第4章　安定化処理と修理

（1）紙を素材とする文化財の安定化処理

水洗可能な紙を素材とする文化財の安定化処理方法

東北地方太平洋沖地震、その後に襲来した大津波によって、多くの文化財が海水損しました。中でも、古文書や書画のように、海水損後真菌や細菌が繁殖し、劣化が急速に進む紙を素材とする文化財（以下、紙製文化財）の場合、被災後なるべく早い段階で的確な処理を施し、その形態と学術情報の保全を図る必要があります。

2011年4月2日と3日、岩手県立博物館（以下、岩手県博）に、陸前高田市立図書館から救出された膨大な数の紙製文化財が搬入されました。当時の東北地方北部太平洋岸の日平均外気温は10℃以下と低かったにもかかわらず、救出された紙製文化財のほとんどに泥や土砂、植物の葉などの天然物、様々な生活物質が固着していました。腐敗臭を発し、白色や青色、黒色を呈する真菌が発生した資料も多数みられました。

被災した紙製文化財を再生させるには、固着する様々な物質の除去（以下、除泥）、腐朽要因となる真菌や細菌の殺菌・除去（以下、除菌）、含有される塩分の除去（脱塩）が不可欠で、これらを確実に実施するためには、水洗が最も有効な方法であることはいうまでもありません。救出された紙製文化財を注意深く観察すると、ａ：炭や鉛筆を描画材料としていて水洗可能なもの、ｂ：水溶性の染料や絵の具を描画材料としていて、水洗不能なもの、ｃ：描画材料の水洗は可能であるものの、軸装類や絵図のように、資料形態保持のためなんらかの措置を施す必要があるものの、３つに大別されました（図1）。

水洗不能な紙製文化財に対する安定化処理方法は未確立です。一般に、ドライクリーニングで大凡の土砂を除去した後、くん蒸により殺菌して保管する方法がとられますが、この方法では海水がもたらした塩分を除去することは不可能で、劣化要因を抱えたままの状態にあることはいうまでもありません。他に、有効な方法が確立されるまで、冷凍保管する方法もとられています（図2）。現在、描画材料が溶出する心配がない領域を部分的に湿らせ、吸水紙を使って局所的に脱塩する、描画材料を固定した後脱塩するなどの方法が検討され、実験が行われていますが、実資料に適応できる状況には至っておりません。

本章第2節1）で詳述するように、水洗可能な紙製文化財については除泥、脱塩、除菌を行い、長期に渡って安定的に保管するための安定化処理技術が確立され、多くの被災紙製文化財に適用されています。以下に紙製文化財の除泥、脱塩、除菌の具体的方法について説明します。

水洗可能な紙製文化財の除泥

紙製文化財に固着する様々な物質については水道水に浸漬し、刷毛や筆を使い可能な限り除去します。混在す

Chapter 4　Stabilization and Restoration

(1) Stabilization of Paper-based Assets

Stabilization methods for washable paper-based assets

Many cultural assets were damaged by seawater in the Great East Japan Earthquake and subsequent tsunami. Cultural assets made of paper (hereinafter referred to as “paper-based cultural assets”), such as old documents, calligraphy, and paintings that rapidly deteriorated because of fungal and bacterial growth following seawater exposure. They needed to be appropriately treated at an early stage after being damaged to preserve their intact forms and the scientific usefulness they had.

On April 2 and 3, 2011, a large amount of paper-based cultural assets was salvaged from the Rikuzentakata City Library and brought to the Iwate Prefectural Museum (hereinafter referred to as the “IPMM”). Even though the average daily temperature at the time on the Northern Pacific coast of the Tohoku Region was 10°C or lower, natural materials, such as dirt, sand and plant leaves, and various other substances produced for everyday use affixed onto most of the salvaged paper-based cultural assets. This gave them a putrid odor, and white, blue and/or black fungus was observed on many items.

The following treatments are indispensable when restoring disaster-damaged paper-based cultural assets: 1) removal of different types of attached material (hereinafter referred to as “dirt removal”), 2) sterilization and removal of deteriorating factors such as fungus and bacteria (hereinafter referred to as “sterilization”), and 3) removal of the contained salinity (desalination). In order to perform these treatments thoroughly, rinsing in water is an effective method. Following detailed observation, it was found that the salvaged paper-based cultural assets could be categorized into the following three types: a) washable items drawn with India ink, charcoal or pencils, b) non-washable items with soluble dyes and paints, and c) items which were made with washable drawing materials but must be given some form of treatment to maintain their intact shapes such as hanging scrolls and pictorial maps (Fig. 1).

No completely effective method has been established for restoring non-washable paper-based cultural assets. The method generally used consists of removing most of the dirt and sand by a thorough cleansing and drying, and storing the item after sterilizing it with fumigation. However, the salinity cannot be removed with this method. Because of this, items treated with this method will obviously still contain a degradation factor. Another possibility is utilizing freezer storage until effective restoration methods can be established (Fig.2). Currently, different methods are being developed and tested, including a method in which localized desalination is performed using water absorbing paper by wetting the areas of the items where there is no possibility of damaging the image. An additional method is where desalination is performed after protecting the drawing material in order to prevent elution from occurring. However, further evaluation and testing is needed before these methods can be used on genuine assets.

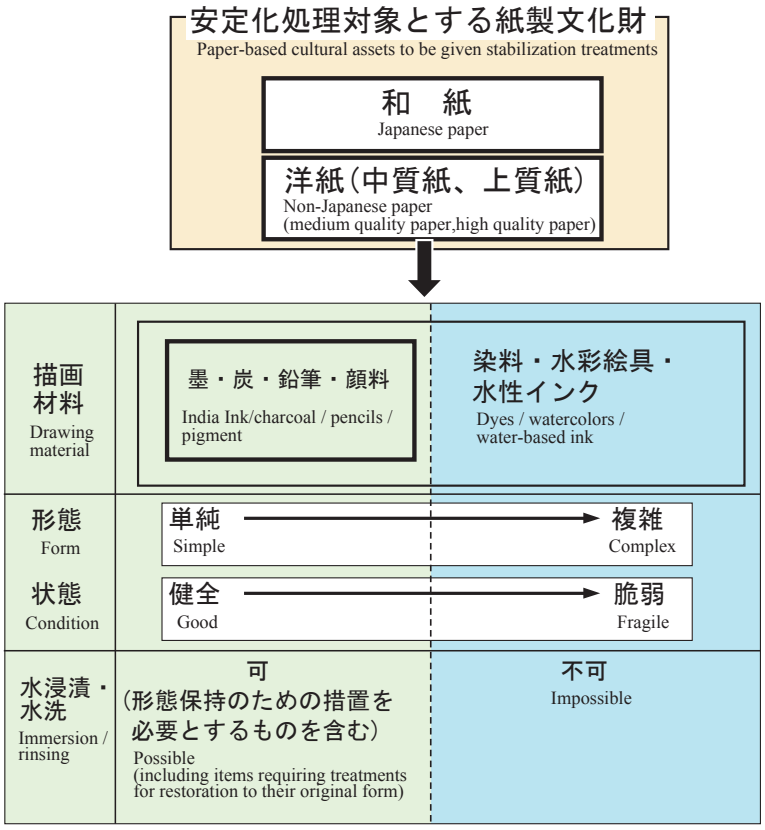


図1　安定化処理する紙製文化財の分類
Fig. 1　Classification of paper-based cultural assets undergoing stabilization treatment

図2　岩手県立博物館敷地内に設置された冷凍庫
Fig. 2　A freezer installed on the premises of the Iwate Prefectural Museum

る微細粒子については、超音波洗浄機を使用しその除去を図っています。超音波洗浄機による洗浄は、紙製文化財の他に、木を素材とする文化財、金属を素材とする文化財、および木・金属を素材とする複合文化財等に用いられていて、除泥に一定の成果を上げています。ただし、連続して超音波洗浄し続けた場合、紙を構成するセルロースに悪影響を与える可能性のあることが指摘されていることをふまえ（新田ほか2013）、その処理時間を15分以下に設定しています。

水洗可能な紙製文化財の除菌

除菌は文化財を次亜塩素酸ナトリウム水溶液に浸漬する方法で行われています。次亜塩素酸ナトリウムは、食品製造や医療をはじめとする様々な分野で多用されている殺菌剤で、水に溶け易く、殺菌効果が迅速で、脱臭効果を有すること、および安価であることがその大きな理由です。岩手県博では紙製文化財の安定化処理開始後約２ヶ月が経過した時点で導入しました。現在、水道水で約400 ～ 600ppmに希釈した水溶液を用いています。

次亜塩素酸ナトリウムには本来除去すべき塩化物イオンが相当量含まれていますが、海水損した文化財には実際に使用する次亜塩素酸ナトリウム水溶液を上回る塩化物イオン（Cl^-）が含有されています。使用後十分に洗浄することで、薬剤に含有される塩化物イオンをほとんど取り除くことができることが確認されました。

水洗可能な紙製文化財の脱塩

脱塩は不織布で保護した紙製文化財を24時間ごとに浸漬液を交換しながら５日間水道水に浸漬する方法で行っています。５日後、浸漬した紙製文化財を水道水から引き揚げ、精製水で超音波洗浄します。上記方法による脱塩の有効性については、楮紙を用いて作成した150丁の堅帳（図3）を、陸前高田市広田湾から採水した海水に３週間浸漬した後脱塩処理し、以下に示す３つの方法で確認しました（木戸脇ほか2012）。

ア．脱塩液中に溶出された塩化物イオンとナトリウムイオン（Na^+）濃度のイオンクロマトグラフ法による分析

イ．紙製文化財に含有されるナトリウム（Na）、カリウム（K）および塩素（Cl）のEPMA分析

ウ．紙製文化財に含有されるNa、K、マグネシウム（Mg）およびClの蛍光Ｘ線分析

実験の結果、楮紙を用いて作成した堅帳と実資料の脱塩液の塩化物イオン濃度とナトリウムイオン濃度は、いずれもほぼ同様に低減しています（図3）。海水損前の堅帳のEPMA分析ではNa、Cl、Kのいずれも検出されませんでしたが、海水損した堅帳の繊維表面からは多量のNa、K、Clが検出されました。一方、脱塩処理した堅帳のNa、K、Cl濃度は海水損前とほぼ同程度にまで低減されています（図4）。同様の結果は、蛍光Ｘ線分析からも確認されました（図5）。脱塩液に含有される塩化物イオン濃度とナトリウムイオン濃度の測定では、海水損した

As described in detail in 1) of Chapter 4 (2), stabilization techniques for washable cultural assets that enable stable, long-term storage involving dirt removal, desalination and sterilization have been established and applied to numerous disaster-damaged paper-based cultural assets. Specific methods for performing dirt removal, desalination and sterilization for paper-based cultural assets will be explained further.

Dirt removal for washable paper-based cultural assets

Various substances attached to the paper-based cultural assets were removed as much as possible using large and small brushes after soaking the items in tap water. Microscopic particles also present in the items were removed by using an ultrasonic cleaner. In addition to paper-based cultural assets, ultrasonic cleaning has also been used on cultural assets made of wood and/or metal. This method has been very effective for dirt removal. However, we limited the treatment time to 15 minutes in consideration of the possibility that continuous ultrasonic cleaning may have a deleterious effect on the cellulose molecules in the paper (Nitta et al. 2013).

Sterilization of washable paper-based cultural assets

Sterilization was performed by immersing the cultural assets in a sodium hypochlorite aqueous solution. Sodium hypochlorite is a disinfectant widely used in many different fields including the food manufacturing and medical industries. The main reasons we use it are because it dissolves readily in water, enables rapid disinfection, has deodorizing effects and is inexpensive. The solution currently used at the IPMM is prepared by diluting the disinfectant to a level of 400 to 600 ppm in tap water.

Sodium hypochlorite contains a considerable amount of chloride ions which must be removed from the seawater-damaged cultural assets. It was confirmed that cultural assets containing a larger amount of chloride ions in comparison to those contained in the sodium hypochlorite solution could be treated with a high-ion solution. It was also observed that there is very little effect from the residual chloride ions in the solution when the items were thoroughly washed after their treatment using the solution.

Desalination for washable paper-based cultural assets

Desalination was performed by immersing paper-based cultural assets protected by nonwoven fabric in tap water for five days while changing the water of the immersing bath every 24 hours. Following this five-day cleaning, the immersed items were taken out of the tap water bath and cleaned by ultrasonic cleaning using purified water. The effectiveness of desalination on paper-based cultural assets using this method was confirmed by testing the following three methods after immersing a control, a 150-page double-leaved book created using Japanese kozo (mulberry) paper (Fig. 3), in seawater taken from Hirota Bay in Rikuzentakata City for three weeks and then performing desalination (Kidowaki et al. 2012).

A) Measurement of chloride ions (Cl^-) and sodium ions (Na^+) contained in the desalination solution by ion chromatography

B) Analysis of sodium (Na), potassium (K) and chlorine (Cl) contained in the paper-based cultural assets by electron probe micro-analyzer (EPMA)

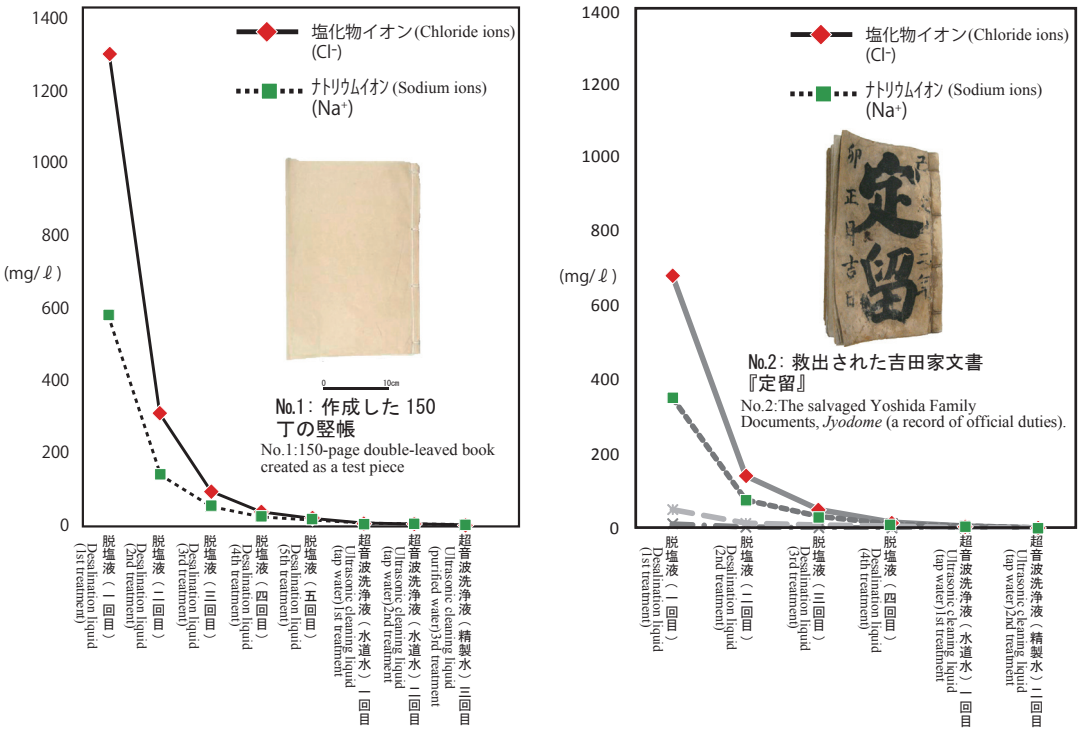


図3　脱塩液に含有される塩化物イオンおよびナトリウムイオン濃度の推移（イオンクロマトグラフ法による）。１回から５回の脱塩は水道水を用い、脱塩液を24時間ごとに交換。

Fig. 3　Changes in the concentrations of chloride and sodium ions contained in the desalination liquid (measured by ion chromatography). Tap water was used for the first through fifth desalination steps. The water in the desalination bath was changed every 24 hours.

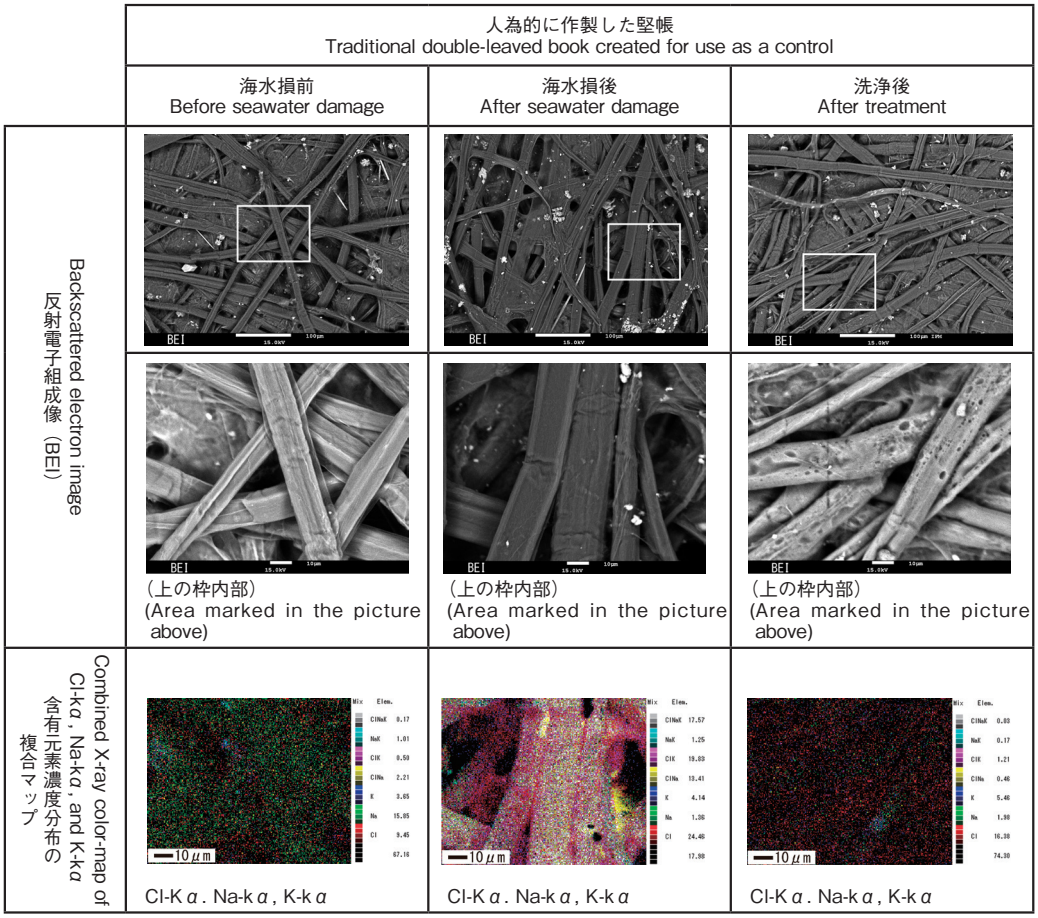


図4　No.1竪帳に含有されるNa・K・Cl濃度分布のEPMAによる分析結果

Fig. 4　Analytical results of the elemental concentration distribution of Na, K and Cl contained in the double-leaved document by EPMA (No.1)

紙製文化財から確実に塩分が取り除かれているという現象を確認できますが、それでも紙製文化財そのものに相当量の塩分が残っている可能性があり、脱塩が十分になされたかどうかを明確にすることは困難です。処理した紙製文化財そのものを表面分析し、Na、Cl、Kが検出されないことが確認されたことにより、構築した安定化処理法の有効性が確かめられました。

水洗が困難な紙製文化財に対する安定化処理

救出された紙製文化財の中には、描画材料の溶出という点では問題がないものの、脆弱なため水洗による形状保持が困難なものが相当数みられます。紙を素材とする軸装類や繊維染色製品はその代表的な例です。

上記資料の除泥および脱塩はいずれも、あらかじめ不織布などで保護した後作業台の上に置き、その上から霧吹きで精製水を噴霧し十分に湿らせ、資料から溶出してきた塩分はもとより、様々な固着物を含む水を、刷毛を使って除去する方法で行われています（本章第2節3)･4)･8)）。

排液の塩化物イオン濃度の推移は図3とほぼ同様の傾向を示していて、この方法でも十分な除泥、脱塩効果が得られることが確かめられました。浸漬が困難な資料については、この方法で洗浄および脱塩が進められています。

救出から安定化処理に至るまでの作業手順

いうまでもなく、海水損した文化財の安定化処理方法は未確立です。除泥・除菌・脱塩処理を施した文化財が今後どのように推移するか、定期的に経過観察する必要があります。岩手県博では現在、救出された海水損文化財を、図6に示す手順で処理し、再生を図っています。

赤沼英男（岩手県立博物館）

C) Analysis of Na, K, magnesium (Mg) and Cl contained in the paper-based cultural assets using X-ray fluorescence spectrometry

The analytical results indicate that the concentrations of chloride ions and sodium ions in the desalination liquids of the double-leaved book used as a control and the actual cultural asset both decreased in a nearly identical pattern (Fig. 3). According to the analysis of the control by EPMA, Na, Cl and K were not detected prior to seawater damage, but were detected in large amounts in the fibers of the control after seawater exposure. The concentrations mostly reverted to their original state after the seawater-damaged control was washed (Fig. 4). Similar results were obtained by X-ray fluorescence analysis (Fig. 5). Even though the measurement of chloride and sodium ion concentrations in the water used for desalination demonstrated that salinity was removed from the seawater-damaged paper-based cultural assets, it is difficult to clarify whether or not the desalination had been performed sufficiently. This is because there is the possibility that a considerable amount of salt remains in the item itself. However, we were able to confirm the effectiveness of the stabilization method we developed by conducting a surface analysis of the treated paper-based cultural assets which confirmed that no Na, Cl or K was detected.

Stabilization for paper-based cultural assets which are difficult to clean with water

A considerable number of salvaged paper-based cultural assets were too fragile for cleansing in water, even though there was no concern of drawing material elution, as such treatment may damage their intact shapes. Typical examples of these items include hanging scrolls mainly made of paper and dyed fiber products.

The fragile items were all treated by placing them on a work table after covering them with materials such as nonwoven fabric, then sufficiently saturating them by spraying purified water from above, and finally removing salt and other attached substances contained in the elution liquid using large brushes (see 3), 4) and 8) of Chapter 4 (2)).

The chloride ion concentration of the runoff decreased in a pattern nearly identical to the pattern shown in Fig.3, showing that sufficient dirt removal and desalination can be achieved with this method. It has been used for the cleaning and desalination of items for which immersing cannot be performed because of the difficulty in maintaining their intact shapes throughout the process.

Work procedure from salvage to stabilization

Of course, stabilization methods for seawater-damaged cultural assets have not yet been established. The conditions of the cultural assets treated by dirt removal, sterilization and desalination must be periodically observed to record any changes. Salvaged seawater-damaged cultural assets are currently being stabilized and repaired at the IPMM by the procedure shown in Fig. 6 in order to return them to their original state.

Hideo Akanuma (Iwate Prefectural Museum)

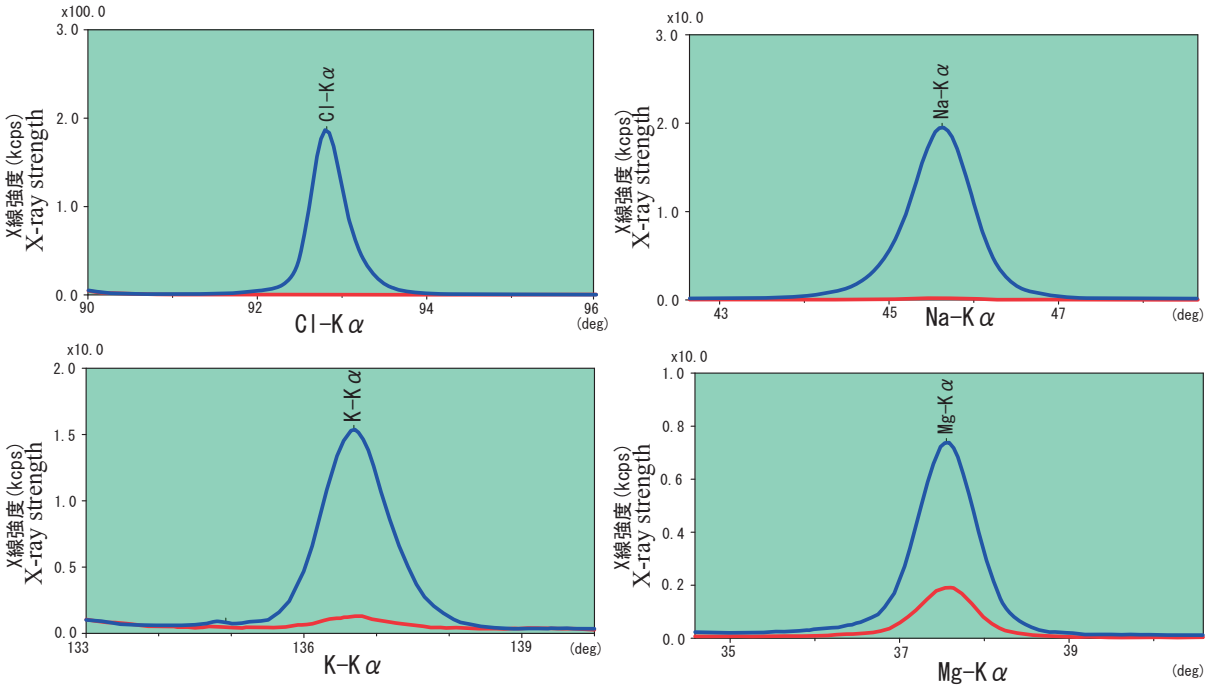
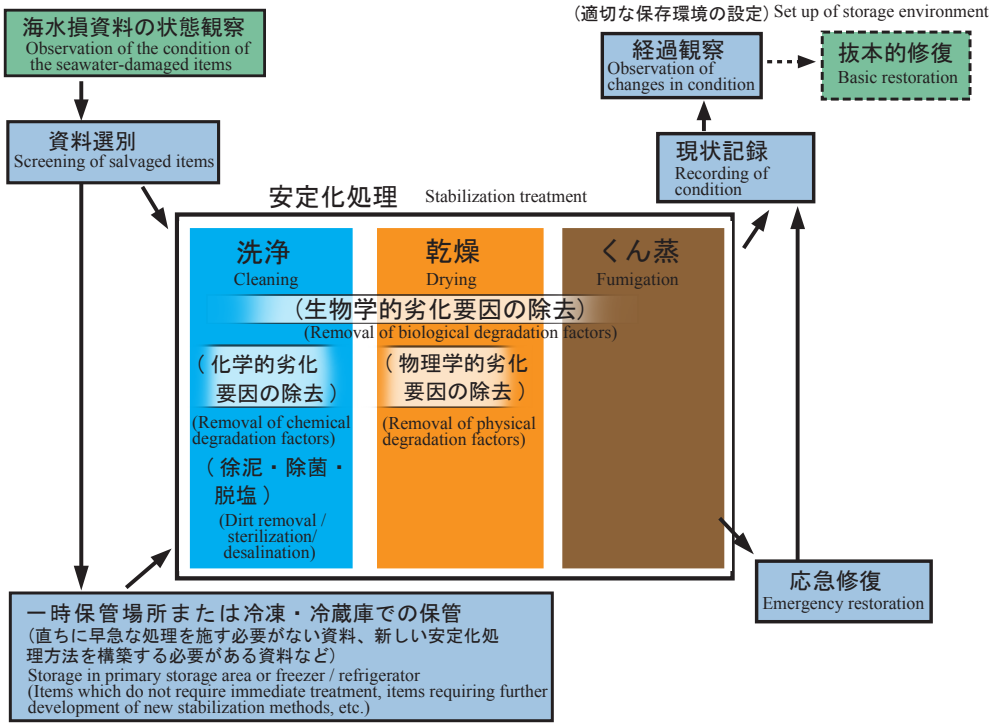


図5　No.1 堅帳の蛍光X線分析法による分析結果　青線＝脱塩処理前の堅帳、赤線＝脱塩・洗浄処理後の堅帳
Fig. 5　Analytical results of elemental concentration of Na,K,C and Mg contained in No.1 double-leaved document by X-ray fluorescence spectrometry. Blue line: *Kozo* (mulberry) paper of No.1 double-leaved book before desalination. Red line: *Kozo* (mulberry) paper of No.1 double-leaved book after desalination and cleaning.



※安定化処理：資料劣化および収蔵施設の環境汚染につながる要因を可能な限り除去し、長期に渡り安定的に保管できる状態を確保すること。

*Stabilization: A treatment to remove as many factors causing degradation of the items and environmental pollution of storage facilities as possible, and to ensure that the items are in suitable condition for long-term storage .

図6　岩手県立博物館における海水損資料再生手順
Fig. 6　Stabilization and Restoration procedure for seawater-damaged items used at the Iwate Prefectural Museum