of Fibers From Group D..........................100
34. IR Spectrum of Fibers From Group E..........................101
35. IR Spectrum of Fibers From Group F..........................102
CHAPTER I
INTRODUCTION

In October 1990, a trunk containing waterlogged and degraded textiles was recovered from the site of the S.S. Central America, a steamship which sank off the coast of the Carolinas in 1857. The contents were removed and assessed (Jakes and Mitchell, in press). Supported by a fiberglass screen and immersed in baths of distilled water, textiles from the trunk were unrolled and examined. The garments were in apparent good condition and withstood the operation of unrolling. Small samples were taken from inconspicuous locations of some of the textiles. The textiles from the trunk were stained in random patterns with black, green-black, and rust-red colors (Jakes and Wang, accepted for publication). The proper methods of unfolding and drying, of identification and characterization, and of the cleaning and preservation of these textiles have become important topics of research.

Since the retrieved items have stayed in the marine environment for over a hundred years and have undergone long term degradation, the conservation treatments of these waterlogged items are different from those employed for archaeological objects recovered from soil burials. In order to keep these marine textiles in a stable condition for
further study, it is important to first understand the condition of the materials and how they have degraded in the deep ocean environment.

So rarely are textiles retrieved from the marine environment only a few studies have been conducted and reported. Previous studies have primarily addressed the cleaning and consolidation treatments of the retrieved textile items (e.g. Bengtsson 1975a, Morris and Seifert 1978, Ryder 1983) but the reports have not addressed the mechanisms which operate to alter the textile structures in the ocean. The need for research in water-degraded archaeological textiles has been noted (Peacock 1990, Jenssen 1987). In addition, few studies address the techniques employed in the identification and characterization of the fiber; the need for such study has also been stated (Jakes and Wang, accepted for publication).

Other studies of historical textiles (e.g. Brothwell 1969, Ballard 1989, Hersh 1989, Ryder 1984, Ryder and Gabra-Sanders 1985) provide information about the analytical methods employed in the examination of small samples of historic and archaeological textile material. These methods include optical microscopy, scanning electron microscopy, infrared spectroscopy and other physical property testing, and may be applied to the study of marine textiles as well.

Research on fiber damage during burial (Cooke, 1990) provides knowledge about the fiber degradation in burial soil environment and may provide some insights about fiber
degradation through aging. However, textiles in a marine environment undergo different conditions than those in burial soil. "Seawater is a unique solution made up of the solvent (water) and a complex mixture of chemical constituents, particulate matter and gas bubbles" (Florian, 1987). Textiles suffer a combined damage as a function of the ocean conditions including chemical composition, pH, oxidation potential, temperature and microbiological composition (Florian, 1987).

Initial examination (Jakes and Wang, accepted for publication) showed that the textiles from different locations in the retrieved trunk display different staining patterns. Some textiles display variable staining all over while others are less stained and the stains are localized. When examined under the microscope, most fibers removed from the textiles were recognizable; the fibers were cotton, flax, silk, and wool. Some fibers were encrusted with black deposits which prevented their identification by morphological characteristics. X-ray microanalysis of the black staining in selected fibers has shown the combined elements of iron, sulfur, chlorine, copper and others (Jakes and Wang, accepted for publication, Jakes and Mitchell, in press). No study has been conducted on the effect of the presence of metal on the degradation of textiles in the marine environment, therefore this is one area of necessary research. The lack of information in the research literature combined with the recovery of a large number of historic marine textiles which
require conservation treatment further indicates the need for research on the degradation of textiles in the marine environment. In the research design, a control group of textiles is required in order to assess the changes in textiles and fibers after they have been immersed in the marine environment for varying periods of time. There also is a need to determine the proper methods for the evaluation of the degradation which the textiles have undergone, and to establish the classification categories of fiber morphology characteristics which result from the fiber degradation.

**Research Objectives**

Given the opportunity to work with the Columbus-America Discovery Group, a research plan was developed to study the degradation of cellulose textiles in the marine environment by using contemporary fabrics.

The objectives of this study are to evaluate the effect of a 3 month exposure to the deep ocean environment on the morphological shapes and physical and chemical properties of flax fiber/linen fabric. Copper and iron metal squares were used to simulate influences of metal in the contained environment of trunks. The following research objectives were generated to guide the study:

1. To explore and describe the microscopic morphological characteristics of flax fiber after being immersed in the marine environment for 3 months alone, in the presence of
iron, and in the presence of copper.

2. To explore and describe the physical and chemical microstructure changes of flax fiber after being immersed in the marine environment for 3 months alone, in the presence of iron, and in the presence of copper.

3. To determine which physical and chemical characteristics, of the ones measured in this work, are strongly related to degradation in the marine environment as an aid to future research in marine textile degradation.

Limitations of the study

This study is a part of a larger research project and the only material discussed is linen which was immersed for 3 months. Complex conservation questions are not addressed in this study. It is assumed that any disruption or change of the fibers caused by the effects of sampling are insignificant in effect compared to the consequences of the 3 month period of degradation.
Definition of Terms

Absorbance - the ability of a layer of a substance to absorb radiation, expressed mathematically as the negative of the common logarithm of transmittance (McCrone 1967).

Brightfield Illumination - The usual form of microscope illumination by means of a substage condenser and mirror with the image of the sample on a bright, evenly lit field (McCrone 1967).

Bulging - Fibers display bulging along their length at regular or irregular intervals due to degradation or growth condition on the side of the fiber. It is distinguished from swelling in that no fibrils are evident as distinct entities in the bulge.

Conservation - Refers to treatments in a laboratory setting whose purpose usually is to bring the object back to an appearance as similar as possible to the original and to stabilize its condition (Kajitani, 1977). The treatment must not influence the material or any possible aesthetic qualities of the object (Lodewijks, 1972).

Cracks - A fiber which exhibits a crack shows a marked fissure in the fiber. It can be distinguished from a transverse marking because the fiber is separated at the point of the fissure.

Darkfield Illumination - Illumination of the specimen by indirect light; no light is admitted directly to the objective (McCrone 1967).
Differential Interference Contrast (DIC) - The differential interference contrast technique is a qualitative technique for making more visible those specimens lacking contrast with ordinary brightfield microscopy. DIC microscopy is best with specimens of path difference between $\lambda/10$ and $1\lambda$. When fibers are examined under DIC, the surface structures are enhanced (Fatou, 1978).

Dislocation - A distinct disruption of the surface of the fiber. It can be evenly spaced or irregularly spaced.

Fibrillation - A fiber is characterized as showing "fibrillation" if fibrils are apparent within the fiber structure. The fibrils may or may not show separation from each other within the fiber structure.

Historic marine textiles - refers to waterlogged items from a historic period, retrieved from the marine environment.

Infrared crystallinity ratio - The ratio of absorbance at 1372 cm$^{-1}$ (O-H bending) and 2900 cm$^{-1}$ (O-H stretching) in the IR spectrum proposed for indicating relative crystallinity in cellulosic materials (Nelson and O'Connor 1964).

Morphological Characteristics - These include such identifying physical characteristics as shape, surface characteristics, homogeneity, transparency, color in transmitted light and color in reflected light, refractive indices and birefringence for identification with a light microscope (McCrone 1967).
Phase contrast Microscope - A microscope giving enhanced image contrast by interference between the direct and diffracted beams from the specimen (McCrone 1967). It increases contrast and is suitable for phase specimens with optical path differences of up to \( \lambda /2 \) but works best with specimens of \( \lambda /10 \) retardation. The internal structure of fibers can be made more apparent when examined under phase contrast (Fatou, 1978).

Polarized light - A bundle of light rays with a common propagation direction and a single vibration direction. The vibration direction is always perpendicular to the propagation direction. It is produced from ordinary light by reflection, by double refraction with a suitable crystal, or by absorption, again with a suitable crystal (McCrone 1967). The interference color of fiber under the polarized light is an indication of the birefringence of the fiber (Fatou, 1978).

Preservation - As opposed to conservation, includes all those treatments that contribute to guaranteeing the life of the objects. "Care" and "maintenance" are used synonymously with "preservation" (Kajitani, 1977).

Transverse markings - Marks running across the fiber's width which are distinct from cracks, because there is no fissure apparent. The transverse marking also is distinct from the dislocation because the marking is a surface only phenomenon which does not result from
folding of the fibrils in growth.

**Working Distance** - The distance between the preparation and the nearest portion of the objective (McCrone, 1967).
CHAPTER II

THE REVIEW OF LITERATURE

Historic textiles are highly perishable; they are often very fragile. Analysis of historic textiles has been carried out with variable success, in part because of the fragile condition of the specimens. In this chapter, the literature review is presented covering the studies of marine textiles, as well as some techniques employed in the study of historic and archaeological fibers and fabrics, which include optical microscopy, scanning electron microscopy (SEM) and infrared spectroscopy (IR). The historic background of the sinking of S.S. Central America and the deep ocean environment of the shipwreck also is included.

Studies on Marine Textiles

Historic textiles from marine environments rarely have been retrieved; few studies have been done in this area. Of these, most of the studies deal with cleaning treatments of the fabrics and few report the methods used in the identification and characterization of textiles.

Bengtsson (1975a) reports the unfolding, identification and preservation of the sails from the royal warship Wasa, which sank in 1628 in Stockholm harbor. Although Bengtsson
does classify the fibers as "vegetable" fibers (1975b), there is no information given describing the method employed for the determination that the fibers were "vegetable", nor is information reported concerning the condition of the fibers. Ryder (1983), however, does report the microscopic examination of the fleece type found in a sample of wool textiles from the Wasa; fiber diameter and dye information alone are described. Jakes and Wang (accepted for publication) describe the examination and characterization of textile samples from the passenger’s trunk retrieved from the site of S.S. Central America. Fiber samples were examined by light microscopy and scanning electron microscopy. Some degradation mechanisms which altered the fiber structures are discussed.

The conservation of leather and textiles from the Defence (an American privateer sunk in 1779) has been addressed by Morris and Seifert (1978). They described the treatment of textiles with 5% oxalic acid but they do not indicate how they identified the linen, hemp, and silk fibers with which they worked. They found that iron staining could be seen on the surface of the leather and textiles and also intruded into their structure. The effects of the presence of metal salts on the condition of the textiles are not discussed.

Studies which deal with the effects of metal on textiles in soil burial may have some implications for marine textiles research. Cooke (1990) found that metal salts, e.g. the corrosion products of iron, copper and its alloys, inhibit
biodeterioration. At the same time these species catalyze the hydrolysis and oxidation of both cellulose and protein. "The formation of negative casts or positive pseudomorphs may preserve much of the surface and structural detail of the fiber, despite the almost total destruction of the textile itself" (Cooke 1990). Vollmer (1975) similarly found that textiles in contact with copper, bronze, iron, or silver may result in "casts" (i.e. impressions) or metallized fragments (called "textile pseudomorphs"). Textiles in these conditions may be preserved in nearly perfect form (King, 1978). No research has been conducted on the effect of iron and copper on the degradation of textiles in marine environment prior to the initiation of the work reported herein.

Techniques of Textile Fiber Analysis

Light Microscopy

Light microscopy is a technique which has been effectively used by researchers to identify fiber content and is recommended as a means of identifying the fiber content of archaeological textiles (e.g. King, 1978, Jakes, 1990). Information can be obtained from the fiber appearance and from the behavior of fibers when examined under polarized light, phase contrast, and DIC. With brightfield and darkfield examination, the fiber bundles are apparent. Under polarized light, the fiber exhibits colors which reflect the orientation of the crystallites of that fiber. With phase contrast, the
lumen or other internal structures can be made more apparent. With differential interference contrast, surface structures are enhanced (Jakes, 1990).

Optical microscopy can be used to provide information regarding changes in fiber morphology caused by the degradation which the fibers have undergone in long term storage. Archaeological fibers are particularly difficult to identify because they are aged, decayed, fossilized or charred. Experience is needed to interpret and identify archaeological fibers (Goodway, 1987). Degraded bast fibers can be hard to differentiate. Sometimes microscopic examination is impeded by mineral encrustation requiring micro-chemical cleaning just to see the fiber (King, 1978). Appleyard and Wildman (1969) have described the examination and identification of several animal fibers from archaeological sites.

Kadolph (1984) selected historic textile pieces from a steamboat that sank in 1865 to verify fiber content, document morphological characteristics of historic fibers, and document changes in the morphology of historic fibers when compared to contemporary fibers. She found that the major morphological characteristics in the degraded fiber included cracks, bulges and fibrillation. Sibley, Jakes, and Song (1989) describe the stress cracks and fibrillation observed in archaeological bast fibers from textiles from Etowah, Georgia (1200 A.D.).
Jakes (1990) also has described a variety of information provided by examining archaeological fibers with polarized light, phase contrast, and differential inference contrast techniques. Light microscopy and phase microscopy methods were used to characterize the stains and images on the Shroud of Turin (Jumper, Adler, et al. 1984).

A recent study by Jakes and Wang (accepted for publication) employed light microscopy in the identification and characterization of textile fibers from a trunk retrieved from the site of the ship S.S. Central America. The morphological characteristics of fiber samples are summarized and categorized.

**Scanning Electron Microscopy**

Another major technique for fiber identification and other research work in fiber science is scanning Electron Microscopy (SEM). SEM has a great depth of field and better resolution than light microscopy, and provides an excellent three-dimensional view in the study of textile yarns and fibers.

Bresee and Goodyear (1986) report the study of fracture of historic silk fibers; SEM was used to examine the morphology of fractured fiber ends. They found that the fragility of naturally aged historic samples resulted from a decrease in interfibrillar cohesion rather than from excessive embrittlement. SEM also has been used to examine textile
fragments from Etowah to confirm the processing of fiber and yarn by prehistoric people of North America (Sibley, Jakes, and Song, 1989). In 1989, Ballard, et. al. used SEM-EDS (Energy Dispersive Spectroscopy) to examine historic silk flags in the National Museum of American History. The presence of mordants, weighting materials, and colorants is discussed with reference to the embrittlement of the silk. They also discuss the correlation between fiber deterioration and elemental composition.

SEM has also been used in the study of marine textiles. Ryder (1984) used SEM to identify the wool fiber content of textiles recovered from the Mary Rose, a warship which sank in 1632. Although these fibers were identified, their chemical and macromolecular physical structures were not characterized.

The information provided by SEM is not limited to fiber identification alone. The causes of fiber damage can also be inferred. Cooke (1990) studied fiber damage resulting from different environments, i.e. during preparation, manufacture, use, and burial. Hann (1990) also uses SEM to study the fibers from mummy textiles and found a "hosepipe effect" on the fibers, which could be due to chemical contraction or due to heat.

**Infrared Spectroscopy**

Infrared spectroscopy has been used as an analytical tool for the identification of unknown materials because it
provides selective molecular information. Infrared spectroscopy can be used in the identification of textile fibers, coatings, and finishes. The crystalline forms and stereochemical structures of polymers used in textiles can also be examined, as well as compositional changes resulting from their thermal degradation.

The IR spectra of solid samples usually are recorded in transmission either by pressing samples into KBr pellets or grinding samples up as Nujol mulls. The first technique is often used for the analysis of textile fibers. There are several applications in the study of textiles. Liang and Marchessault (1959 and 1960) conducted an in-depth study on the IR analysis of cellulose. They used polarized light to examine the spectral differences displayed by cellulosics I and II.

Although oxidative changes, hydrolytic changes and other changes in textile fibers associated with the natural ageing process should be apparent in the IR absorption spectra, it is difficult to characterize the fiber. When preparing KBr discs, problems exist in surface irregularities, lack of sensitivity, and the necessity for sample destruction (Cardamone, Gould and Gordon, 1987). Fibers may not transmit infrared radiation well.

The development of FT-IR spectrometers, with their inherent advantages over grating instruments, has increased the usefulness of this technique for the analysis of work of
archaeological textiles.

"FT-IR has several important advantages over conventional methods. The most important of these is the efficient and rapid collection of data. FT-IR is also less susceptible to stray radiation. In addition, because a computer is necessary to obtain the Fourier transform, many scans can easily be performed to improve the signal-to-noise ratio. Digital subtraction (that is, point-by-point subtraction of the separate spectra by a computer) can also be used to produce good difference spectra. The most important advantage of the FT-IR spectrometer are listed as follows:

1. Multiplexing of spectral information: Information from all frequencies in the spectrum is gathered simultaneously.

2. Enhanced spectral throughput: Because no entrance and exit slits of the monochromator are used the amount of energy falling on the detector is greatly enhanced.

3. Frequency accuracy: Because the instrument uses a laser to monitor the position of the moving mirror in the main interferometer, the frequency of the measured spectrum is very accurate" (Hon, 1986).

Yang, Perenich and Fateley (1989) employed FT-IR photoacoustic spectroscopy to study the finishing agents distribution in foam finished fabrics. Jakes and Wang (accepted for publication) also use FT-IR to identify and confirm the fiber content of textile samples from the ship S.S. Central America.

Nelson and O’Connor (1964) conducted a comprehensive study on the IR analysis of cellulose, and proposed a new infrared ratio $1372 \text{ cm}^{-1} / 2900 \text{ cm}^{-1}$ for measuring crystallinity in cellulosic materials. It can be applied to both cellulose I and II. A group of bands in the 1200-1400 cm$^{-1}$ region (assigned to C-H and O-H bending and CH$_2$ wagging motions)
appear to be related to crystallinity and not a lattice type. The absorption band at 1372-1375 cm\(^{-1}\) (C-H bending) was chosen as being most suitable for indicating crystallinity. This absorption band should not be affected by differences in the amount of water absorbed onto the cellulose. The band at 2900 cm\(^{-1}\) (C-H and CH\(_2\) stretching) was chosen to take a ratio with the one at 1372 cm\(^{-1}\) because it is less affected by changes in crystallinity, and therefore provides a kind of internal standard to compensate for the sources of variation mentioned. Using this ratio, Nelson and O’Connor (1964) reported a correlation coefficient of 0.860 between the IR ratio and X-ray analysis measurement of crystallinity. Basch and Lewin (1973) also correlated the crystallinity of cellulose using this IR ratio and X-ray diffraction and reported a R value of 0.882.

**Historic Background of the S.S. Central America**

At the time of her sinking, the *S.S. Central America* was one of two luxury passenger steamships engaged in regular bimonthly service on the Atlantic leg of a route from San Francisco to New York. During the period of the Gold Rush, an efficient route between the east and west coasts of the United States was by way of Panama. Passengers finished the first part of their journey from San Francisco to Panama on the *S.S. Sonora*. "After a four-hour train ride across the isthmus, the travelers boarded the *S.S. Central America* at Aspinwall for the
ten-day journey to New York" (Noonan, 1992a). The ship left Aspinwall on September 3, 1857, "carrying 578 passengers and crew, three tons of gold, and forty thousand pieces of mail" (Noonan, 1992a). It encountered a powerful hurricane and sank on September 12, 1857. The shipwreck of the S.S. Central America claimed 425 lives of the passengers and crew.

The ship and associated artifacts were located by the Columbus-America Discovery Group in 1987 by using side scan sonar technology and probability mapping based on historical records. Many artifacts along with gold coins and bars have been recovered from the wreck by deep sea diving submersible Nemo. Nemo is a remotely operated vehicle or robot capable of performing heavy work in the deep ocean. Two passenger trunks were retrieved "from the debris field surrounding the ship's rotting hull" (Noonan, 1992a). One was recovered in September 1990, another one was recovered in October 1991.

The trunks were transported to Columbus, Ohio, where they were opened and the contents removed and assessed. Textiles from the trunks were unrolled while immersed in distilled water. "These garments appeared contiguous and withstood the operation of unrolling without obvious damage" (Jakes and Mitchell, in press). Small samples were taken from inconspicuous locations. Supported on fiberglass screens, the garments were quickly frozen at 19° Fahrenheit below zero for freeze-drying. The cleaning and restoration of these garments is still under study. The results of this research will help
historians and conservators in the conservation and historic analysis of the garments retrieved from the trunks.

**Underwater environment**

The *S.S. Central America* is located "near the edge a sloping plain known as the Blake Ridge, eight thousand feet below the surface of the Atlantic and about 180 miles east of the Carolinas" (Noonan, 1992b). The temperature of water is near freezing. It is dark on the site, the pressure is 240 atm and the current is very slow (Herdendorf, personal communication). "The area where the ship went down is a virtual biological desert, yet the ship swarms with life. At least five new species of life have been found at the wreck, including several new species of sponge" (Noonan, 1992a). At the same site, a 21 feet long Greenland shark was also viewed by Nemo. This is 4,000 feet deeper than any other Greenland shark has been found and at least 1,000 miles farther south than any other Greenland shark has been seen.

In the normal marine environment, the oxygen dissolved in the sea water is about 1 cc/l at depth of 610m, and the pH ranges from 7.5 to 8.4 (Florian, 1987). The moment any artifact material comes in contact with seawater, some degree of solubilization occurs. Even on metal surfaces metal ions are freed and become involved in corrosion reactions.

It is assumed that reactions occur extremely slowly in the deep sea. This is partially due to the low concentrations
of many of the reactants in seawater. But at the interface between water and metal boundaries, the reactants are concentrated resulting in increased reaction rates (Florian, 1987).

Florian (1987) summarized the chemical constituents of seawater. "The major constituents of seawater are dominated by the presence of six ions, i.e. Cl\(^-\), Na\(^+\), SO\(_4\)\(^{2-}\), Mg\(^{2+}\), Ca\(^{2+}\) and K\(^+\) which constitute 99.5% of dissolved constituents." She states that "iron is one of the most important minor constituents of seawater. The ferric valence Fe\(^{3+}\) is the dominant form in oxidizing seawater and the principal species is Fe(OH)_3. In reducing water the lower valence Fe\(^{2+}\) is prevalent." She also notes that "the principal gases dissolved in seawater are oxygen and carbon dioxide. Their solubility decreases with increased temperature and chlorinity. In seawater, dissolved oxygen varies from 0-8.5 ml/l. The pH of seawater usually falls between the range of pH 7.5 and 8.4." In this study, she also states that "the significance of marine organisms in respect to conservation of excavated artifacts from wreck-sites is limited" and "the significant organisms are fouling assemblages as a whole, wood and stone borers, fungi and bacteria."

Bacteria are everywhere in the ocean. As soon as an object enters the seawater it is covered with a film of diatoms or bacteria and the cycle of biodeterioration starts.
Summary

So rarely are textiles retrieved from marine environment, few have been studied. Little is known concerning the mechanisms of degradation of textiles in the marine environment. There is a need to conduct experiments with standard materials to observe the progress of degradation the materials undergo while in the marine environment.

Various techniques are employed in the study of the fiber characteristics, including light microscopy, SEM, and infrared spectroscopy. These techniques provide several dimensions of information and can be used in the study of marine textiles.

Two trunks were retrieved from the underwater site in the debris field of the S.S. Central America. Textiles from these trunks have been examined. In the following chapter, the discussion will cover the study of modern linen fabric that was exposed to the deep ocean at the same site as where the trunks were retrieved.
CHAPTER III

METHODOLOGY

This research is concerned with the changes in morphology, physical properties and physical-chemical structure of linen fibers after immersion in the deep ocean environment for a period of 3 months. The methodology for this research is presented in four major sections. The first section describes the fabric samples used in the experiment. The second section discusses the immersion treatment, which includes preparation, immersion, and retrieval of the samples. The third section discusses the procedures for evaluating the morphology, physical properties, and physical-chemical structure changes of the experimental samples. The final section covers the statistical methods for the analysis of the test data.

Sample

Contemporary linen, TestFabrics No. L-53, was used for this study. The fabric is a coarse plain woven fabric with a yarn count of 32x25 yarns/inch. The average diameter of the fiber is 19.5 μm. Four treatment conditions were employed:
1) Cellulosic fabric as a control, not immersed in the marine environment, hereafter labelled control group;

2) Cellulosic fabric only, immersed in the marine environment for 3 months, hereafter labelled group D;

3) Cellulosic fabric placed with copper metal pieces, immersed in the marine environment for 3 months, hereafter labelled group E;

4) Cellulosic fabric placed with iron metal pieces, immersed in the marine environment for 3 months, hereafter labelled group F;

Dependent variables consisted of measured physical and chemical characteristics, which include fiber diameter, yarn count, fabric thickness, L*, a*, b* color coordinates, and IR crystallinity ratio. Samples from each group also were examined with techniques of light microscopy and scanning electron microscopy for changes in morphological characteristics.

**Immersion Treatment**

Linen fabric was coupled with cotton in the immersion experiment. Both fabrics were cut into small circles with diameter of 5.5" each, and inserted in layers in 1 gallon Nalgene plastic jars with ten layers of cotton followed by ten layers of linen, alternating until the jar was filled. Some shifting and compacting of the fabric layers occurred during transport, placement, and recovery. The jars were fitted with
open tubes at both the bottom and the top, which allowed sea water to enter the jars. The fabric circles were placed into three jars, labelled 1D, 1E, and 1F. 1D contained cotton and linen fabric only. 1E contained cotton and linen along with three square pieces of copper (3" x 3" square, 1/8" thickness) at positions near the top, near the bottom and in the middle of the jar. 1F contained cotton and linen fabric and three square pieces of iron (3" x 3" square, 1/8" thickness), at the same positions as that in the jar 1E. The jars were then placed at the 1.5-mile-deep ocean floor site on July 9, 1991 by the deep sea diving submersible Nemo, at the same site as that from which the trunks were retrieved. The jars were tied to stakes on the ocean floor so that they would not move(Figure 1). They were raised on October 5, 1991 with the total immersion period being 89 days. Pinch clamps on the tubing remained open upon immersion but were closed prior to lifting the jars from the ocean floor. The jars were refrigerated in transport to Columbus, Ohio. Ten fabric samples were randomly chosen from different locations from each of the jars on October 22, 1991, and were air dried in a desiccator in the laboratory. This study describes the linen samples only.
Figure 1. Immersion Jars on the Ocean Floor.
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Testing and Evaluation Procedures

All the samples were examined for changes in morphology, physical properties and physical-chemical structures. The tests were conducted according to the methods of the American Society for Testing and Material (ASTM, 1985) or the American Association of Textile Chemists and Colorists (AATCC, 1985) as indicated in Table 1.
Optical Microscopy Examination

To prepare the flax fibers for examination under the optical microscope, they were teased from the yarn and spread out on a slide, a drop of water was added, and then enclosed with a cover slip to form a "whole mount". Diameter measurements of fibers were made at a magnification of 400x by using a precalibrated micrometer eyepiece. Five different points along the length of each fiber were randomly chosen. After the measurement of the diameter, the fibers were examined employing a Zeiss Axioplan research microscope under bright field, dark field, phase contrast, polarized light and Differential Interference Contrast. Photomicrographs were taken with Ektachrome 160 tungsten film at 400x magnification.

After the initial examination, a checklist was developed which categorized the characteristics of fiber morphology observed under the light microscope.
# Table 1

**Test Methods, Apparatus, and Number and Size of Specimen**

<table>
<thead>
<tr>
<th>Property</th>
<th>Test Method / Instrument Employed</th>
<th>Number of Specimens</th>
<th>Sample Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morphology Characteristics</td>
<td>Zeiss Axioplan Microscope</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>JEOL JSM-820 SEM</td>
<td>1</td>
<td>0.2x0.2 inch</td>
</tr>
<tr>
<td>Fiber Diameter</td>
<td>Micrometer eyepiece</td>
<td>10</td>
<td>single fiber</td>
</tr>
<tr>
<td>Thread Count</td>
<td>ASTM D 3775-79 Suter Thread Counter</td>
<td>10</td>
<td>1 inch</td>
</tr>
<tr>
<td>Fabric Thickness</td>
<td>ASTM D 1777-64 Randall &amp; Stickney Gauge</td>
<td>10</td>
<td>D2.2 inch Circle</td>
</tr>
<tr>
<td>Color Change</td>
<td>HunterLab Colorimeter</td>
<td>10</td>
<td>D2.2 inch circle</td>
</tr>
<tr>
<td>Crystallinity Ratio</td>
<td>Perkin Elmer 16 PC FT-IR Spectrometer</td>
<td>10</td>
<td>Single Fiber</td>
</tr>
</tbody>
</table>

**SEM Examination**

One small piece of fabric (about 0.2x0.2 inch) from each treatment level was taken for SEM examination. The fiber samples were coated with a thin layer of carbon in order to eliminate the build up of negative charge due to lack of electrical conductivity of the fibers. The samples were first mounted on a carbon planchet and then coated with a thin layer of carbon. Each sample was then seated on a metal sample stage, which requires a 39 mm working distance for sample examination. A JEOL JSM-820 scanning electron microscope
employing a 15 kv accelerating voltage was used in this work. At least one photograph was taken of each yarn sample using Polaroid Type 55 film.

**Yarn Count**

One reading of yarn count per inch in the warp direction and one in the filling direction were taken for each fabric at each treatment level. Average readings for the warp and filling were computed. The Suter Thread Counter apparatus was used following the procedure outlined in ASTM Test Method D 3775-79 (Annual Book of ASTM Standards, 1985).

**Thickness**

The Randall and Stickney Gauge was used to measure fabric thickness. Three readings were taken at random from different areas of the untreated and treated fabrics. The averages were calculated. Test procedures were followed according to ASTM D 1777-64 (Annual Book of ASTM Standards, 1985).

**Evaluation of color changes**

Color coordinates and color difference between each treatment were evaluated by using L*, a*, b* readings generated by a HunterLab Labscan Spectrocolorimeter. The Hunter L,a,b, system is a uniform color scale based on the opponent-colors theory of vision. The instrument was zeroed and standardized with the standard 1.75 inch illuminated area
port, 10° Standard Observer, D_65 Illuminant. A single fabric was employed for color measurement.

The total color difference (ΔE) was calculated by

\[ ΔE = \left( (ΔL^*)^2 + (Δa^*)^2 + (Δb^*)^2 \right)^{1/2} \]

where ΔL is the change in value of lightness or darkness, Δa is the change in shade of red or green and Δb is the change in shade of yellow or blue with respect to a standard.

Four readings of L*, a*, b* were made of each of the samples. These readings were taken in the warp and fill directions in the locations of the center front and the center back. There were 10 samples per treatment. Average L*, a*, b* and ΔE then were calculated for each sample.

**Infrared Spectroscopy**

Small fiber samples from each fabric sample at each treatment level were taken for infrared spectroscopic examination. Fibers were cut 1-2 mm long and blended with KBr powder. A KBr pellet containing fiber samples was made on a CARVER Laboratory Press, model C, under 20,000 pounds applied load. In order to remove air and moisture, a vacuum pump was connected to the press while making the pellets. A Perkin Elmer Model 16 PC FT-IR spectrometer was used to collect IR spectra.

The spectra were collected at 32 scans, 4000-700 cm\(^{-1}\) scanning range. Scanning energy was moderated close to 10,000 units. The spectra were saved and processed employing the
Perkin Elmer IR Data Manager software program. The spectrum of each treated linen sample was compared to the spectrum of untreated linen to see if there are any differences in the absorbance bands, wave number, or peak intensity. An infrared ratio, i.e. the absorbance intensity ratio at 1372 cm\(^{-1}\) and 2900 cm\(^{-1}\), was calculated as an indicator of crystallinity of samples at each treatment level. The calculation method is summarized in the following:

1. Smooth the spectrum to reduce the noise in the spectrum. A smoothing factor of 3 and 13 data points are used in the smoothing calculation.

2. Flattening: The flattening operation levels the baseline so peak intensity can be measured from a consistent baseline. Usually three points, i.e. 3700 cm\(^{-1}\), 2000 cm\(^{-1}\), and 1000 cm\(^{-1}\) are selected to correct the curvature of the baseline. The "curve" function in the IRDM software program is used to correct the curvature and make the line flatter.

3. The "TAAT" command was used to convert the vertical axis from transmission percentage to absorbance.

4. The vertical cursor was used to identify the absorbance value and wavelength for peak A at 2900 cm\(^{-1}\) and valley B to the left of it. The absorbance difference AC indicates the amount of crystallinity for the peak near 2900 cm\(^{-1}\).

5. For the peak near 1375 cm\(^{-1}\), the vertical cursor was used
to identify the absorbance value and wavelength for points D, E and F(Figure 2). The absorbance difference EI was calculated as follows:

\[ EI = EH + HI = EH + GF \times DH/DG \]

EI indicates the amount of crystallinity for the peak near 1375 cm\(^{-1}\).

(6) The IR crystallinity ratio of 1375 cm\(^{-1}\)/2900 cm\(^{-1}\) is calculated as the ratio of EI/AC.
Figure 2. Calculation of FT-IR Crystallinity Ratio
**Statistical Analysis**

Mean values and standard deviations were computed for data obtained from each of the tests, i.e. the diameter, thread count, thickness, L*, a*, b*, ΔE, and the crystallinity ratio.

**Statistical Procedures**

The test data were first examined for normality of distribution by producing normality plots, called Nplots, by means of the Minitab statistical software. The results show that the distributions are not normal for each of the data sets. Transformation of data from (x) to (1/x) was performed but was not successful in achieving normal distributions. Consequently, parametric statistics are not suitable for the data analysis.

Since the distributions under different treatments are different in shapes and in mean values, standard rank-based (parametric) inferences for differences of means do not apply. Inference from the differences of medians must be deduced from simultaneous confidence intervals on the medians themselves (Hsu, personal communication). After discussion with the statistical consultants, Sign Interval analysis was chosen to calculate the confidence intervals for medians of each of the groups and to compare the differences between them. Notched box plots displayed these confidence intervals in a visual manner, useful for interpretation of data and comparison of
groups.

The Minitab statistical package version 8 was used to carry out the analysis and to display the confidence intervals by Notched Boxplots. The notched boxplots graphically display the main features of data distribution of a single variable (Figure 3).

"The middle half of each variable is represented by a box and the median is marked with a '⁺'. 'Whiskers' run from the hinges to the adjacent values on each side. Values between the inner and outer fences are possible outliers, and are plotted with a '⁺'. Values beyond the outer fences are probably outliers, and are plotted with a '₀'. If the median and a notch fall on the same space, the notch will not be displayed. Similarly, if the median and a quartile fall on the same space, the quartile is not displayed." (Minitab Manual, version 8, 1992).

```
1   0       (   *       I     ++-----)
2
   ------(     +    I)------
3
   0     (+     )
4
   ------(     +     )
```

```
27.0 28.5 30.0 31.5 33.0 34.5
```

**Figure 3. Boxplot from Minitab.**

Two groups whose notched intervals do not overlap are significantly different roughly at the .05 level.

In the following pages, the test results of fiber diameter, fabric yarn count, thickness and FT-IR crystallinity index are presented and discussed.
CHAPTER IV

RESULTS AND DISCUSSION

Linen fabric was used in this study to investigate the effects of the deep ocean environment on the degradation of cellulose fibers in the presence of metal or alone. The linen fabric was exposed to four treatments, i.e. group D, cellulose fabric immersed alone; group E, cellulose fabric immersed with copper pieces; group F, cellulose fabric immersed with iron pieces; and the control group which was not immersed. The results of this research are discussed in three sections. The first section discusses the preliminary experimental results for the morphological examination of fibers from each treatment. Results of study by optical microscopy and scanning electron microscopy are then discussed. The second section covers the results of physical testing of each treatment and includes comparison and statistical analysis on each test parameter, i.e. fiber diameter, thread count, thickness, L*, a*, b*, and ΔE. The third section presents the results of infrared analysis and the comparisons of the spectra of fibers exposed to the four treatments. The crystallinity ratios of fibers from each treatment level also are presented.
**Fiber Morphology Examination**

Fibers from each treatment were examined under the microscope employing brightfield, darkfield, phase contrast, polarized light, and differential interference contrast techniques. A checklist was developed categorizing the characteristics of fiber morphology observed under the light microscope. The findings are summarized in Table 2.

**Microscopy Examination Checklist**

Fiber samples were first examined for their morphological characteristics as linen (flax) fiber. Seen under the microscope, the fiber cells appear as long, transparent, cylindrical tubes which may be smooth or striated lengthwise. There are swellings or 'nodes' at many points, and the fibers show characteristic cross-markings. Each fiber cell has a lumen or canal running through the center; the lumen is narrow but clearly defined and regular in width (Cook, 1959). The intense color which the fibers display when examined under the polarized light reflects the orientation of the crystallites of the fibers.

After confirmation that the fibers are, in fact, flax, they were then examined for characteristics of their morphology which indicated degradation. Surface deposits, which vary depending on the sampling location, were noticed in some samples. Some of the fibers are encrusted with deposits; some carry the deposits or stains inside the lumen.
## Table 2. Microscopy Examination Checklist

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Morphology Description</th>
<th>Morphology/Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Polarized Color</td>
<td>Lumen</td>
</tr>
<tr>
<td>L-1D-1</td>
<td>various color</td>
<td>Y</td>
</tr>
<tr>
<td>L-1D-2</td>
<td>various color</td>
<td>Y</td>
</tr>
<tr>
<td>L-1D-3</td>
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<td>Y</td>
</tr>
<tr>
<td>L-1D-4</td>
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<tr>
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<tr>
<td>L-1D-8</td>
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</tr>
<tr>
<td>L-1D-9</td>
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<td>Y</td>
</tr>
<tr>
<td>L-1D-10</td>
<td>various color</td>
<td>Y</td>
</tr>
</tbody>
</table>

Y - This feature is present;
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S - There are some of the feature observed, e.g. 3 or 4 examples per microscope slide;
F - There are a small number of the feature observed, e.g. 1 or 2 examples per microscope slide.
<table>
<thead>
<tr>
<th>Sample Number</th>
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<th>Morphology Description</th>
<th>Biodegradation</th>
<th>Bulges</th>
<th>Cracks</th>
<th>Fibrillation</th>
<th>Stain</th>
<th>Surface Deposit</th>
<th>Other</th>
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<td></td>
<td></td>
<td>F</td>
<td></td>
<td>green</td>
<td></td>
</tr>
<tr>
<td>L-1E-2</td>
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<td>Y Y Y Y</td>
<td></td>
<td></td>
<td></td>
<td>F</td>
<td></td>
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<td>F</td>
<td></td>
<td>green</td>
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<td>S S S</td>
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<td></td>
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<td>F S</td>
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<td></td>
<td></td>
<td></td>
<td>F F</td>
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<td></td>
<td></td>
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<td>S S Y</td>
<td></td>
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<tr>
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<td></td>
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<td>structure</td>
</tr>
<tr>
<td>L-1E-10</td>
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<td>spirals</td>
</tr>
</tbody>
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<tr>
<td>L-1F-1</td>
<td>various color</td>
<td>Y</td>
</tr>
<tr>
<td>L-1F-2</td>
<td>various color</td>
<td>Y</td>
</tr>
<tr>
<td>L-1F-3</td>
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<td>Y</td>
</tr>
<tr>
<td>L-1F-4</td>
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</tr>
<tr>
<td>L-1F-5</td>
<td>various color</td>
<td>Y</td>
</tr>
<tr>
<td>L-1F-6</td>
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S - There are some of the feature observed, e.g. 3 or 4 examples per microscope slide;
F - There are a small number of the feature observed, e.g. 1 or 2 examples per microscope slide.
Several forms of degradation were noticed. The predominant features are bulges, cracks, and fibrillation, which were found in almost every sample. Eaten away areas in the fiber, recognized as a result of biodegradation, are also found in some samples. These characteristics are summarized in the checklist (Table 2) which serves as a tool when examining the fibers under the microscope.

Fibers from Group D

Ten microscope slides containing multiple fibers from fabrics from group 1D were examined under the microscope. The most predominant characteristics which these fibers display are many bulges and a large degree of fibrillation. Several fibers with bulges were found in most of the slides. Bulging is probably caused by bacteria growing under the fiber surface (Jakes and Wang, accepted for publication). Examination under SEM also showed eaten away areas in the fibers. This also is a consequence of biodegradation (Figure 4 and 5). The causative micro-organisms have not been identified. A study of the effects of such bacteria on the structure of textile fibers has not been conducted (Jakes and Wang, accepted for publication).

The fibers in the immersion jar have undergone a stress which is mainly a swelling stress. When the fibers get wet, they swell and expand. The stress on a straight fiber is uniform in all directions but the stress on a bent fiber is different between the outer and inner layers (Figure 6).
Figure 4. Flax Fibers From Group D: SEM, Biodegradation.

Figure 5. Flax Fibers From Group D: SEM, Biodegradation.
The outer layers will be extended and the inner layers compressed (Morton and Hearle, 1972). When the elongation of elements in outer layers is larger than the breaking elongation of the material, breaking starts from the outer layers (Figure 7).

Cracks are also found on the fibers from group D. Such cracks are noted to be related to the decrease of polymer chain length as the fiber polymers degrade (Jakes and Wang, accepted for publication).

**Figure 6. Bending of a Fiber.**

**Figure 7. Bending Break of a Fiber.**
Fibrillation found in most sample slides could be due to the internal failure of the interfibrillar attraction (Figure 8). The decrease of interfibrillar attraction leads to the separation of fibrils. In addition, the swelling of fibrils causes a more pronounced appearance of fibrils in the fiber.

Figure 8. Flax Fiber From Group D, Fibrillation.
L-1D-1: DIC, 400X.

It is possible that cracks or separation of fibrils also could be due to the effect of sampling, during the process of removing the fiber from the fabric and mounting the fiber on the microscope slides. The broken ends and the split in the fiber observed under SEM observation (Figure 9) confirms that
the fibers are brittle. It has been assumed in this work, however, that the damage which might occur in sampling is minimal in comparison to that which occurred in the deep ocean environment.

![Flax Fibers From Group D: SEM, Broken Ends](image)

**Figure 9. Flax Fibers From Group D: SEM, Broken Ends.**

Another interesting finding which stems from the microscopic examination is that there are some holes in the fibers (Figure 10 and 11). The flax fiber has a lumen or canal running through the center. As the fiber swells, the fiber may suffer a swelling stress (Figure 6). As the stress accumulates, a break, tear or split starts from the lumen and develops across the fiber from inside to outside as well as internally along the fiber’s length (Figure 11).
Figure 10. Flax Fibers From Group D, Broken Bulge.
L-1D-7: DIC, 400X.

Figure 11. Flax Fiber From Group D, A Hole in a Fiber.
L-1D-1: Polarized Light, 400X.
Fibers from Group E

Multiple fibers from group E, which contained linen fabric and copper pieces, and mounted on the microscope slides, display some green spots on the fiber surfaces. The predominant feature of group E fibers are cracks and pronounced nodes. A spiral structure due to fibrillation is found in some fiber samples (Figure 12).

A regular pattern of cracks or breaks (Figure 13 and Figure 14) is observed in most of the fiber slides. The cracks could be the consequence of swelling stress, but it is also possible that cracks were introduced during sampling. The presence of cracks in most of the fiber slides

Figure 12. Flax Fiber From Group E, Spiral Structure. L-1E-4: Bright Field, 400X.
Figure 13. Flax Fibers From Group E, A Crack.
L-1E-4: Pol., 400X.

Figure 14. Flax Fibers From Group E: SEM, A Crack.
Figure 15. Flax Fibers From Group E: SEM, A Bulge.

demonstrates that the fiber is brittle. Some bulges are also found but they are not as frequent as those displayed by fibers from group D (Figure 15). These findings suggest that the fibers are weaker than the fibers from the untreated standard linen.

Compared to modern flax fiber, the examination of fibers from group E shows that some fibers have pronounced nodes larger in size than nodes in untreated linen (Figure 16 and Figure 17). Because polarization color reflects the orientation of the crystallites of the fiber, "examination of the fibers in polarized light shows whether the inherent orientation of the cellulose crystallites is preserved or dislocations have taken place" (Kleinert 1972). Examined under the polarized light, these pronounced areas show
polarization colors which are different from those displayed by fibers from the standard fabric (Figure 18), which indicates that the crystallite orientation in this region is distorted.

Pronounced nodes can be seen as protrusions of the dislocation. Searle notes the increased reactivity of the nodal area of linen. "It is well known that the dislocation marks show a differential staining with iodine solution, and it has been suggested that there is a depolymerisation of the cellulose wherever they occur." (Searle 1924). Because the dislocation area in flax fibers is more vulnerable to attack by chemicals and bacteria enzymes, i.e. it is more easily oxidizable or hydrolyzable than the remainder of the cellulose fiber, it may result in an increased node size.

No biodegradation was observed in the examination of these fibers. This result is reasonable since it is known that copper and its alloys inhibit biodegradation (Cooke, 1990). Although copper is known to catalyze the hydrolysis of cellulose fiber (Cooke, 1990), in the deep ocean environment the oxygen concentration is very low, and the temperature is very low, thus slowing hydrolytic reactions. Despite the catalytic presence of copper, fibers are not totally degraded.
Figure 16. Flax Fibers From Control Group: SEM.

Figure 17. Flax Fiber From Group E: SEM, Pronounced Nodes.
Figure 18. Flax Fiber From Group E, Pronounced Nodes.
L-1E-7: Pol., 400X.

Figure 19. Flax Fiber From Group E, Wrinkled Surface.
L-1E-5: DIC, 1000X.
When examining fibers under DIC, some fibers with a very rough surface were observed (Figure 19). Similar surfaces were observed under SEM (Figure 20). The fibers appear wrinkled on the surface. The source of this wrinkling is unclear, but it is a distinct characteristic for group E fabrics, and therefore must be related to the influence of metal in the degradation process.

**Fibers from Group F**

Ten microscope slides containing multiple fibers from group F, which contained linen and iron metal pieces, display many surface stains in a quantity greater than that from group E. Deposits are seen on the fiber surfaces (Figure 21); and also are found inside the lumen. The fibers display more fibrillation than those removed from either group D or E. Most of the fibers contain bulges and cracks.

The spiral structure of the component fibrils also is found in some fibers (Figure 22 and 23), and to some degree, the fibrils have separated. Unseparated fibrils also are visible when fibers are examined under the SEM (Figure 24). A similar form of degradation is apparent in the fibers from group 1E (Figure 12). By some mechanism the metal ions result in swelling and separation of fibrils which does not operate with the fabric which was immersed alone.
Figure 20. Flax Fibers From Group E: SEM, A Wrinkled Fiber.

Figure 21. Flax Fibers From Group F: SEM, Deposits on Fiber Surface.
Searle's study (1924) shows that when pressing a normal fiber in a solution of calcium chloride, "a very large number of spirally placed striations became visible and (when pressing) with sufficient pressure, the fiber can be so disintegrated that the component spirals are separated from one another as discrete fibrils." Flax fibers are composed of fibrils which spiral around in fibers building the fiber structure layer by layer. It consists of bundles of individual fibrils held together by gummy materials. Once the interfibrillar gummy materials are damaged in the ocean environment, the fiber no longer appears as a single fiber but as an "untwisted rope". Thus the metal ions act in some way in deteriorating inter-fibrillar gummy materials.

Figure 22. Flax Fibers From Group F, Spiral Structure.
L-1F-9: DIC, 1000X.
Figure 23. Flax Fiber From Group F, Spiral Structure.  
L-1F-9: DIC, 400X.

Figure 24. Flax Fibers From Group F: SEM,  
Unseparated Fibrils.
Summary

In summary, the fibers exposed to the deep ocean environment for 89 days exhibit changes in their surface morphology in comparison to modern flax fibers. The major changes include bulges, cracks, and fibrillation. The bulges could be due to bacteria growing under the surface of the fiber (Jakes and Wang, accepted for publication). Cracks and fibrillation could be attributable to swelling stress of the fiber. Some eaten away areas were found in group D and probably are due to bacterial deterioration in the fiber. The morphological characteristics of fibers from each treatment were discussed and summarized in Table 2.

Light microscopy and SEM are valuable tools to assist in the examination of the morphological changes of fibers. The chemical structure and the physical properties of the fibers may also changed. In the following pages, the findings and discussion of physical properties and chemical-physical structural changes of the linen fabric retrieved from marine environment is presented.
**Physical Properties**

Linen fabric samples were evaluated for fiber and fabric size changes and fabric color differences in order to evaluate the overall degradation effects on the linen fabric attributable to 3 months exposure to the marine environment in presence and absence of metal. The parameters measured were fiber diameter, fabric yarn count, fabric thickness and fabric color coordinates. The test results were statistically evaluated. Medians and sign intervals of each of the tests are included in Tables 3 & 4.

**Test Results**

Standard linen fabric, Testfabric L-53, is a coarse plain woven fabric with a yarn count of 32x25 yarns/inch. The mean diameter of the untreated fiber is 19.5 μm. The mean fabric thickness is 0.0242 inch. After immersion treatment, the mean yarn count for group D, E, and F is 32.2x26.9, 32.5x26.6, and 33.1x26.7 yarn/inch respectively. The mean fiber diameter of group D, E and F is 21.8μm, 21.8μm and 21.1μm respectively. The fabric thickness is 0.0279, 0.0273, and 0.0272 inch for group D, E and F respectively. When comparing the treated fabrics to the standard, the yarn count does not change much while the diameter of the fiber and the thickness of the fabric appear to increase (Table 3).

The L*, a*, b* color coordinates of 10 fabric samples from each treatment group were obtained on the HunterLab
spectrocolorimeter. Mean and standard deviations are listed in Table 4. The mean value of L* for group D, E, F and control group is 67.233, 62.667, 65.410 and 69.614 respectively. The mean value of a* for group D, E, F and control group is 1.0738, 0.7960, 1.3285 and 1.0156 respectively. The mean value of b* for group D, E, F and control group is 7.407, 8.429, 8.107 and 5.9994 respectively. The mean value of total color difference ΔE for group D, E and F compared with the control group is 3.000, 7.462 and 4.837 respectively. The mean value of total color difference ΔE for group E and F compared with group D is 4.985 and 2.662 respectively. Group E has the largest total color change among the three treatment groups.

Table 3

<table>
<thead>
<tr>
<th>samples</th>
<th>yarn count (yarn/inch)</th>
<th>diameter (μ)</th>
<th>thickness (inch)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>warp</td>
<td>fill</td>
<td></td>
</tr>
<tr>
<td>1D</td>
<td>32.1±2.1</td>
<td>26.9±4.6</td>
<td>21.8±2.5</td>
</tr>
<tr>
<td>1E</td>
<td>32.5±0.8</td>
<td>26.6±2.6</td>
<td>21.8±3.8</td>
</tr>
<tr>
<td>1F</td>
<td>33.1±0.6</td>
<td>26.7±3.3</td>
<td>21.1±3.4</td>
</tr>
<tr>
<td>Control Group</td>
<td>32.0±0.9</td>
<td>25.0±3.3</td>
<td>19.5±3.1</td>
</tr>
</tbody>
</table>
### Table 4

**Mean Values and Standard Deviation of Fabric Color Coordinates**

<table>
<thead>
<tr>
<th>Sample</th>
<th>HunterLab Color Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L*</td>
</tr>
<tr>
<td>Group D</td>
<td>67.233 ±1.758</td>
</tr>
<tr>
<td>Group E</td>
<td>62.667 ±1.356</td>
</tr>
<tr>
<td>Group F</td>
<td>65.410 ±0.934</td>
</tr>
<tr>
<td>Control Group</td>
<td>69.614 ±0.544</td>
</tr>
</tbody>
</table>

**Statistical Analysis Results**

As discussed earlier, the normality of distribution of each set of the data was examined and it was found that the data were not normally distributed. Transformation of the data was executed but the transformed data were still not normally distributed. A nonparametric statistical analysis, the Sign Interval, was therefore used to compare the differences of each of the medians of each of the treatments.

**Fiber Diameter**

Statistical analysis shows that there is no significant difference in median diameter between the control group and that of each of the immersed groups (Table 5). Comparison of
<table>
<thead>
<tr>
<th>Measurement</th>
<th>Sample</th>
<th>Sample Number</th>
<th>Median</th>
<th>Confidence Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fiber Diameter (μm)</strong></td>
<td>Group D</td>
<td>10</td>
<td>22.50</td>
<td>(22.25, 22.75)</td>
</tr>
<tr>
<td></td>
<td>Group E</td>
<td>10</td>
<td>21.38</td>
<td>(21.00, 21.75)</td>
</tr>
<tr>
<td></td>
<td>Group F</td>
<td>10</td>
<td>21.12</td>
<td>(20.75, 21.50)</td>
</tr>
<tr>
<td></td>
<td>Control Group</td>
<td>10</td>
<td>21.73</td>
<td>(21.73, 21.73)</td>
</tr>
<tr>
<td><strong>Fabric Thickness</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(inch×10⁻³)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Group D</td>
<td>10</td>
<td>2.770</td>
<td>(2.730, 2.810)</td>
</tr>
<tr>
<td></td>
<td>Group E</td>
<td>10</td>
<td>2.720</td>
<td>(2.710, 2.730)</td>
</tr>
<tr>
<td></td>
<td>Group F</td>
<td>10</td>
<td>2.750</td>
<td>(2.730, 2.770)</td>
</tr>
<tr>
<td></td>
<td>Control Group</td>
<td>10</td>
<td>2.435</td>
<td>(2.420, 2.450)</td>
</tr>
<tr>
<td><strong>Fabric Yarn Count</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(yarn/inch)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Group D</td>
<td>10</td>
<td>33.00</td>
<td>(33.00, 33.00)</td>
</tr>
<tr>
<td></td>
<td>Group E</td>
<td>10</td>
<td>32.50</td>
<td>(32.00, 33.00)</td>
</tr>
<tr>
<td></td>
<td>Group F</td>
<td>10</td>
<td>33.00</td>
<td>(33.00, 33.00)</td>
</tr>
<tr>
<td></td>
<td>Control Group</td>
<td>10</td>
<td>32.00</td>
<td>(32.00, 32.00)</td>
</tr>
<tr>
<td><strong>Warp</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Fill</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Group D</td>
<td>10</td>
<td>27.50</td>
<td>(27.00, 28.00)</td>
</tr>
<tr>
<td></td>
<td>Group E</td>
<td>10</td>
<td>28.00</td>
<td>(28.00, 28.00)</td>
</tr>
<tr>
<td></td>
<td>Group F</td>
<td>10</td>
<td>28.50</td>
<td>(28.00, 29.00)</td>
</tr>
<tr>
<td></td>
<td>Control Group</td>
<td>10</td>
<td>26.50</td>
<td>(26.00, 227.00)</td>
</tr>
</tbody>
</table>
the mean value of the diameter of each of the immersed groups to that of the standard group, however, points toward an increase in fiber diameter in each of the immersed groups relative to the diameter of the standard fibers (Table 3). Thus, visual appraisal of the data may provide an indication of a trend which is not shown by statistical analysis at .05 confidence level.

Increase in fiber diameter is anticipated to be a consequence of immersion. Swelling with water alone is sufficient to alter fiber diameter. Flax fibers contains crystalline and amorphous regions. As a fiber absorbs water, the polymer chains in amorphous areas are pushed apart. Water molecules form hydrogen bonds with the polar groups, such as the hydroxyl (OH), on the cellulose chain. Because water cannot enter the intermolecularly associated crystalline regions, some areas remain closed and unaffected by water uptake in the fibers. Both adsorption and absorption take place in the amorphous region and stop as the amount of water adsorbed reaches a saturation point (McCawley, 1977). When water enters the fiber, there is a disruption of intermolecular associative forces between the molecular chains. When the sample dries, free water contained in the fiber and some bonded water on the cellulose chains is removed, but some water molecules remain bound in the amorphous regions, and some bonding sites for water are satisfied by intermolecular bonding (Florian, 1987). Thus
although dry, fibers which have swollen with water do not return to their original size.

In addition to the effect of water, another reason that the fiber diameter could increase due to treatment in the deep ocean is that the salts from the sea water remain inside the fiber as water is removed. The salts provide a physical barrier to movement of the fiber polymers.

Finally, the forces of degradation can influence the consequent fiber diameter. "Fiber swelling is limited by the interchain forces holding the polymers together in the crystalline areas; only when these forces are broken in degradation processes can the fiber swell more" (Jakes and Howard, 1986). The fact that the median diameters of the groups were not statistically different at the .05 confident level indicates, therefore, that the 3 month exposure was not sufficient to cause enough polymer movement and degradation to result in permanent fiber swelling. However, the fact that there is a trend reflected of an increase in the mean diameter of the treated samples relative to the control samples indicates that this parameter should be examined again for samples exposed to a longer period of immersion. The fibrillar structure observed in samples from jar 1E and 1F confirms that there are some examples of fibers which have undergone degradation such that there is an increase in fiber size when the fiber structure swells (Figure 22 and 23).
Fabric Yarn Count

In terms of median yarn count, no differences are observed between each treatment group (Table 5). Statistical analysis shows there is no significant difference between each treatment group and the control group at the .05 level.

The result is due to the possibility that increase in fiber diameter only reduced the space between the fibers in a single yarn, and this change is not big enough to cause the yarn to increase in size. In addition, because yarn interlacing in the fabric restricts yarn swelling, the change in fabric structure and yarn count is limited.

Fabric Thickness

Statistically comparing the results of fabric thickness, no significant difference in median fabric thickness was found between each of the immersed groups, i.e. group D (immersed alone), group E (immersed with copper) and group F (immersed with iron), but each of the medians are different in fabric thickness from that of the control group (Table 5). This indicates that the presence of metal did not make any difference in fabric thickness while the immersion treatment in sea water increased the fabric thickness.

The reason for this is the same as that for change in fabric yarn count. Because the swelling of fibers did not cause significant changes in yarn size, the concomitant fabric thickness does not change significantly either. Because the
swelling of fibers was restricted by the yarn and fabric structure, and the increase in fiber size was very small, there was no significant change in yarn and fabric size.

**Color Change**

Result of Sign Interval analyses of the median values of L*, a*, b* color coordinates reveals that immersion treatment and the presence of metal did make a difference in fabric appearance which is statistically supported (Table 6). Significant differences are also noted in median L*, a* and b* values for each group, each of which contribute to the total color difference. For group D and the control group, there is no significant difference in median a* value, while difference in median L* and b* value contributed more to the total color difference. A similar situation is found in median b* value for group D and F, which show no statistically significant difference, where the difference in median a* and L* were the major contributors to the total color difference.

When examining the mean value of the total color difference value ΔE, significant differences were found between each of the treatment groups and the control group as well as group E & F and group D (Table 7). Comparison of ΔE of the three treatment groups with that of the control group shows that fabrics from group D have the smallest total color change, while fabrics from group E have the largest total color change (Table 7). The larger ΔE in fabrics from group
E results from the larger changes in ΔL* and Δb* value. Comparisons of the mean value ΔE of group E and F with group D show that fabrics from group E have larger color changes than that from group F.

Examining the three components separately, it can be seen that the mean ΔL* value of each of the treatment groups is smaller than the mean ΔL* value of the control group, i.e. the samples from group D, E and F are all darker than the control group (Table 7). The ΔL* values of group E and F compared with group D also show that the samples from group E and F are darker than those from group D. Samples from group E are the darkest group among the three treatment groups. The degradation of cellulose itself can make the fabric appear darker in color. In addition, the sample from groups E and F were stained by metal products. The staining from the corrosion of metal pieces results in the treated samples which have a darker color than the untreated fabrics and the fabrics immersed without metal.
<table>
<thead>
<tr>
<th>Measurements</th>
<th>Sample</th>
<th>Sample Number</th>
<th>Median</th>
<th>Confidence Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>L*</td>
<td>Group D</td>
<td>10</td>
<td>67.10</td>
<td>(65.46, 68.60)</td>
</tr>
<tr>
<td></td>
<td>Group E</td>
<td>10</td>
<td>62.64</td>
<td>(61.69, 63.53)</td>
</tr>
<tr>
<td></td>
<td>Group F</td>
<td>10</td>
<td>65.18</td>
<td>(64.59, 66.27)</td>
</tr>
<tr>
<td></td>
<td>Control Group</td>
<td>10</td>
<td>69.69</td>
<td>(69.33, 69.96)</td>
</tr>
<tr>
<td>a*</td>
<td>Group D</td>
<td>10</td>
<td>1.062</td>
<td>(0.952, 1.166)</td>
</tr>
<tr>
<td></td>
<td>Group E</td>
<td>10</td>
<td>0.743</td>
<td>(0.649, 0.971)</td>
</tr>
<tr>
<td></td>
<td>Group F</td>
<td>10</td>
<td>1.274</td>
<td>(1.151, 1.474)</td>
</tr>
<tr>
<td></td>
<td>Control Group</td>
<td>10</td>
<td>1.020</td>
<td>(0.980, 1.038)</td>
</tr>
<tr>
<td>b*</td>
<td>Group D</td>
<td>10</td>
<td>7.394</td>
<td>(6.984, 7.877)</td>
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<tr>
<td></td>
<td>Group E</td>
<td>10</td>
<td>8.040</td>
<td>(7.02, 10.18)</td>
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<td></td>
<td>Group F</td>
<td>10</td>
<td>7.564</td>
<td>(7.050, 9.049)</td>
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<tr>
<td></td>
<td>Control Group</td>
<td>10</td>
<td>5.994</td>
<td>(5.774, 6.231)</td>
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### Table 7.

Mean Values and Standard Deviation of Changes in Fabric Color Coordinates

<table>
<thead>
<tr>
<th>Compared with Control Group</th>
<th>Group D</th>
<th>Group E</th>
<th>Group F</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔL*</td>
<td>-2.381</td>
<td>-6.948</td>
<td>-4.204</td>
</tr>
<tr>
<td>±1.664</td>
<td>±1.502</td>
<td>±1.248</td>
<td></td>
</tr>
<tr>
<td>Δa*</td>
<td>0.0581</td>
<td>-0.2196</td>
<td>0.3129</td>
</tr>
<tr>
<td>±0.1412</td>
<td>±0.2604</td>
<td>±0.2290</td>
<td></td>
</tr>
<tr>
<td>Δb*</td>
<td>1.408</td>
<td>2.429</td>
<td>2.107</td>
</tr>
<tr>
<td>±0.490</td>
<td>±1.577</td>
<td>±1.292</td>
<td></td>
</tr>
<tr>
<td>ΔE</td>
<td>3.000±</td>
<td>7.462</td>
<td>4.837</td>
</tr>
<tr>
<td>1.237</td>
<td>±1.787</td>
<td>±1.401</td>
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</table>

<table>
<thead>
<tr>
<th>Group E &amp; F Compared with Group D</th>
<th>Group D</th>
<th>Group E</th>
<th>Group F</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔL*</td>
<td>/</td>
<td>-4.567</td>
<td>-1.824</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±2.738</td>
<td>±2.275</td>
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<tr>
<td>Δa*</td>
<td>/</td>
<td>-0.2778</td>
<td>0.255</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±0.3059</td>
<td>±0.326</td>
</tr>
<tr>
<td>Δb*</td>
<td>/</td>
<td>1.021</td>
<td>0.700</td>
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<tr>
<td></td>
<td></td>
<td>±1.680</td>
<td>±1.634</td>
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<tr>
<td>ΔE</td>
<td>/</td>
<td>4.985</td>
<td>2.662</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±2.686</td>
<td>±2.095</td>
</tr>
</tbody>
</table>

Comparisons of mean Δa* value of the treated groups with control group show that there is no significant difference between group D and the control group, while group E has a smaller value and group F has a larger value than the control group (Table 7). A similar trend was found when comparing group E and F (immersed with metal) with group D (immersed without metal). Group E has a smaller value while group F has a larger value than group D. The results indicate that samples from group E are more green in color shade than the control group and group D, while samples from group F are more red in color shade than the control group and group D. The
findings are reasonable because the cuprous and cupric ions and the ferrous and ferric ions respectively yield green and red colored products.

Comparisons of the mean Δb* values of treated groups D, E and F with the control group show that they are larger than the Δb* value of the control group. Comparisons of the Δb* values of group E and F with group D also show that they are larger than group D (Table 7). The textiles in the treated groups are more yellow in color than the control ones and textiles from group E and F (immersed with metal) are more yellow than textiles immersed without metal. Textiles immersed with metal have undergone a more obvious change in color than those immersed without metal in the deep ocean environment.

The immersion treatment did make some changes in fabric appearance. Because the samples were chosen from different locations from the jar rather than randomly chosen from the jars according to a random number selection, and the spectrocolorimeter measurement was conducted consistently in the center of each sample, there are many sources of variation in the results. Some test locations were in the areas with dark stains and some were in the areas with light stains. Such large variation indicates that a more controlled method of color coordinate evaluation is necessary. In further study, more samples should be examined and the test location could be chosen as the area which is visually darkest.
Summary

In general, the mean fiber diameters display a trend toward increase in size (Table 3) which warrants further monitoring. The fabric yarn count did not change statistically after immersion in the marine environment for three months. There is no significant difference in fabric thickness between the three immersion groups while the thickness of the immersion groups are all different from the control group. There is significant difference in fabric color coordinates between treatment groups and control group, as well as group E & F and group D. In future work, fiber diameter should be evaluated, while fabric yarn count and thickness may not be parameters to measure.

Chemical-Physical Molecular Structure Change

The degradation of linen fabrics in the marine environment was further studied by FT-IR spectroscopy. The IR spectra of 10 fiber samples from each treatment group were recorded and were compared to the spectra of the control sample. In addition, infrared ratios of 10 fiber samples from each treatment group were calculated as an indication of relative crystallinity of the fibers.

FT-IR Spectra

The IR spectra of immersed fibers exhibit the structure typical of cellulose. The peaks shown in the spectra are
similar to that in Kleinert's study (1972). He reports that "the strong absorption at 3430 to 3400 cm\(^{-1}\) is evidence for the presence of bonded hydroxyl groups and the related O-H stretching vibrations, whereas the absorption at 2920-2910 cm\(^{-1}\) and 2840 cm\(^{-1}\) can be ascribed to stretching vibrations of C-H bonds in various groups." He found that strong absorption between 1650 and 1660 cm\(^{-1}\) indicates unsaturated C-C bonds. The absorption at 1372-1375 cm\(^{-1}\) is due to C-H bending bonds. The absorptions at 1420 cm\(^{-1}\) and 1320 cm\(^{-1}\) are due to O-H bending and O-H deformation vibrations of carboxylic hydroxyl-groups. "Moreover, the absorption maximum at 1070 cm\(^{-1}\) and the bands at 1155 to 1125 cm\(^{-1}\) may indicate C-O stretching and O-H bending in C-O-H." Two bands of the control fabric 1000 cm\(^{-1}\) and 990 cm\(^{-1}\) are more intense than the same bands displayed in samples employed in Kleinert's study.

As the immersion treatment was only 3 months, it is possible that the time period was not long enough to create enough chemical change such that the absorptions in the IR spectra would be altered. In comparing the treated sample spectra with that of the standard untreated linen, most of the absorptions show no differences. No new bands were introduced by the immersion treatment and there is no readily visible evidence in the IR spectra of the contamination of iron or copper.

The absorption in the region of 1740 cm\(^{-1}\) in the spectra of samples from group D and E and in particular from group F,
is weaker than that in the untreated linen. There are no concomitant increases in absorption apparent in the absorbance bands related to carboxylic acid groups. There are no increases in 1420 cm\(^{-1}\), 1370 cm\(^{-1}\), 1070 cm\(^{-1}\) or 1155-1125 cm\(^{-1}\) observed in comparison of the spectra of the treated samples and that of the standard linen. Thus the possible decrease in quantity of aldehyde group which is reflected in the decreased intensity of the 1740 cm\(^{-1}\) absorption band is not accompanied by an increase in carboxylic acid hydroxyl moieties, as proposed by Kleinert (1972). The change in intensity at 1740 cm\(^{-1}\) is so slight its significance is presently unknown. Much further study of the infrared spectra is required in order to determine whether the apparent decrease in aldehyde groups is a real one, and to determine the mechanism for such a decrease.

In the following paragraphs, the absorption intensity ratio at 1372 cm\(^{-1}\) /2900 cm\(^{-1}\), which is used for indicating relative crystallinity in cellulose materials, is discussed.

**Crystallinity Measurement**

The supramolecular structure of flax fiber is thought to be fringed fibrillar in nature. Polymer chains pass repeatedly through crystalline, oriented, and amorphous regions (Figure 25). The crystal units are regularly distributed throughout the whole fiber, and show preferred orientation parallel to the long fiber axis (Jakes and Howard,
Crystallinity in polymeric materials represents an ordering at the molecular level which is related to both the ordering of the segments of a chain and the ordering of all molecular chains. The degree of order in a segment of a chain can vary. As cellulose fibers degrade, the order of the segments of molecular chains gradually increases from short order regions to longer order regions, and the molecular chains line up relative to each other to increase the degree of order (Atalla, 1981) (Figure 26). The crystallinity of the fiber, therefore, can increase. The crystallinity index of a fiber can be used as an indicator of the crystalline content of cellulose (Caulfield, 1969).

Figure 25. Fringed Fibrillar Internal Structure of Cellulose Fiber.
Suitable infrared absorption bands are used as primary measures of crystallinity in polymers. "The application requires that the band bear a simple and unambiguous relationship to the crystalline or amorphous character of the polymer, and that absorption data can be obtained or inferred for the pure crystalline and amorphous polymers" (Billmeyer, 1984). The absorption at 1372 cm\(^{-1}\), which appears to be affected by the amorphous content of the sample rather than by the lattice type, and the absorption at 2900 cm\(^{-1}\), which is unaffected by changes in crystallinity, are chosen for the measurement of crystallinity in cellulosic materials (Nelson and O'Conner, 1964). The mean value and standard deviation were also calculated and listed in Table 8.

---

**Figure 26. Sequence of Structures with Increasing Order.**
Table 8

Mean Value and Standard Deviation of Crystallinity Ratio of Samples from Each Treatment

<table>
<thead>
<tr>
<th>Samples</th>
<th>Group D (Fabric Only)</th>
<th>Group E (With Copper)</th>
<th>Group F (With Iron)</th>
<th>Control Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infrared Ratio</td>
<td>0.80±0.05</td>
<td>0.76±0.02</td>
<td>0.90±0.05</td>
<td>0.74±0.02</td>
</tr>
</tbody>
</table>

Table 9

Summary of Sign Interval Statistical Analysis on the Crystallinity Ratio of Samples from Each Treatment

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Sample</th>
<th>Sample Number</th>
<th>Median</th>
<th>Confidence Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallinity Ratio</td>
<td>Group D</td>
<td>10</td>
<td>0.8054</td>
<td>(0.8034, 0.8074)</td>
</tr>
<tr>
<td></td>
<td>Group E</td>
<td>10</td>
<td>0.7646</td>
<td>(0.7630, 0.7662)</td>
</tr>
<tr>
<td></td>
<td>Group F</td>
<td>10</td>
<td>0.8937</td>
<td>(0.8935, 0.8940)</td>
</tr>
<tr>
<td></td>
<td>Control Group</td>
<td>10</td>
<td>0.7474</td>
<td>(0.7467, 0.7481)</td>
</tr>
</tbody>
</table>
Results of Statistical Analysis

Sign Interval analysis and the boxplots were conducted on the obtained IR crystallinity ratios. The results show that there are significant differences in crystallinity between each of the treatment groups, and there are significant differences between the treatment groups and the control groups (Table 9).

Samples from group D have a mean crystallinity ratio higher than group E and the control group but lower than group F (Table 8). According to Kleinert's study (1972), the overall crystallinity of aged linen was of high order similar to that of the modern linen, although the crystallites were short. The results in this study indicate that the crystallinity of each treated group is higher or close to the untreated samples. The fabrics suffered a combined damage in the deep ocean environment. It is likely that the degradation reactions occurred primarily in the amorphous regions resulting in alteration of relative crystallinity. "As amorphous areas are damaged, rearrangement of associated chains can occur, resulting in an increased quantity of crystallinity. As degradation ensues, the polymer chains decrease in length, and their mobility increases, once again encouraging the formation of more ordered crystallite regions" (Jakes and Foreman, in press) and consequently caused the increasing of order in molecular chains. As a consequence, the crystallinity of group D becomes higher than the untreated
Group E has the lowest crystallinity among the three treatment groups, but the crystallinity of fibers from group E is statistically higher than that of the control group. The reason for this is not entirely clear. Copper is known to inhibit microbiological degradation, which should preserve fiber structure, yet copper also acts as a catalyst of oxidative degradation, which should result in significant change in relative crystallinity. On the other hand, because the linen fabric was immersed in an environment with copper metal, some preservation of structure may result. In the process of pseudomorph formation, "copper ion is exchanged for the proton of carboxyl groups in cellulose, under appropriate conditions" (Jakes and Howard, 1986). If a similar mechanism is occurring in the deep ocean environment, copper in linen fiber can aid to maintain the fiber internal molecular structure.

Samples from group F have the highest crystallinity ratio among the treatment groups. This may indicate that the amorphous region of the fibers in group F are degraded more than the crystalline areas. Iron catalyzes oxidative degradation and in contrast to copper ion, appears to operate to degrade fiber polymers in amorphous region.
Summary

In comparison of the IR spectra with the untreated linen, no new IR absorption bands were introduced in the spectra of the fibers exposed to each treatment. Small differences in relative intensity of the 1740 cm\(^{-1}\) certain bands between the treated groups and the untreated one was noticed. There is a slightly weaker absorption at 1740 cm\(^{-1}\) for all treated samples, which is attributable to aldehyde groups. Much further study of the infrared spectra is required in order to determine whether the apparent decrease in aldehyde groups is a real one, and to determine the mechanism for such a decrease. The crystallinity ratio median of each treatment group is statistically higher than that of the untreated group.

As amorphous areas are attacked by degrading forces, crystalline areas remain less affected. Thus the relative crystalline composition can increase compared to that of the untreated fibers. In addition, fiber swelling can result in molecular rearrangement in the amorphous regions such that chains align and, therefore relative crystallinity increases. FT-IR spectroscopy can be used to study chemical structural changes in fiber. Through calculation of the crystallinity ratio, an indication of the relative crystalline component is produced.
CHAPTER V

CONCLUSION AND SUMMARY

The ultimate goal of this study is to contribute to the understanding of the mechanisms of degradation of textiles in the marine environment by characterizing the chemical and physical condition of fibers from textiles recovered from a deep ocean site. The work presented herein has three major objectives:

1. To explore and describe the microscopic morphological characteristics of flax fiber after being immersed in the marine environment for 3 months, alone, in the presence of iron, and in the presence of copper.

2. To explore and describe the physical and chemical microstructure changes of flax fiber after being immersed in the marine environment for 3 months, alone, in the presence of iron, and in the presence of copper.

3. As an aid to future research in the evaluation of marine textile degradation, to determine which physical and chemical characteristics, of the ones measured in this work, are strongly related to degradation in the marine environment.

To address the first objective of this study, the linen fabric which was exposed to four treatments, i.e. group D,
cellulose fabric immersed alone; group E, cellulose fabric immersed with copper pieces; group F, cellulose fabric immersed with iron pieces; and the control group which was not immersed, were first examined for morphological characteristics. The major changes in their surface morphology in comparison to modern linen include cracks, bulges, fibrillation, and biodeterioration.

Fibers from group 1D (immersed without metal) display more bulges along the fiber than found in fibers from other treatments. Eaten away areas are found in the fibers as well. Compared to fibers from the other two groups, the fibers from group D appeared to have been subject to bacterial attack to a greater extent than fibers from the other treatments.

Fibers from jar 1E, which contained copper pieces, have nodes which protrude more prominently than fibers from other treatments. More samples need to be examined to confirm that this is due to the presence of copper and to determine the mechanism of this swelling.

Fibers from jar 1F, which contained iron pieces, display fibrillation along the fiber and, in some areas, display disintegration into separated fibrils. No biodegradation was found in either group 1E or 1F, probably because the metal species have some effect on inhibiting biodegradation.

Separated spiral fibrillar structures appear only in fibers from group 1E and 1F. These fibers are more fibrillated because the presence of metal ions in the system
had some effect on the interfibrillar gummy materials, resulting in separation of fibrils, and/or the metal irons encouraged fibrillar swelling, resulting in distinction between individual fibrils.

Addressing the second objective of this work, the experimental linen samples also were evaluated for fiber and yarn size changes and fabric color differences. Statistical analyses show that there is no significant difference in median diameter and yarn count between the control group and that of each of the immersed groups (Table 5), while the mean fiber diameter displays a trend toward increase in size (Table 3). There are no significant differences in fabric thickness between the three immersion groups while the thickness of the immersion groups are all different from the thickness of the control group (Table 5). The swelling of the fiber and the barrier of salts in the fiber could lead to the increase in fiber size even upon fiber drying, but the swelling is insufficient to influence yarn size.

Statistical examination also shows that there are significant differences in the total color difference value ΔE between each of the treatment groups and the control group. There are also significant differences in the total color difference value ΔE between group E & F and group D. Significant differences are also noted in L*, a*, and b* values for each group, which contribute to the total color difference.
Flax fibers from each of the treatments also were examined for chemical-physical molecular structure changes using infrared spectroscopy. No new bands were introduced by the immersion treatment and there is no readily visible evidence in the IR spectra of the contamination of iron or copper. The absorption band at 1740 cm\(^{-1}\) in spectra of samples from group D, E and F is apparently slightly weaker than that in the untreated flax fibers.

The crystallinity ratios show that there are significant differences in crystallinity between fibers from each of the treatment groups and between the treatment groups and the control groups (Table 9). Samples from group D have a crystallinity ratio higher than that of group E and the control group but lower than that of group F. Group E has the lowest crystallinity ratio among the three treatment groups, but is higher than that of the control group, while samples from group F have the highest crystallinity ratio among the treatment groups. The reasons for this result have been discussed in the previous chapter. The crystalline areas are less affected by degrading forces than the amorphous areas. Thus, as degradation proceeds, the relative crystalline composition can increase compared to that of the untreated fibers. In addition, fiber molecular chain alignment can increase during the process of fiber swelling, resulting in an increase in relative crystallinity.
In general, fibers from the immersion treatments have undergone surface morphological changes, which are slightly different with each of the treatment conditions, as well as some small physical and physical-chemical changes in the deep ocean environment. However, because the immersion environment is dark, the temperature is just above freezing, and there is a low oxygen concentration, the degradation reactions proceed slowly. In order to evaluate the effect of the marine environment on the structure of textile materials, it is necessary to examine samples which have been exposed for longer time periods than those employed in this study.

Addressing the third objective of this work, the need for refinement in methodology has been demonstrated. The test results indicate that, in future work, fiber diameter should be evaluated, while fabric yarn count and thickness may not be parameters to measure. In addition, in order to reduce the standard deviation of the test results, more samples should be examined. To reduce variation in colorimetric measurements, the test location could be chosen as the area which is visually darkest. A more strict random sampling method also could be used to choose the samples from the immersion jar.

Suggestion for Future Study

Areas for future study suggested by the results of this study include the following:
1. Examine samples exposed for longer periods in the deep ocean environment and compare those results with the results of this study to evaluate the effect of time on the degradation of linen fabric in the marine environment.

2. Compare the results of a longer period of immersion with the results of this study to see which chemical or physical characteristics of flax fibers display a dramatic change over time period.

3. Compare flax fibers with cotton fibers retrieved from the same immersion jars to evaluate whether they behave in a similar manner in the marine environment.

4. Compare the results of cellulosic fabrics degraded in the marine environment with that of protenaceous fabrics from the same treatments to compare the effect of the ocean environment on the degradation of cellulose and protein textile materials.

5. Consider the findings of this work in the design of future methodology in the examination of textiles exposed to the marine environment.

6. Simulate the marine environment in the lab to explore which variable (e.g. temperature, pH value, salinity or chlorinity, oxygen concentration) is critical in changing fiber morphology and physical and chemical properties.

The last and probably the most important recommendation for future research deals with the need for continuation of
the present research. The repeated measurement of fiber morphology, and physical and chemical properties of fabrics from other experiment groups will enhance the validity of the microscopic checklist developed and could serve as a means of standardization. Further measurement of physical and chemical properties will confirm or deny proposed theories on degradation mechanisms. Such research should reveal some clues to the degradation mechanism of textiles in the marine environment.
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Appendix A

Sign Interval Boxplots of Test Results
1 - without metal
2 - with copper
3 - with iron
4 - standard

---(---I + I---------)---

2 ----(---I +----)

3 ----(---I + )

4 ( + I-)------

-----------------+-----------------+-----------------+-----------------+-----------------+-----------------+-----------------+-----------------+-----------------+-----------------+

Fill

22.5 25.0 27.5 30.0 32.5

Figure 27. Boxplot of Linen Fabric Yarn Count: Fill

1  O (* I +--------)

2

3

4

Warp

27.0 28.5 30.0 31.5 33.0 34.5

Figure 28. Boxplot of Linen Fabric Yarn Count: Warp
Figure 29. Boxplot of Flax Fiber Diameter

Figure 30. Boxplot of Linen Fabric Thickness
Figure 31. Boxplot of Linen Fabric Color Coordinates L*

Figure 32. Boxplot of Linen Fabric Color Coordinates a*
Figure 33. Boxplot of Linen Fabric Color Coordinates b*
Appendix B

Infrared Spectra of Linen Samples
Figure 34. Infrared Spectrum of Flax Fiber from Group E