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# The complexation of Fe(III)-ions in cellulose fibres: a fundamental property

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**Abstract**

In alkaline aqueous solution cellulose fibres, e.g. cotton, viscose, modal and lyocell fibres, show a distinct tendency to complex Fe(III)-ions by ligand-exchange reactions with iron(III)–D-gluconate (DGL), iron(III)–hepta-D-gluconate (HDGL) complexes. Two regions of high-binding capacity are identified at pH 8 and 13, respectively. Using a solution containing 0.001 mol $l^{-1}$ of the Fe(III)-complex, accumulation of Fe(III)-ions is observed in the fibre; depending on the type of cellulose fibre $0.7–3.6 \times 10^{-3}$ mol Fe(III) per kg of fibre are complexed at pH 8, which corresponds to 40–200 mg $kg^{-1}$ Fe(III). At pH 13, higher amounts of Fe(III)-ions up to $2.1 \times 10^{-2}$ mol $kg^{-1}$ (1150 mg Fe(III) $kg^{-1}$) are analysed in the fibre. The equilibrium of the ligand-exchange reaction between fibre and complex in solution is dependent on the type of ligand used (DGL, HDGL) and the fibre type (cotton, viscose, modal, lyocell). The amount of iron complexed remains below the carboxylic number of the cellulose. This finding points to an involvement of the carboxylic groups in the complex formation, which is in agreement with structures of soluble iron–carbohydrate complexes.

The results permit identification and quantification of structural sites able to complex Fe(III)-ions and lead to a more detailed understanding of the mechanism of catalytic damage of cellulose fibres during peroxide bleach.


*Keywords:* Cellulose; Fibre; Iron; Complexes; Viscose; Lyocell; Modal; Gluconate

## 1. Introduction

Approximately 50% of the annual production of textile fibres are based on the natural polymer cellulose. This corresponds to an amount of 25 million tons of cellulose fibres per year, e.g. Co (cotton), Fl (flax), CV (viscose), CMD (Modal), μCMD (micro-modal), CLY (lyocell) (Anon, 2002). A considerable part of the textile processing like pretreatment, bleach and dyeing is performed in alkaline aqueous solution.

To avoid catalytic damage of the cellulose polymer during the peroxide bleaching processes, the removal of heavy metal ions particularly Fe(III)-ions during alkaline pretreatment processes has to be as complete as possible. For this purpose powerful complexing agents are applied.

Sugar acids like D-gluconic acid, hepta-D-gluconic acid are well known to form stable complexes with Fe(III)- and Fe(II)-ions over a wide range of pH (Bechtold, Burtscher, & Turcanu, 2002; Escandar, Gandolfo, & Sala, 1990; Escandar, Olivieri, Gonzales-Sierra, & Sala, 1994; Gonzalez-Velasco, 1980; Nagy et al., 1986; Pecsock & Sandera, 1955; Whitfield, Stoikovski, & Sarkar, 1993). This property has lead to a number of applications, e.g. use as medicinal application (Shepherd et al., 1993) or complexing agent for corrosion inhibition (Lahodny-Sarc, 1995). The remarkable stability of the complexes at high pH is utilised in the formulation of auxiliaries for cellulose fibre pretreatment (Engbers & Dierkes, 1992; Mehltretter, Alexander, & Rist, 1953). At present, a distinct part of technical products contains D-gluconic acid or sugar acids because these compounds are easily biodegraded in the wasted water.

According to Chen, Martell, Motekaitis, Miu, and McManus (1999) in alkaline solutions carbohydrates like sorbitol, mannitol can form complexes with Fe(III) but precipitation is observed in the pH range 4–11. Similarly, the cellulose polymer can be understood as an insoluble carbohydrate type ligand for heavy metal complexation.

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In general, the structure of cellulose fibres can be divided in regions of higher degree of order of the macromolecules (crystalline zones) and regions of lower order so-called amorphous zones (Gruber, 1998). According to the models given in the literature, part of the fibre is accessible for small molecules by diffusion processes.

In aqueous medium, the uptake of water into cellulose fibre leads to intensive swelling of the polymer structure and a hydro-gel structure is formed (Bredereck, Gruber, Otterbach, & Schulz, 1996). In this state, the surface of the polymer structure as a defined physical border disappears and the structure resembles a dissolved carbohydrate. As a result, the physical and chemical behaviour of this heterogenous hydro-gel can be expected to be similar to dissolved carbohydrates and carbohydrate acids, respectively (Pecsock & Sandera, 1955; Sharkov & Akim, 1968).

In this paper, the ability of different cellulose fibres to serve as insoluble ligand for Fe(III)-ions is investigated. The properties both of native and man-made cellulose fibres to extract ions from soluble complexes of D-gluconate (DGL), hepta-D-gluconate (HDGL) and amino-tri-methylene-phosphonic-acid (ATMP) are described.

The ligand-exchange reaction between dissolved complexes and cellulose fibres was studied at various pH and as function of temperature.

The experimental results given are of interest both for the description of the accessibility of a certain cellulose fibre and for an improved understanding of the transport pathways of iron(III)-ions in alkaline treatment baths.

## 2. Experimental

### 2.1. Material

The experiments were performed with ring spun yarn samples. The specification of the different types of yarn/fibres are given in Table 1.

To achieve rapid and complete wetting of the samples in the complexation experiments, the raw cotton yarn Co2 was wetted twice with 2 g $l^{-1}$ wetting agent (Leophen MC, BASF, Ludwigshafen, Germany) at a liquor ratio 1:100 (1 g yarn in 100 ml liquid) followed by rinsing with distilled water.

Table 1
Specification of yarn/fibres

| Sign | Fibre | State | Yarn count (m $g^{-1}$) | Fibre count (dtex) |
|---|---|---|---|---|
| Co1 | Cotton | Bleached | 63 | – |
| Co2 | Cotton | Raw | 68 | – |
| CV1 | Viscose | Raw | 20[a] | – |
| CV2 | Viscose | Raw | 68 | 1.3 |
| CMD | Modal | Raw | 68 | 1.3 |
| μCMD | Micro-modal | Raw | 68 | 1.0 |
| CLY1 | Lyocell | Raw | 68 | 1.4 |
| CLY2 | Lyocell | Raw | 68 | 1.3 |
| CLY3 | Lyocell | Raw | 68 | 1.3 |

[a] Experimentally determined value, other values given by supplier.

All other material samples were easily wetted in the alkaline complex solution and thus no additional pretreatment was required.

### 2.2. Chemicals

$Fe(NO_3)_3{\cdot}9H_2O$, $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$, glycine, NaOH, $NH_4Ac$, AcOH, HCl, $NH_2OH{\cdot}HCl$, 1,10-phenanthroline-hydrochloride were analytical grade chemicals (Merck, Darmstadt, Germany). Na-D-gluconate (DGL) with >99% purity was used. HDGL (CHT, Tübingen, Germany) and amino-trimethylene-phosphonic-acid-sodium salt (ATMP, Sequion 20Na38, Bozzetto, Filago, Italy) were technical grade chemicals and used as received.

### 2.3. Formation of the Fe(III)–cellulose complexes

A stock solution containing 0.01 mol $l^{-1}$ $Fe(NO_3)_3$ and 0.01–0.2 mol $l^{-1}$ ligand was prepared. Ten millilitres of this solution were adjusted to the desired pH value by addition of 0.1 ml $l^{-1}$ glycine solution and 0.1 mol $l^{-1}$ NaOH solution and filled to a final volume of 100 ml. Caustic soda solution with c(NaOH) = 1 mol $l^{-1}$ was used as stock solution for preparation of the pH 13 solution.

The composition of the complex solutions are given in Table 2.

One gram of cellulose fibre was yarn treated in 100 ml of complex solution for 24 h in a shaking water bath (Julabo SW 21) at a temperature in the range of 25–80 °C. After the impregnation step, the yarn was removed from the solution and rinsed twice at room temperature with 100 ml distilled water.

### 2.4. Analytical methods

The analytical determination of the iron content in the fibre after impregnation was performed by extraction with hydrochloric acid and photometry of the Fe(II)-1,10-phenanthroline complex at 510 nm (DIN, 1983).

For this purpose, the iron was extracted from the yarn sample with 50 ml 1 mol $l^{-1}$ HCl for 30 min at 90 °C. An aliquot of 5 or 10 ml extract then was used for the photometrical analysis. The extract was pipetted into a 100 ml volumetric flask, neutralised with 5 ml acetate buffer (40 g $NH_4Ac$, 50 ml AcOH in 100 ml buffer) and diluted with distilled water. Two millilitres of 1.43 mol $l^{-1}$ $NH_2OH{\cdot}HCl$ and 2 ml 0.021 mol $l^{-1}$ 1,10-phenanthroline solution were added to form the complex and the flask was filled to 100 ml. The absorbance was measured after a reaction time of 50 min at a wavelength of 510 nm (Hitachi UV 2000, double beam spectrophotometer).

A calibration curve was established using defined amounts of $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$.

The determination of the carboxylic group content was performed according to Tappi method (T 237 om-88, 1989).

Table 2
Composition of complex solutions

| No. | pH | $c$ (ligand) (mol $l^{-1}$) | $c$ ($Fe^{3+}$) (mol $l^{-1}$) | $v$ (glycine) (ml) | $v$ (NaOH) (ml) | $v$ ($H_2O$) (ml) |
|---|---|---|---|---|---|---|
| *DGL* | | | | | | |
| 1 | 8 | 0.0012 | 0.001 | 47.5 | 2.5 | 40 |
| 2 | 9 | 0.0012 | 0.001 | 42.5 | 7.5 | 40 |
| 3 | 10 | 0.0012 | 0.001 | 30.0 | 20.0 | 40 |
| 4 | 11 | 0.0012 | 0.001 | 25.0 | 25.0 | 40 |
| 5 | 12 | 0.0012 | 0.001 | 22.5 | 27.5 | 40 |
| 6 | 13 | 0.0012 | 0.001 | – | 25 (1 mol $l^{-1}$) | 65 |
| *DGL* | | | | | | |
| 7 | 8 | 0.002 | 0.001 | 47.5 | 2.5 | 40 |
| 8 | 9 | 0.002 | 0.001 | 42.5 | 7.5 | 40 |
| 9 | 10 | 0.002 | 0.001 | 30.0 | 20.0 | 40 |
| 10 | 11 | 0.002 | 0.001 | 25.0 | 25.0 | 40 |
| 11 | 12 | 0.002 | 0.001 | 22.5 | 27.5 | 40 |
| 12 | 13 | 0.002 | 0.001 | – | 25 (1 mol $l^{-1}$) | 65 |
| *HDGL* | | | | | | |
| 13 | 8 | 0.002 | 0.001 | 47.5 | 2.5 | 40 |
| 14 | 9 | 0.002 | 0.001 | 42.5 | 7.5 | 40 |
| 15 | 10 | 0.002 | 0.001 | 30.0 | 20.0 | 40 |
| 16 | 11 | 0.002 | 0.001 | 25.0 | 25.0 | 40 |
| 17 | 12 | 0.002 | 0.001 | 22.5 | 27.5 | 40 |
| 18 | 13 | 0.002 | 0.001 | – | 25 (1 mol $l^{-1}$) | 65 |
| *ATMP* | | | | | | |
| 19 | 8 | 0.002 | 0.001 | 47.5 | 2.5 | 40 |
| 20 | 9 | 0.002 | 0.001 | 42.5 | 7.5 | 40 |
| 21 | 10 | 0.002 | 0.001 | 30.0 | 20.0 | 40 |
| 22 | 11 | 0.002 | 0.001 | 25.0 | 25.0 | 40 |
| 23 | 13[a] | 0.002 | 0.001 | 5.0 | 45.0 | 40 |

DGL, Na-D-gluconate; HDGL, Hepta-D-gluconate; ATMP, amino-trimethylene-phosphonic-acid-sodium salt.
[a] Precipitation.

## 3. Results and discussion

### 3.1. Composition of dissolved complex

In this series of experiments, Fe(III)–DGL complexes were used as dissolved complex system for the formation of the Fe(III)–cellulose complexes (solutions 1–12). The general reaction scheme for the formation of the Fe(III)–cellulose complex at a molar ratio in solution of Fe(III):DGL of 1:1.2 at pH 11 (solution 4) is shown in Scheme 1. The style of the chemical formula shown in Scheme 1 is according to the formula used for the description of metal-complexes formation (Martell & Motekaitis, 1992).

In the first step, the alkaline stable complex of Fe(III)–DGL is formed. Eq. (1) gives an example for such a complex described by Bechtold et al. (2002). In the presence of cellulose fibres, a ligand exchange occurs. In solution 4, the complex $[Fe_2H_{-7}(DGL)_2]^{3-}$ is present as main species. In solutions 7–12, complexes with Fe:DGL 1:2 stoichiometry are present. The number of protons released from the cellulose ligand is dependent on the type of complex formed in the fibre and the pH of the solution, thus the Fe(III)–cellulose complex is written in more general form as $[FeH_{-x}Cell]^{3-x}$. According to Eq. (2), $DGL^-$ is released and diffuses back into the bulk solution.

Suited chemical sites in the swollen cellulose fibres can act as heterogenous polymer carbohydrate ligand and an equilibrium for the Fe(III)-center-ions is established between the dissolved $DGL^-$ and the insoluble cellulose polymers (Eq. (2)).

During rinsing, the pH of the solution is lowered, the iron(III)–cellulose complex in the fibre looses stability and precipitation of $Fe(OH)_3$ inside the fibres occurs (Eq. (3)). This reaction can be observed visually in experiments at high pH values, e.g. solutions 6 and 12 when a high concentration of complex is formed in the fibre. While the complex in the fibres $[FeH_{-x}Cell]^{(3-x)}$ is almost colourless, the precipitation of $Fe(OH)_3$ leads to the development of yellow–light brown coloured fibres.

In experiments with molar ratio of Fe(III)–DGL of 1:1, a certain tendency for precipitation of $Fe(OH)_3$ was detected, thus experiments were performed with solutions containing the molar ratio Fe(III):DGL 1:1.2 and 1:2 (solution 1–6 and 7–12).

The iron content determined in bleached cotton Co1 as function of the two different molar ratios Fe(III):DGL 1:1.2

Formation of complex in solution

$$2\,Fe^{3+} + 2\,DGL^- \rightleftharpoons [Fe_2H_{-7}(DGL)_2]^{3-} + 7H^+ \quad (1)$$

Formation of Fe(III)-cellulose complex - Ligand exchange

$$[Fe_2H_{-7}(DGL)_2]^{3-} + 2\,Cell + (7\text{-}2x)\,H^+ \rightleftharpoons 2\,[FeH_{-x}Cell]^{(3-x)} + 2\,DGL^- \quad (2)$$

Rinse of sample - Decomposition of complex

$$[FeH_{-x}Cell]^{(3-x)} + 3\,H_2O \rightleftharpoons Cell + Fe(OH)_3 + (3\text{-}x)\,H^+ \quad (3)$$

Scheme 1. Reaction scheme for the uptake of Fe(III)-ions by cellulose fibres from the dissolved Fe(III)–DGL complex at pH 11 at a molar ratio of Fe(III):DGL of 1:1.2 (solution 4).

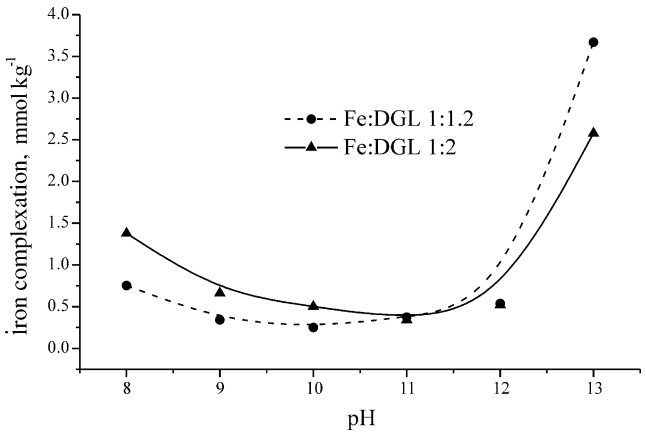


Fig. 1. Iron content in bleached cotton Co1 as function of pH of the impregnation solution, for different composition of the solution, molar ratio Fe:DGL 1:1.2, 1:2 (solutions 1–6 and 7–12), 25 °C.

and 1:2 in the impregnation solution as function of the pH are shown in Fig. 1.

The results given in Fig. 1 should be discussed under consideration of the structure of the Fe(III)–DGL complexes present in solution. For the pH range between 8 and 12, the composition of the Fe(III)–DGL complex has been proposed in the literature (Bechtold et al., 2002). In the case of a molar ratio Fe(III):DGL of 1:1.2, a bimolecular complex with the structure $[Fe_2H_{-7}DGL_2]^{2-}$ is present in solution at pH 8–12 (solutions 1–6).

Applying a molar ratio of Fe(III):DGL of 1:2 $[FeH_{-3}DGL]^{2-}$ is formed at pH 8–11 (solutions 7–12) and above pH 11 increasing amounts of $[FeH_{-4}DGL]^{3-}$ are present in solution (solutions 11 and 12). For the pH range above 12 assumptions for the composition of the dissolved Fe(III)–DGL system are given in the literature (Pecsock & Sandera, 1955).

Independent of the stoichiometric composition of the complexes in solution strong complexation of iron in the fibre is found in the experiments at pH 8–9 (solutions 1, 2, 7, 8) and at pH 13, where an enormous increase in complex binding capacity is observed (solutions 6 and 12). At pH 8, iron(III)-complexation capacity of 0.75–$1.38 \times 10^{-3}$ mol kg$^{-1}$, 42–77 mg Fe(III) per kg fibre was determined, while at pH 13 $3.67 \times 10^{-3}$ mol, 205 mg Fe(III), respectively, were analysed per kg of cotton fibre.

The study was not extended to higher pH value because at high alkalinity distinct structural changes of the cellulose fibre will cause additional effects.

The differences between the curves shown in Fig. 1 could be attributed to several effects.

- *Kinetic effects due to slow establishment of equilibrium between the complexes*. As known from the literature, particularly the Fe(III)–carbohydrate complexes show very slow reaction rates and equilibria are reached rather slowly (Bechtold et al., 2002; Chen et al., 1999; Escandar et al., 1990). As in the experiments, there was given sufficient time for equilibration, kinetic effects should be of minor relevance.
- *Formation constants of dissolved complex species and cellulose complexes*. In solutions containing Fe:DGL with 1:2 stoichiometry formation of the more stable 1:2 complex shifts the equilibrium, according to Eq. (2), to the left side. As a result lower concentrations of Fe(III)-complex are found in experiments with 1:2 stoichiometry (solutions 7–12).
- *Experimental conditions during washing step*. In case of solutions 7–12, a higher concentration of DGL is present in the fibre and thus a redissolution of freshly precipitated $Fe(OH)_3$ can occur.

### 3.2. Influence of temperature on iron uptake

Complex equilibria show distinct sensitivity to temperature. To study the influence of temperature on the amount of iron complexed in cellulose fibres a series of ligand-exchange experiments was performed with Co1 at temperatures between 25 and 80 °C, at a molar ratio Fe:DGL 1:2. The experiments were performed in the pH range 8–13 (solutions 7–12). The results are given in Fig. 2.

As can be seen from Fig. 2, a distinct increase in the iron content is found at elevated temperatures at any pH between 8 and 13. At higher temperature increased iron concentrations of up to $4.29 \times 10^{-3}$ mol kg$^{-1}$, 240 mg Fe(III) per kg of fibre are determined at pH 8. At pH 13, the iron content increases from $2.57 \times 10^{-3}$ mol kg$^{-1}$ at 25 °C to $23.8 \times 10^{-3}$ mol kg$^{-1}$ (1331 mg kg$^{-1}$) at 80 °C which corresponds to an increase in iron uptake of a factor of approx. 10 compared to results found at a temperature of 25 °C (Fig. 2).

In general, the higher uptake with increased temperature can be attributed to several effects.

- Increased rate of diffusion of dissolved molecules and higher accessibility of the porous fibres.

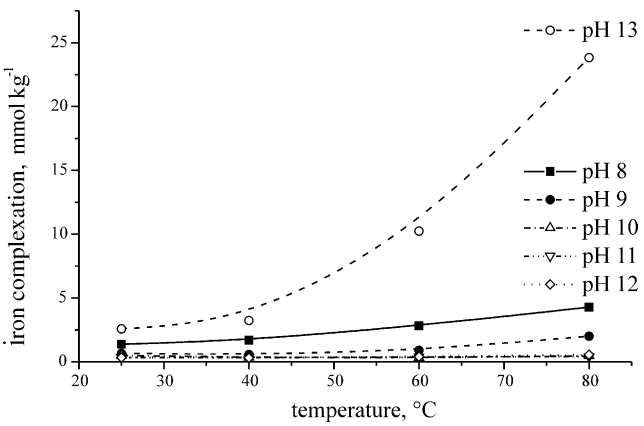


Fig. 2. Iron uptake by cotton Co1 from Fe(III):DGL 1:2 at pH 8–13 at 25, 40, 60 and 80 °C (solutions 7–12).

- *Lowered complex stability of the Fe(III)–DGL system present in solution*. As the increase of iron-uptake is found over the complete range of pH investigated in the study, the main factor to explain the experimental results is the changed stability of the dissolved complex at elevated temperature.
- At pH 13 and elevated temperature, (oxidative) side reactions of the cellulose polymer chain also have to be taken into account. An influence of oxidative side reactions in alkaline solutions could be quoted in the series performed at pH 13 but the increase of the iron content in the fibres found at pH 8–10 does not support such argumentation. Generally in the investigated range of conditions, the effect of oxidation reaction will be of minor relevance, which will be supported by results given below.

### 3.3. Influence of ligand

The complexation of iron by cellulose binding sites is in competition with the complexation by the ligand present in solution. As a result, the stability of the dissolved complex determines the observed iron uptake into the fibre.

To study this effect in more detail, the iron uptake in the presence of three different ligands DGL, HDGL and ATMP was studied. Two different types of cellulose fibres were used in this series: cotton Co1 and viscose CV1. The experiments were performed at 60 °C and at Fe(III):ligand ratio 1:2. (solutions 7–12, 13–18, 19–23). The results of the experiments are shown in Fig. 3.

The influence of complex stability of the ligand in solution can be seen by comparison of the results obtained with the different ligands DGL, HDGL and ATMP. The higher the stability of the complexes formed in solution at given pH the lower the iron content determined in the fibre.

Due to the higher complex stability of Fe(III)–HDGL at pH 8, $1.69 \times 10^{-3}$ mol kg$^{-1}$, 94.3 mg kg$^{-1}$ Fe(III) and at pH 13, $1.68 \times 10^{-3}$ mol kg$^{-1}$, 93.7 mg kg$^{-1}$ Fe(III) are determined. In the presence of Fe(III)–DGL, $2.82 \times 10^{-3}$ mol kg$^{-1}$, 158 mg kg$^{-1}$ and $9.27 \times 10^{-3}$ mol kg$^{-1}$, 518 mg kg$^{-1}$ Fe(III), respectively, were analysed in cotton Co1.

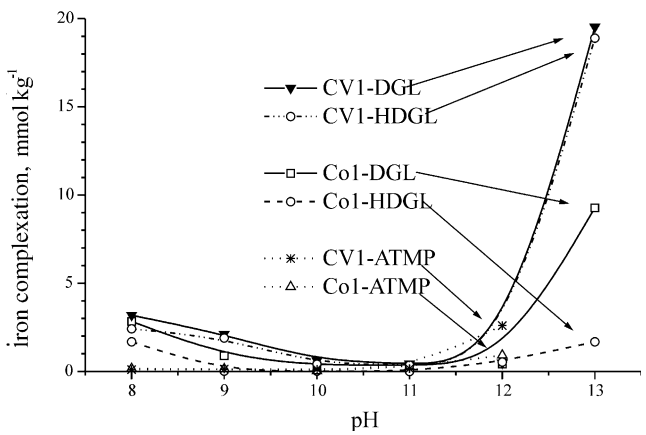


Fig. 3. Iron complexation in cellulose fibres cotton Co1 and viscose CV1 in the presence of different ligands DGL, HDGL, ATMP Fe(III):ligand ratio 1:2 at 60 °C in the pH range of 8–13 (solutions 7–12, 13–18, 19–23).

The high stability of ATMP complexes up to pH 12 is demonstrated by very low values up to pH 11. The behaviour of ATMP is comparable for both cotton Co1 and viscose CV1 and is typical for a powerful complex ligand, which establishes the equilibrium according to Eq. (2) with main weight on the left side. Thus, very low Fe(III) concentrations (below $0.18 \times 10^{-3}$ mol kg$^{-1}$, 10 mg kg$^{-1}$) are analysed in the fibres up to pH 12, where an increase to $2.60 \times 10^{-3}$ mol kg$^{-1}$, 145 mg kg$^{-1}$ is observed.

Blank samples analysed after a treatment of cotton Co1 in iron-free solutions 8–12 showed values of 0.21–$0.48 \times 10^{-3}$ mol kg$^{-1}$ and 12–27 mg kg$^{-1}$ Fe(III), respectively. At pH 12, the stability of the ATMP complexes in solution reaches its limit and precipitation of $Fe(OH)_3$ occurs at pH 13. Thus, the Fe(III)-values at pH 12 tend to increase, however, precipitation of $Fe(OH)_3$ hinders a detailed analysis of the iron content at this pH because of the difficulty to distinguish between complexed Fe(III)-complex and deposited $Fe(OH)_3$.

As can be seen from the curves in Fig. 3, both the capacity for the iron complexation in viscose CV1 and the stability of the iron complexes in the fibre are higher for viscose CV1 in comparison to cotton Co1. The results indicate different number of binding sites in the fibre and higher stability of the complexes in the fibre.

In case of viscose CV1, differences in the values between DGL and HDGL are low which indicates a strong complexation of the Fe(III) by viscose fibres. At pH 13, more than $17.9 \times 10^{-3}$ mol kg$^{-1}$, 1000 mg kg$^{-1}$ Fe(III) are determined while at pH 8, values remain similar for cotton Co1 and for CV1.

The low Fe(III)-complexation in the fibres found at pH 13 for HDGL as ligand (solution 18) supports the above assumption that oxidative side reactions are of minor importance for an explanation of the high Fe-complexation found in the presence of DGL.

### 3.4. Influence of fibre type

The results presented in Section 3.3 indicated that the Fe(III)–DGL 1:2 system could be used to quantify structural differences in fibres by determination of the iron binding capacity at pH 8 and 13. Thus, the uptake of Fe(III)-ions in different cellulose fibres was investigated for a set of cellulose fibres, e.g. cotton, viscose, modal, lyocell fibres. For these investigations, yarn samples with very similar physical fibre and yarn properties were selected (Table 1).

As carboxylic groups are known to be of importance for the formation of iron(III)–carbohydrate complexes, the carboxylic group content was determined according to Tappi-methods (T 237 om-88, 1989). The values for

Table 3
Fibre characterisation by iron-complexation at pH 8 and 13 at 60 °C (solutions 7 and 12) and carboxylic group number of untreated material and after impregnation at pH 13

| Sign | Iron uptake (mmol kg$^{-1}$) | | Carboxylic number untreated (mmol kg$^{-1}$) | Carboxylic number impregnation (mmol kg$^{-1}$) |
|---|---|---|---|---|
| | pH 8 | pH 13 | | |
| Co2 | 3.69 | 8.93 | 28.8 | 25.6 |
| CV2 | 1.36 | 20.59 | 37.6 | 40.2 |
| CMD | 1.11 | 17.28 | 19.3 | 21.8 |
| μCMD | 1.15 | 19.34 | 19.6 | 27.6 |
| CLY1 | 0.70 | 14.25 | 20.8 | 87.7 |
| CLY2 | 1.18 | 18.10 | 77.2 | 52.7 |
| CLY3 | 1.08 | 18.67 | 18.6 | 29.9 |

the different fibres are given in Table 3. To check changes in carboxylic number during the impregnation step, the carboxylic number of a set of samples was determined before and after a treatment for 24 h at 60 °C in solution 12. Remarkable changes in the carboxylic number only were found in the case of lyocell-fibres (Table 3). CLY1 and CLY2 are crosslinked types and CLY3 is a normal lyocell fibre so the observed change in carboxylic number for CLY 1 and CLY2 can be attributed to hydrolysis effects of the crosslinker present in the fibre.

According to the results presented above, experiments at pH values 8 and 13 were used to characterise the different cellulose fibres. The results obtained are shown in Fig. 4.

While at pH 8 and 60 °C, considerable complexation of Fe(III) ($2.33–3.68 \times 10^{-3}$ mol kg$^{-1}$, 130–206 mg kg$^{-1}$) is observed for cotton fibres Co1 and Co2, lower amounts of iron ($0.72–1.36 \times 10^{-3}$ mol kg$^{-1}$, 40–76 mg kg$^{-1}$) are bound in the different regenerated cellulose fibres CV2, CMD, μCMD, CLY.

A reverse situation is found at pH 13, where the values for cotton Co1 and Co2 reach $7.16–11.82 \times 10^{-3}$ mol kg$^{-1}$, 400–660 mg kg$^{-1}$, while regenerated cellulose fibres bind $14.32–20.59 \times 10^{-3}$ mol kg$^{-1}$, 800–1150 mg kg$^{-1}$ Fe(III)-ions.

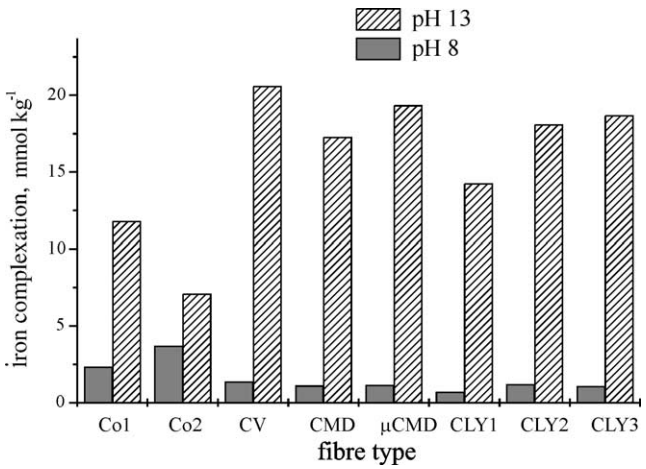


Fig. 4. Complexation of Fe(III)-ions by different types of cellulose fibres. System: Fe(III):DGL 1:2, pH 8 and 13, 60 °C (solutions 7 and 12).

This indicates a distinct change in accessibility, number of binding sites and complex stabilities between cotton and regenerated cellulose fibres by a change in pH from 8 to 13.

When the binding capacity for Fe(III)-ions determined at pH 8 and 13 is compared to the carboxylic group content of the fibre, the carboxylic group number seems to form an upper limit for the iron(III)-binding capacity. At pH 8, the iron complexation stabilises at a level which is much lower than the carboxylic group content, while at pH 13, the capacity for iron(III)-complexation stabilises near the value of the carboxylic group content of the fibre. Only for crosslinked lyocell type fibres, the carboxylic group content exceeds the iron-complexation capacity considerably, which can be attributed to the influence of the crosslinker.

## 4. Conclusions

In the presence of suited soluble Fe(III)-complexes like Fe(III)–DGL and Fe(III)–HDGL, a ligand exchange of the iron(III)-center ion between dissolved ligand and insoluble cellulose is observed and cellulose fibres behave as solid ligands.

In the investigated range of experimental conditions a maximum binding capacity was found at pH 8 and 13. Depending on the type of cellulose fibre at pH 8, a binding capacity of 40–200 mg Fe(III) per kg of fibre, corresponding $0.7 \times 10^{-3}–3.6 \times 10^{-3}$ mol kg$^{-1}$ Fe(III) was analysed. At pH 13, much higher uptake of Fe(III)-ions is observed and up to 1150 mg Fe(III) per kg cellulose ($21 \times 10^{-3}$ mol kg$^{-1}$) were determined. The carboxylic group number of the fibres forms an upper limit for the Fe(III)-complexation at pH 13. The small changes of the carboxylic group numbers during a treatment at higher temperature prove the minor importance of oxidative side reactions in the cellulose polymer. The increase of the Fe(III)-concentration analysed in the fibre following to treatments at 60 or 80 °C thus rather can be attributed to lowered stability of the dissolved Fe(III)-complexes, which favours the formation of Fe(III)–cellulose complexes.

In the presence of ligands which form complexes with higher formation constant, e.g. ATMP, very low Fe(III)–cellulose complex concentrations are found in the fibres.

The given method can be applied as an analytical technique to quantify binding sites suited to form iron(III)-complexes in the fibre and to characterise accessibility of the fibre in swollen state. The complexation of Fe(III)-ions is very sensitive to changes in the cellulose structure. Thus, the method can be used to describe differences between various cellulose fibres, e.g. Co, CV, CMD, CLY fibres.

The results given permit a more detailed understanding of the interaction of Fe(III)-ions, complexing agents and

cellulose fibres during alkaline processing and indicate the importance of a proper selection of suited auxiliaries. At high pH, a competition for Fe(III)-ions between dissolved soluble ligands and fibre cellulose leads to ligand-exchange reaction and formation of Fe(III)–cellulose complexes. In such cases, the complexing agent expected to remove and mask iron(III)-ions by complexation and dissolution can be identified as source which actually introduces Fe(III)-ions into the cellulose fibres.

Complexing agents, which are able to form comparable stable Fe(III)-complexes, will stabilise Fe(III)-ions in solution and ligand-exchange reactions will not occur to a remarkable extent. Complexing agents which form Fe(III)-complexes with comparable low formation constant will cause precipitation of $Fe(OH)_3$ in alkaline baths. As a result $Fe(OH)_3$ will be deposited on the fibres.

The found tendency of cellulose fibres to complex Fe(III)-ions by ligand-exchange reactions can be seen as a possible source for catalytic damage during the following up peroxide bleach.

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## References

Anon, (2002). World production: 59 million tons textile fibres. *Man-made fibre year book*. Frankfurt a.M., Germany: International Business Press, p. 21.

Bechtold, T., Burtscher, E., & Turcanu, A. (2002). $Ca^{2+}$–$Fe^{3+}$-D-gluconate-complexes in alkaline solution. Complex stabilities and electrochemical properties. *Journal of Chemical Society, Dalton Transactions*, 2683–2688.

Bredereck, K., Gruber, M., Otterbach, A., & Schulz, F. (1996). Die Hydrogelstruktur von Cellulosefasern und ihre Bedeutung für Fasereigenschaften und Textilveredlung. *Textilveredlung*, *31*, 194–200.

Chen, D., Martell, A. E., Motekaitis, G. J., Miu, S., & McManus, D. (1999). Potentiometric determination of the equilibrium constants for formation of Fe(III)–sorbitol complexes. *Inorganica Chimica Acta*, *293*, 206–209.

DIN 38 406 (1983). *T1, Bestimmung von Eisen, photometrische Verfahren*. Weinheim, Mai: Wiley-VCH, pp. 1–9.

Engbers, B. J. J., & Dierkes, G. (1992). *Sequestriermittel und Ionenaustauscher für die Textilveredlung, textilpraxis intern*, *47*, 365–368. see also pp. 557–560.

Escandar, G. M., Gandolfo, F. H., & Sala, L. F. (1990). Complex formation between aldonic and uronic acids and ferric ion in aqueous solution. *Anales de la Asociacion Quimica Argentina*, *78*(1), 37–48.

Escandar, G. M., Olivieri, A. C., Gonzales-Sierra, M., & Sala, L. F. (1994). Iron(III) complexes of lactobionic acid: Equilibrium and structural studies in aqueous solution. *Journal of Chemical Society, Dalton Transactions*, 1189–1192.

Gonzalez-Velasco, J. (1980). Electromigration behaviour of complexes between Fe(III) and Cu(II) ions and gluconic acid. *Anales de Quimica*, *76*, 17–21.

Gruber, M (1998). *Untersuchungen zur supramolekularen Struktur und Farbstoffadsorption von Cellulosefasern*. Doctoral thesis. Institut für Textil- und Faserchemie, University of Stuttgart.

Lahodny-Sarc, O (1995). Critical review and new results on gluconates, environmentally acceptable inhibitors. *Annali dell' Universitá di Ferrara, Sez. 5 Suppl (1995)*, *10* (*Eighth European Symposium on Corrosion Inhibitors*), 1, 421–433.

Martell, A. E., & Motekaitis, R. J. (1992). *Determination and use of stability constants* (2nd ed.). New York: VCH Publishers, Inc..

Mehltretter, C. L., Alexander, B. H., & Rist, C. E. (1953). Sequestration by sugar acids. *Industrial Engineering Chemistry*, *45*, 2782–2784.

Nagy, L., Burger, K., Kürti, J., Mostafa, M. A., Korecz, L., & Kiricsi, I. (1986). Iron(III) complexes of sugar-type ligands. *Inorganica Chimica Acta*, *124*, 55–59.

Pecsock, R. L., & Sandera, J. (1955). The gluconate complexes. II. The ferric-gluconate system. *Journal of American Chemical Society*, *77*, 1489–1494.

Sharkov, V. V., & Akim, L. E. (1968). Comparative study of the accessible internal surface of cellulose fibres by sorption of alkali, copper, and iron. *Trudy Leningradskogo Tekhnoligicheskogo Instituta Tsellyulozno-Bumazhnoi Promyshlennosti*, *21*, 220–237.

Shepherd, R. E., Isaacson, T., Chensny, L., Zhang, S., Kortes, R., & John, K. (1993). Lactobionic and gluconic acid complexes of $Fe^{II}$ and $Fe^{III}$; control of oxidation pathways by an organ transplantation preservant. *Journal of Inorganic Biochemsitry*, *49*, 23–48.

T 237 om-88 (1989). Carboxyl content of pulp, 1988. *Tappi test methods*. Atlanta, GA, USA: Technology Park.

Whitfield, D. M., Stoikovski, S., & Sarkar, B. (1993). Metal coordination to carbohydrates. Structures and function. *Coordination Chemistry Review*, *122*, 171–225.