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Influences of saltwater immersion on properties of wood-cellulosic paper

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ABSTRACT

The saltwater immersion method was developed to inhibit mould growth on flood- or tsunami-damaged paper. Commercially available fine paper used for printing and writing showed decreased tensile indices after saltwater immersion. The salt remaining in the paper tended to increase the moisture content because of the salt deliquescence and moisture in the air. The tensile index was restored by removing salt from the paper. Crystallization and distribution of salt in interfibre pores were also considered to influence interfibre rebonding. The difference in the fibre responses to saltwater depended on the relationship between nano-scaled pores in the fibre walls, osmotic pressure, and the degree of sizing, which resulted in low water retention values. More of the starch applied as a surface sizing agent was dissolved or dispersed during distilled water immersion than saltwater immersion. This loosened the fibre network, which was a factor that decreased the sizing degree of the paper.

1. Introduction

Tsunamis and floods may destroy paper-made cultural properties such as historical and political documents, paintings, and photographs. If left wet for extended periods, bacteria or moulds can cause these properties to biodegrade (Magaudda, 2004). Moreover, the functional properties and aesthetic values possessed by these documents are spoiled by the impaired physical and chemical properties of the biodegraded paper (Konkol, McNamara, Hellman, & Mitchell, 2012).

The saltwater immersion method was introduced earlier. It was confirmed that no mould grew on paper immersed in artificial seawater with a salt concentration of 3.2% or higher. The growth of three types of fungi that grow on paper (*Trichoderma reesei*, *Aspergillus terreus*, and *Aureobasidium pullulans*) was effectively inhibited by increasing the salt concentration (Higashijima, Hori, Igarashi, Enomae, & Isogai, 2012). In addition, it was found that salt had beneficial effects, such as preventing dye ink dissolution (Higashijima, 2012). As a follow up to these results, the interaction between salt and paper and its influence on paper properties should be studied.

In the material sciences, the addition of NaCl is reported to improve tensile strength of medium density fibreboard. NaCl-containing fibres swelled in water because of the osmotic pressure of free Na^+ ions (Uraki, Nemoto, Yanaga, Koizumi, & Hirai, 2005). NaCl coexisting with a retention aid worked to improve the retention and flocculating effects in the papermaking process (Linstrom & Glad-Normark, 2005).

Commercially available copy paper manufactured from chemical pulp was used as a sample of the document paper most frequently used. Copy paper for printing and writing has some common components. It was completely composed using AKD as an internal sizing agent, added during stock preparation in the papermaking process. The purpose of adding AKD is to control wetting

Abbreviations: AKD, alkylketene dimer; ASA, automatic absorptometer; HBKP, hardwood bleach kraft pulp; Py–GCMS, pyrolysis–gas chromatography mass spectrometer; SEM-EPMA, scanning electron microscope with electron probe microanalyzer; w/w, weight by weight; WAR, water-absorption rate; WRV, water retention value.

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of paper and aqueous liquid absorption and penetration into paper (Neimo, 2000). The surface sizing of paper is chosen in order to improve the surface strength, water resistance, and printing quality (Moutinho, Kleen, Figueiredo, & Ferreira, 2009). Starch is typically used for surface sizing (Carceller & Juppo, 2004; Prinz & Schultz, 2007; Moutinho, Figueiredo, & Ferreira, 2011). Paper fillers are used to increase the paper opacity and brightness. By combining it with fine paper, the result could be used as a candidate for studying salt-affected paper.

The aim of this research was to study advantageous or adverse effects of saltwater immersion on paper properties and the mould inhibition effect. If the properties of the paper after immersion in saltwater are not harmed, the saltwater immersion method is expected to be a comprehensive system. This study determined how paper properties changed after immersion in saltwater. The moisture content, tensile index, degree of fibre swelling, and the stability of additives in the copy paper such as starch, sizing agents, and fillers were evaluated. These results would indicate the best process for the recovery and storage of paper treated using the saltwater method.

2. Material and methods

2.1. Preparation of paper samples

Commercially available A4 fine paper (Fine PPC, Kishu paper, Japan, referred to as 'copy paper') with a grammage of 70 g m^{-2} was used in this experiment. It was strongly sized internally and externally with starch.

2.2. Saltwater immersion procedure

The experiment was carried out following the scheme shown in Fig. 1. Copy paper was immersed in a sodium chloride (NaCl, Wako Pure Chemical Industries, Ltd., Japan) solution at 3.5% (w/w) for 24 h. Desalination was performed using a washing technique in which the sample was gently immersed in 500 mL deionized water per sheet for 60 s. Non-desalted samples were prepared by restraint drying the sheets fixed in rings after they were taken out of saltwater.

Additional samples of Copy paper were immersed in deionized water without the addition of salt, for 24 h as a control sample. The paper properties of the original, deionized water, non-desalted, and washed paper samples were then compared.

2.3. Measurement of paper properties

2.3.1. Moisture content and physical properties

The moisture content, tensile index and single-sheet thickness were measured according to ISO standards ISO 1924-2:2008, ISO 534:205, and ISO 287:2009, respectively. However, the temperature was set to 25 °C and the relative humidity (RH) was set to 60%, which is different from the conditions specified in the standards. Paper samples were conditioned in the same temperature and relative humidity for all measurements of fibre and paper properties unless otherwise specified.

2.3.2. Residual salt in paper

Dried samples were weighed before and after immersion. The change in the paper mass was calculated and reported as the residual salt in paper.

2.3.3. Water absorption rate (WAR)

The WAR was determined using an automatic scanning absorptometer (ASA, Kumagai Riki Kogyo Co., Ltd., Japan). The volume of water absorbed by the paper dried after immersion in the NaCl solution was recorded over time. The WAR was calculated using the slope of the linear section of the absorption volume curve against time in the 10–20 s range. The WAR is closely related to the degree of sizing of the paper.

2.3.4. Water retention value (WRV)

To observe the swelling behaviour of fibres induced by immersion in a salt solution, Copy paper was treated according to the following process obtained by modifying SCAN-C 62:00. Copy paper with a mass of approximately 1.7 g was disintegrated in 230 mL of water. Salt powder was added during this disintegration until a salt concentration of 3.5% (w/w) was reached, and the suspension was allowed to stand for 24 h. A glass filter (no. 1GP16, SIBATA SCIENTIFIC TECHNOLOGY LTD, Japan) was used to form test pads. The WRV of laboratory handsheets prepared from a beaten hardwood bleached kraft pulp (HBKP) was also measured for comparison.

2.3.5. Ash contents

Ash in copy paper immersed in the NaCl solution was measured according to ISO 1762:2001. The incineration temperature for the ash content was 525 °C.

2.3.6. Alkylketene dimer (AKD) analysis

The AKD content was determined using pyrolysis gas chromatography/mass spectrometry (Py–GC/MS: GCMS-QP5050A, Shimadzu, Co. Ltd.). A dispersion of AKD (Harima Chemicals Group, Inc., Japan) was first diluted with water to adjust the AKD concentration and a known AKD mass. The NaCl solution-immersed, distilled water-immersed, and original copy papers were also cut to the same size. *N*-eicosane was applied to all the samples as the internal standard. Pyrolysis was performed at 500 °C and the detector temperature was set to 280 °C. For the GC/MS operation that followed, the injection and initial column temperatures were 250 and 150 °C, respectively. The column was heated from 150 to 300 °C at a rate of 5 °C min^{-1}. The analysis time was 50 min.

2.3.7. Salt distribution analysis using scanning electron microscope-electron probe microanalyzer (SEM-EPMA)

The distribution of Na and Cl elements in the saltwater-immersed copy paper were observed using EPMA-mapping (JXA-8530F Electron Probe Micro Analyzer, JEOL, Co. Ltd.).

2.4. Amount of starch dissolved in salt solution

The starch content of the NaCl solution resulting from dissolving from the copy paper was measured according to the following process obtained by modifying TAPPI Method T 419 om-91. A 2 g piece of copy paper was taken out of the 300 mL NaCl solution after immersion for 24 h. A 20 mL sample of the NaCl solution with starch dissolved in it was taken and a 0.25 mL KI-I_2 solution (7.5 g KI and 5 g I_2 per litre) was added to a 50 mL volumetric flask. Deionized water was added to adjust the volume. Absorbance of the mixture was measured using a UV-spectrometer at 580 nm. To make a quantitative measurement, the amount of the dissolved starch was calculated by referencing the UV absorbance calibration curve as a function of the starch concentration (Oxidized starch, Oji corn starch, Co. Ltd., Japan).

3. Results and discussion

3.1. Effect of saltwater immersion on tensile index of paper

Fig. 2 shows the tensile indices as a function of the dry-basis moisture content including salt-induced moisture. The copy paper had a higher moisture content which tended to reduce the tensile

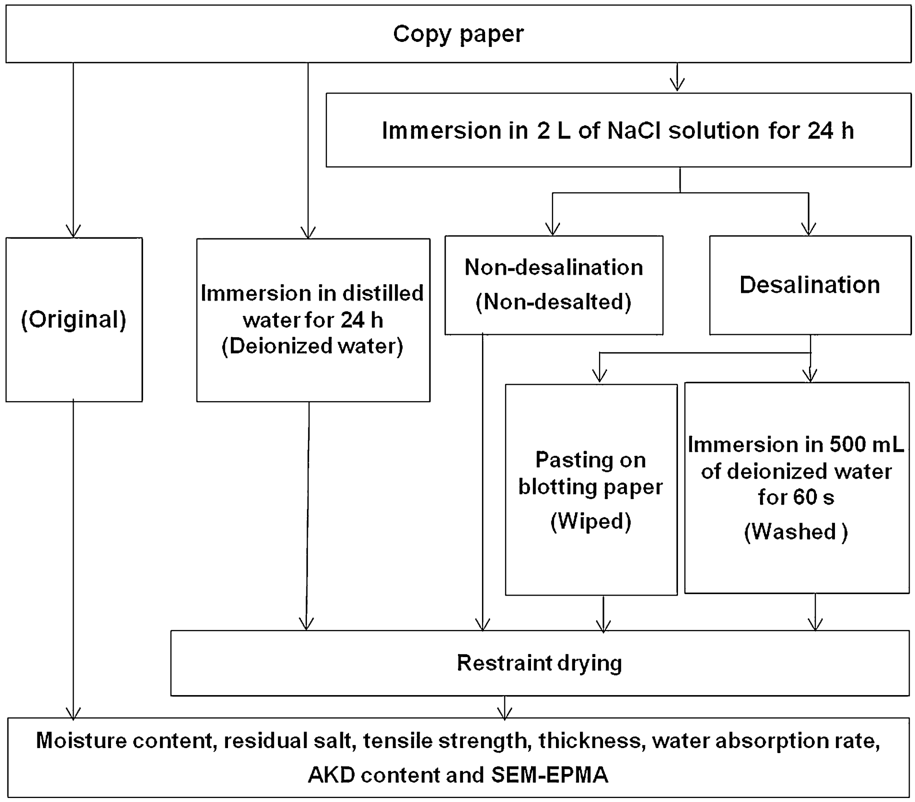

Fig. 1. Experimental flow diagram of salting and desalting processes for copy paper.

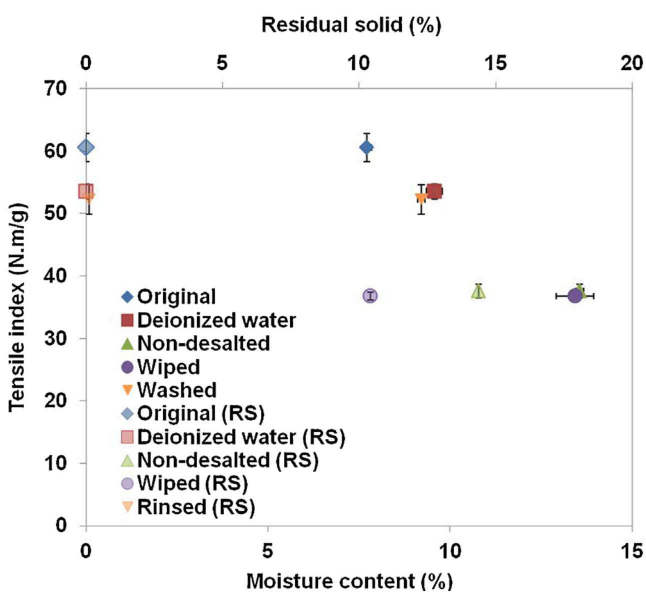

Fig. 2. Influence of immersion in NaCl solution on strength of copy paper.

index. To understand this result in more detail, several aspects of the salt–paper interaction were taken into account.

The first aspect is the moisture content. Salts introduce moisture depending on the salt-water affinity. The lower moisture content of the copy paper which was washed for 60 s is considered to lead to a higher tensile index. The second aspect is the crystallization. Non-desalted samples of copy paper with larger amounts of residual salt provided the lowest tensile index. This was likely because the number and dimension of the generated crystals were the largest in this case.

The third aspect is the sizing degree. During immersion, salt ions could not gain access to the nano-scaled pores in the fibre walls through the cloudy hydrated ionized carboxyl groups or solutes of starch and other paper components. Therefore, water was not likely to perfectly penetrate the nano-scaled pores in the fibre walls without the external pressure overcoming the osmotic pressure. Crystal growth at the crossing points of several neighbouring fibres probably inhibits the rebonding between the fibres after hydrogen bonds are broken during fibre swelling. Water was used to wash salt off the paper. This recovered some of the strength of the paper, although all samples experienced the same salty condition as the non-desalted samples.

3.2. *Effect of residual salt on moisture content*

Salt particles were found to remain in inter-fibre pores, or were attached to paper surfaces, and caused the paper mass to increase by immersion.

Fig. 3 shows the distributions of Na (on the right) and Cl (on the left) of the deionized water, non-desalted, and washed copy paper samples. The non-desalted sample was found to contain a large amount of NaCl. However, the washing process decreased the Na^+ and Cl^- contents to almost the same as that of the deionized water sample.

Fig. 4 shows the component ratios of variously treated copy paper. The moisture content was determined and presented based on the mass of oven-dry paper. The residual solid was predominantly NaCl. The difference between the moisture in the original copy paper and that in variously treated copy paper was regarded as the moisture induced by NaCl. Consequently, the moisture content of the NaCl solution-immersed sample was higher than those of the deionized water and original samples. The large amount of salt that remained on the paper introduced a great deal of

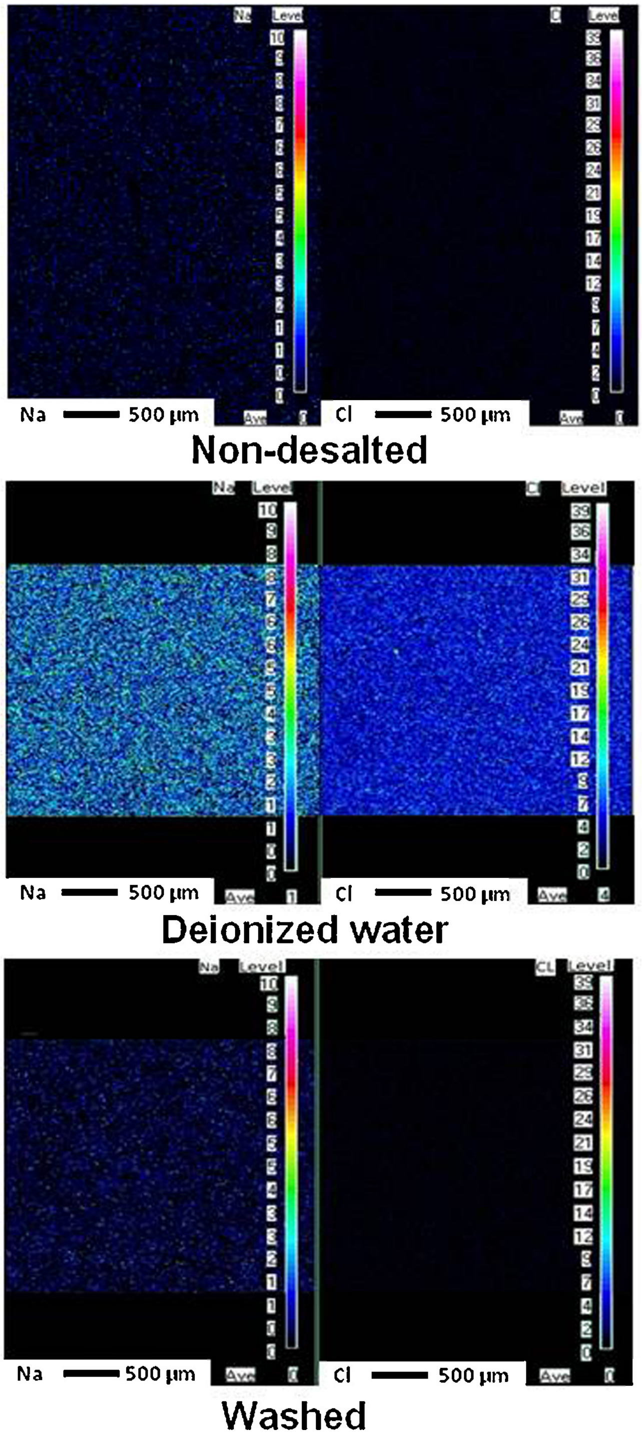

Fig. 3. Electron probe microanalyzer (EPMA) mapping of Na and Cl distributions over Original and NaCl solution-immersed copy paper.

moisture, which had a dominant effect on the moisture content of copy paper.

This fact means that there was moisture adsorbed on salt in addition to the water on three main components: polysaccharides in fibres, starch film on paper surfaces, and, if hydrophilic, paper filler. Moisture adsorption on salt is regarded as the effect of the deliquescent salt remaining in the paper. When NaCl, a strong electrolyte, is placed in water, ion pairs are completely dissociated into Na^+ and Cl^- ions. Both kinds of ions were surrounded by water molecules and Cl^- ions accommodate more water molecule than Na^+ ions (Yang, Meng, & Wang, 2006). When paper is immersed

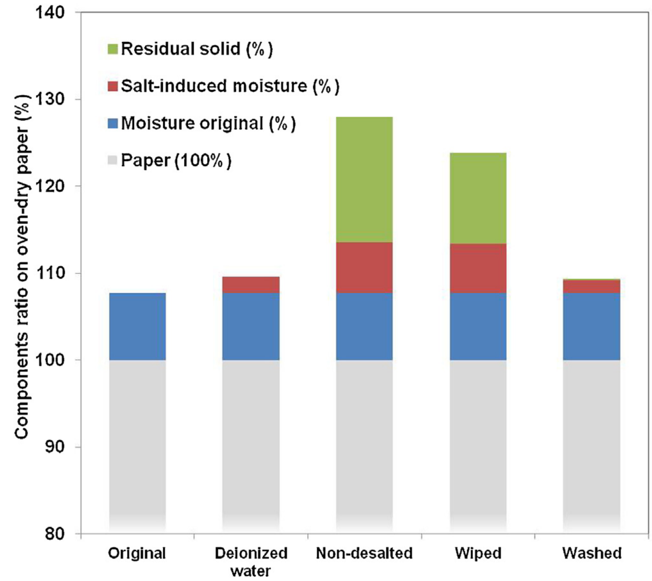

Fig. 4. Effect of residual salt on moisture content of NaCl solution-immersed copy paper.

in a NaCl solution, ions, along with water molecules, penetrate and fill vacant spaces in the paper. After an extended immersion period, water from the paper immersed in the salt solution evaporated during drying at room temperature. When the paper was drying, salt ions situated in pores are still hydrated (Sebastián et al., 2008) while salt ions on fibre surfaces lose water to form crystals. A NaCl crystal shows deliquescence (absorption of water) at approximately 75% or higher RH and a 25% NaCl solution shows efflorese (loss of water) at approximately 45% or lower RH at room temperature (Wise et al., 2012; Cziczo & Abbatt, 2000). As mentioned in the experimental chapter, after immersion in the NaCl solution and drying, the copy paper was conditioned at 60% RH. Thus, NaCl did not pick up any more moisture. Therefore, the salt-induced moisture content the paper originated from the moisture held by salt crystals even after drying because of incomplete dryness above 45% RH.

Desalination by wiping and washing with water were also compared. The results show that placing the wet saltwater-immersed paper on blotting paper was not sufficient to remove the salt ions. This is because salt ions may have been situated in interfibre locations deep in the paper. By washing with water, salt ions in fibre pores and around the fibre wall seem to be effectively washed away, leading to a lower salt-induced moisture content of paper.

3.3. *Effect of salt solution on fibre swelling*

The degree of fibre swelling in a NaCl solution was evaluated in terms of the WRV. Fig. 5 shows that the WRV of fibres in both HBKP and copy paper in a NaCl solution was lower than that in distilled water. In the case of distilled water, water molecules filling pores in fibre walls, which then formed hydrogen bonds with amorphous cellulose, led to swelling and increased the pore size in the fibre walls. In the NaCl solution, the swelling degree is subject to both the pH and salt concentration (Ek, Gellerstedt, & Henriksson, 2009). Higher concentrations of salt ions decrease the thickness of an electric double layer more intensively by holding together the association of carboxyl groups; neither Na^+ ions nor Cl^- ions could create a hydrogen or ionic bond with cellulose (Reid & Breton, 1959). Binding between cellulose and Na^+ may occur by ionic interaction through the dissociation of the carboxyl group on the cellulose chain in alkaline conditions (Fitz-Binder & Bechtold, 2012; Bechtold et al., 2013). Thus, fibre swelling is limited because

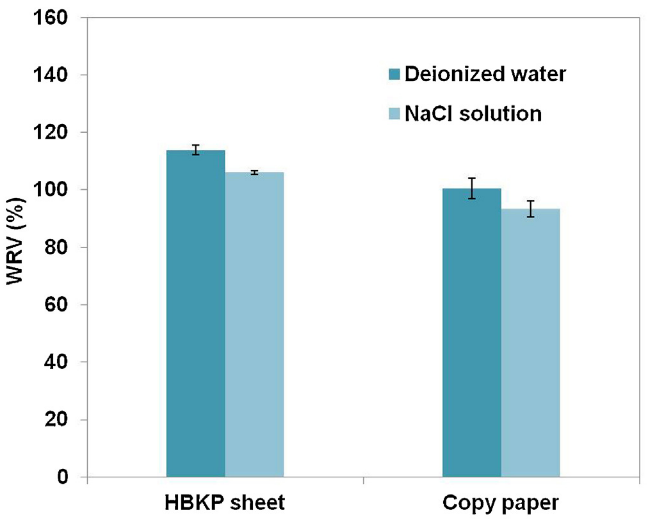

Fig. 5. Influence of NaCl salt on water retention value of copy paper and HBKP sheet.

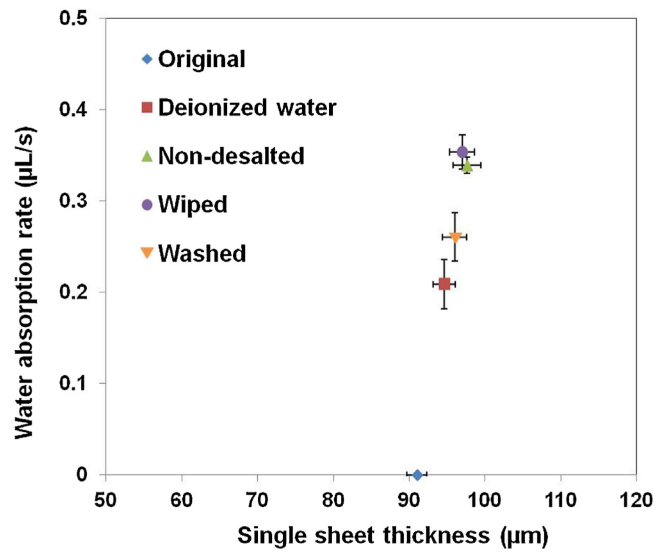

Fig. 6. Changes in thickness and water absorption rate of copy paper due to immersion in NaCl solution.

of the slightly acidic nature of, and high concentration of salt ions in, the 3.5% NaCl solution.

From another point of view, the osmotic pressure between nano-scaled pores in fibre walls, which are difficult for hydrated ions to access, and the external salt solution phase is high at high salt concentrations. This mechanism pulled water molecules from the nano-scaled pores to the external phase, resulting in low water retention and hence, less fibre swelling (Fält, 2003; Hubbe & Rojas, 2008). Fig. 5 also shows that the pulp obtained from disintegrated copy paper had a lower WRV than that of the HBKP. Thus, the sizing agent that reduced the access of water to the fibres resulted in the limitation of fibre swelling. Generally, nano-scaled pores occur during pulping and beating. These pores can be easily closed using two processes: (i) drying immediately after pulping and beating, and (ii) drying repeatedly.

3.4. Sizing degree of saltwater-immersed paper

After immersion, the thickness of dried copy paper samples tended to increase by about 2%, presumably because of the loosened and deformed fibre network. The difference in the change in thickness between the deionized water copy paper and NaCl solution copy paper was not significant. As discussed above, fibre swelling was limited in the salt solution; however, salt crystals deposited during drying inhibited fibre and sheet structure shrinkage, causing the formation of large pores in the paper. This led to an increase in the WAR, as shown in Fig. 6. As a result, the sizing degree of copy paper decreased by immersion in a salt solution followed by drying without salt removal.

Fig. 7 shows percentages of starch that dissolved from the copy paper in distilled water and NaCl solution. Starch film on copy paper was dissociated, detached, and occasionally dissolved via immersion. Oxidized starch is widely used for surface sizing. The carboxylic group on the starch molecules were modified in order to shorten the molecule and maintain the desirable viscosity during film application to the paper surface (Lehtinen, 2000). This carboxylic group is dissociated and releases protons to neutralize the alkaline condition of the solution. Thus, a larger amount of starch detached from paper surface during immersion and subsequently dissolved in water than in NaCl solution (pH of deionized water is 6.5 and NaCl at 3.5% is 5.9).

The AKD contents of the sheets were measured using Py–GC/MS. The detected AKD exhibited two major peaks at retention times of approximately 35 and 39 min. The AKD mass was calculated using

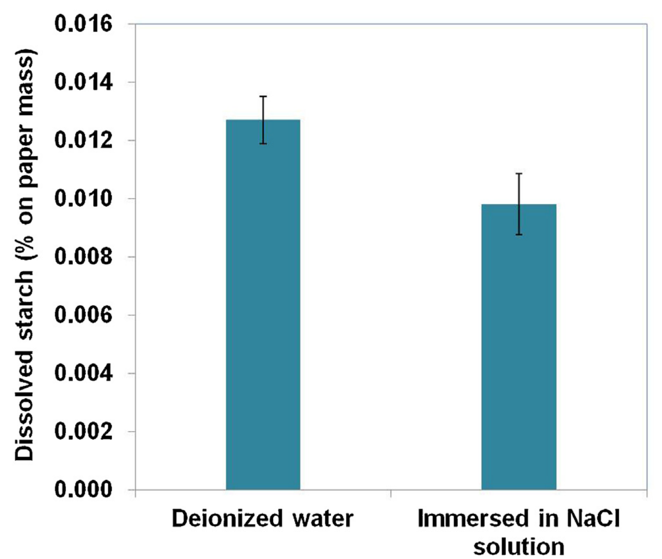

Fig. 7. Dissolution of starch from copy paper during immersion in deionized water and NaCl solution.

the relative total area of the two peaks to that of the *N*-eicosane peak at a retention time of approximately 13 min. Accordingly, the AKD contents of the original and NaCl solution-immersed copy paper samples were determined and compared, as shown in Fig. 8.

These results show that AKD would not be lost when the salt immersion method is applied. The AKD content of the distilled water-immersed copy paper was also at a similar level to that of the original copy paper, although the data are not shown. Therefore, the decrease in the sizing degree by immersion in distilled water or NaCl solution is not due to the loss of AKD, but presumably by the appearance of hydrophilic surfaces through inter-fibre de-bonding during the immersion followed by rebonding during drying, accompanied by a redistribution of AKD (Shen & Parker, 2001).

In this study, the paper filler content was measured as a percentage of the ash content. It was found that the copy paper filler, which was mainly composed of magnesium silicates, was not lost during immersion in water or NaCl solution, as shown in Fig. 8.

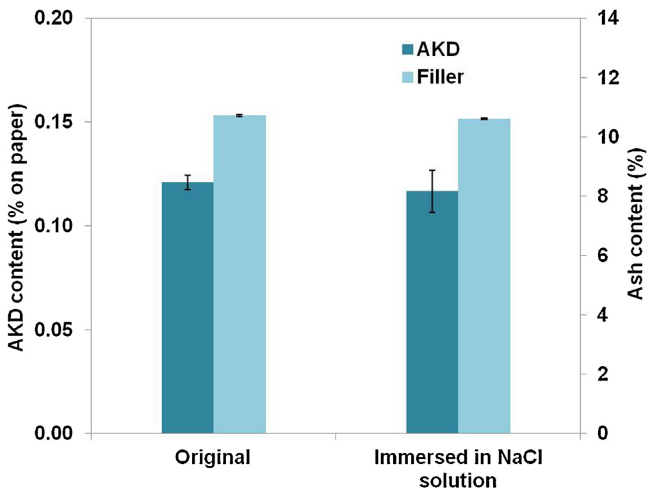

Fig. 8. Stability of AKD and filler of NaCl solution-immersed copy paper.

If the preservation of water-damaged papers using the saltwater immersion method is to be applied, the paper strength after immersion is the main point of concern. Following the discussion above, desalination after saltwater immersion is recommended. There were two desalination techniques included in this study: wiping and washing using water. The wiping technique seems to be ineffective for salt removal because a high amount of salt remains on the paper. Meanwhile, desalination by water rinsing decreases moisture content and maintains paper strength.

4. Conclusions

Salt affected copy paper during and after immersion. When paper was in the salt solution, salt ions stabilized the fibre swelling and paper components. However, the residual salt in the paper introduced additional moisture to dried papers. Moisture and salt crystals in the paper decreased its strength after drying. In consideration of this result, it was suggested that paper strength properties could be recovered by washing the residual salt away with water. Therefore, a desalination process followed by low relative humidity drying should be included in the comprehensive system of the saltwater immersion method.

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References

Bechtold, T., Manian, A. P., Öztürk, H. B., Paul, U., Širokái, B., Široký, J., Soliman, H., Vo, L. T. T., & Vu-Manh, H. (2013). Ion-interactions as driving force in polysaccharide assembly. *Journal of Carbohydrate Polymers*, *93*, 316–323.

Carceller, R., & Juppo, A. (2004). New surface size composition changes paper surface properties for improving ink jet printability of copy paper. *Paperi ja Puu*, *86*(3), 161–163.

Cziczo, D. J., & Abbatt, J. P. D. (2000). Infrared observations of the response of NaCl, $MgCl_2$, NH_4HSO_4, and NH_4NO_3 aerosols to changes in relative humidity from 298 to 238 K. *Journal of Physics Chemistry A*, *104*, 2038–2047.

Ek, M., Gellerstedt, G., & Henriksson, G. (2009). *Pulp and paper chemistry and technology. Paper products physics and technology*. Berlin: Walter de Gruyter GmbH & Co. KG (Chapter 3).

Fält, S. (2003). Influence of electrolytes on the swelling and strength of kraft-liner pulps. *Nordic Pulp and Paper Research Journal*, *18*(1), 69–73.

Fitz-Binder, C., & Bechtold, T. (2012). Ca^{2+} sorption on regenerated cellulose fibres. *Carbohydrate Polymers*, *90*, 937–942.

Higashijima, K., Hori, C., Igarashi, K., Enomae, T., & Isogai, A. (2012). First aid for flood-damaged paper using saltwater: The inhibiting effect of saltwater on mould growth. *Studies in Conservation*, *57*(3), 164–171.

Higashijima, K. (2012). Saltwater immersion method to prevent biological degradation of flood-damaged paper documents. In *Mater thesis*. Japan: The University of Tokyo.

Hubbe, M. A., & Rojas, O. J. (2008). Colloidal stability and aggregation of lignocellulosic materials in aqueous suspension: A review. *BioResources*, *3*(4), 1419–1491.

Konkol, N. R., McNamara, C. J., Hellman, E., & Mitchell, R. (2012). Early detection of fungal biomass on library materials. *Journal of Cultural heritage*, *13*, 115–119.

Lehtinen, E. (2000). *11th Pigment coating and surface sizing of paper*. Jyväskyla: Fapet Oy (Chapter 22).

Linstrom, T., & Glad-Normark, G. (2005). Strategies for improving the retention/formation relationship during papermaking: Part 1. A heteroflocculation approach. In *STFI-Packforsk report, 96*.

Magaudda, G. (2004). The recovery of biodeteriorated books and archive documents through gamma radiation: Some considerations on the results achieved. *Journal of Cultural Heritage*, *5*, 113–118.

Moutinho, I. M. T., Figueiredo, M. L., & Ferreira, P. J. T. (2011). Paper surface chemistry as a tool to improve inkjet printing quality. *BioResources*, *6*(4), 4259–4270.

Moutinho, I. M. T., Kleen, A. M., Figueiredo, M. M. L., & Ferreira, P. J. T. (2009). Effect of surface sizing on the surface chemistry of eucalyptus containing paper. *Holzforchung*, *63*, 282–289.

Neimo, L. (2000). *4th Papermaking chemistry*. Jyväskyla: Fapet Oy (Chapter 7).

Prinz, M., & Schultz, W. S. (2007). Sizing agents for surface and wet end application. *Professional Papermaking*, *1*, 44–49.

Reid, C. E., & Breton, E. J. (1959). Water and ion flow across cellulosic membranes. *Journal of Applied Polymer Science*, *1*(2), 133–143.

Sebastián, E., Cultrone, G., Benavente, D., Fernandez, L. L., Elert, K., & Rodriguez-Navarro, C. (2008). Swelling damage in clay-rich sandstones used in the church of San Mateo in Tarifa (Spain). *Journal of Cultural Heritage*, *9*, 66–76.

Shen, W., & Parker, I. H. (2001). A preliminary study of the spreading of AKD in the presence of capillary structures. *Journal of Colloid and Interface Science*, *240*, 172–181.

Uraki, Y., Nemoto, J., Yanaga, K., Koizumi, A., & Hirai, T. (2005). Preparation of board-like mouldings from composites of isolated lignins and waste paper II: Effect of inorganic salt addition on board performance and evaluation of practical use of MDF. *Journal of Wood Science*, *51*, 589–594.

Wise, M. E., Baustian, K. J., Koop, T., Freedman, M. A., Jensen, E. J., & Tolbert, M. A. (2012). Depositional ice nucleation onto crystalline hydrated NaCl particles: A new mechanism for ice formation in the troposphere. *Atmospheric Chemistry and Physics*, *12*, 1121–1134.

Yang, Y., Meng, S., & Wang, E. G. (2006). A molecular dynamics study of hydration and dissolution of NaCl nanocrystal in liquid water. *Journal of Physics: Condensed Matter*, *18*, 10165–10177.