DIP quality influenced by process water quality

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ABSTRACT: The need for deinking mills to reduce their fresh water consumption has resulted in higher loads of various contaminants in the process water. Lower recovered paper quality also leads to higher contamination levels in the mills. This higher load has an influence on achievable target brightness. The objective of the work was to determine and explain the main reasons for relatively poor deinked pulp quality or poor deinking potential based on the influence of recovered paper composition and process water quality. The process water parameters significantly affect the deinking potential of recovered paper. The test results showed the negative effects of increased water hardness. For standard recovered paper mixtures, flotation selectivity is higher with increasing flotation pH-value. Good results were realized for standard recovered paper with low hardness, low surface tension, and high pH-value. The results for recovered paper containing flexo newsprint could be slightly improved with low hardness, low surface tension, and low pH-value. The results of the test program using design of experiments showed interacting effects of pH-value and surface tension on luminosity and flotation selectivity.

Application: Process water properties of deinking plants vary and significantly affect the deinking potential of recovered paper. There is potential to improve the deinking process, but further investigations are necessary.

For environmental and economic reasons, deinking mills are forced to reduce their fresh water consumption and recirculate process water. This leads to higher loads of various contaminants in the process water. A decrease in recovered paper quality has also led to higher contamination levels in the mills. In the daily operation of the deinking plant, this higher load has an influence on achieving the targeted brightness.

Possible reasons for this effect could be related to the process water quality, which is altered. If colored or colloidal particles are enriched in the water loops, the process water clarification (e.g., by dissolved air flotation) is less efficient. Smaller ink particles resulting from water-based printing inks might affect the process water quality even more than offset inks.

Some studies have dealt with the deinkability of water based print products such as ink jet or flexo [1-7]. Unsatisfying deinking results usually were shown in trials with 100% water-based print products. Because water-borne print products typically are only in smaller portions in the recovered paper furnish, other investigations deal with recovered paper mixtures containing a certain share of water-based print products [8-16]. Further research work is related to improvements of the deinking results of water-borne print products or recovered paper mixtures containing water-based inks by applying other chemistry or process conditions [17-31]. In those investigations, the effect of water-based inks in the recovered paper furnish are observed on deinked pulp (DIP) quality and sometimes also on process water quality. All these laboratory or pilot plant experiences have one commonality: the results are obtained by using fresh water for pulping and dilution, at least in the beginning of the trials. Of course, paper mills use process water and have sometimes experience with water-based print products in their furnish, but usually the effects on deinked pulp quality cannot be traced back to a specific proportion of these prints.

Therefore, the aim of the research project was to study by systematic trials the effect of process water quality on DIP quality of recovered paper furnish containing water-based print products. For this, an investigation was performed in which process water from different paper mills with deinking facilities were used for laboratory trials. The quality of the various process waters was determined and its influence on the optical parameters of the deinking process and the final DIP were observed. By identifying those process water parameters influencing primarily the deinking process, possible solutions for a proper treatment of the process water can be developed to improve the results of the deinking process.

MATERIALS AND METHODS

First, the effect of recovered paper quality on the process water quality was investigated. The effect of different contents of water-based printing inks (flexo and ink jet) on DIP quality of a standard recovered paper mixture was of particular interest.

To cover this influence, a standard paper mixture of 50% offset news, 30% coated offset magazine, and 20% coated rotogravure magazines was used. During the trials, the offset newspapers were substituted by various percentages of flexo and the offset magazines were substituted by various percentages of ink jet prints (**Table I**). As flexo newspaper, a commercial colored newspaper (NP) on standard newsprint was

Sample	Standard	Flexo-NP 10	Flexo-NP 20	Flexo-NP 30	Inkjet-TB 10	Inkjet-TB 20	Inkjet-TB 30	Inkjet-TB 10 Flexo-NP 10	Flexo-NP 15 Inkjet-TB 15
Offset-NP	50	40	30	20	50	50	50	40	35
Offset-LWC	30	30	30	30	20	10	0	20	15
Rotogravure-LWC	10	10	10	10	10	10	10	10	10
Rotogravure-LWC	10	10	10	10	10	10	10	10	10
Flexo-NP	0	10	20	30	0	0	0	10	15
Inkjet-TB	0	0	0	0	10	20	30	10	15

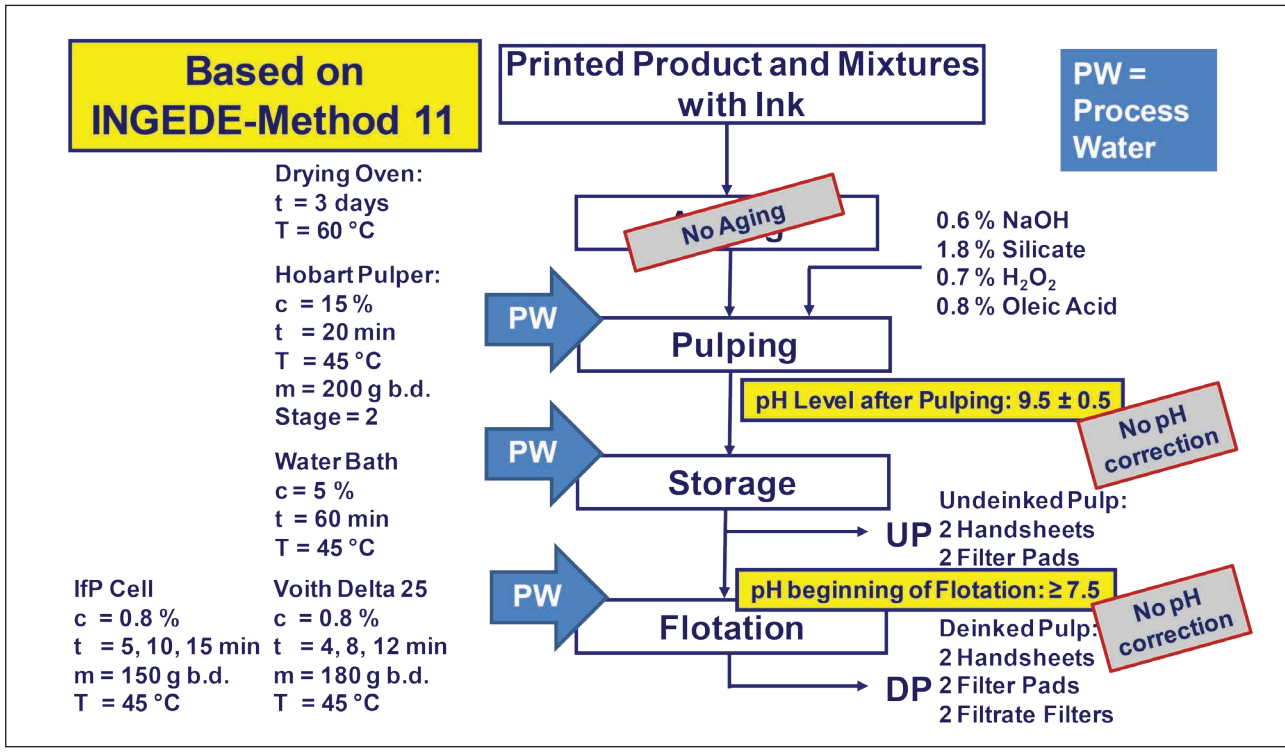
I. Sample composition in percent.

used. For the inkjet paper, a colored inkjet textbook (TB) printed both sides on woodfree paper was chosen.

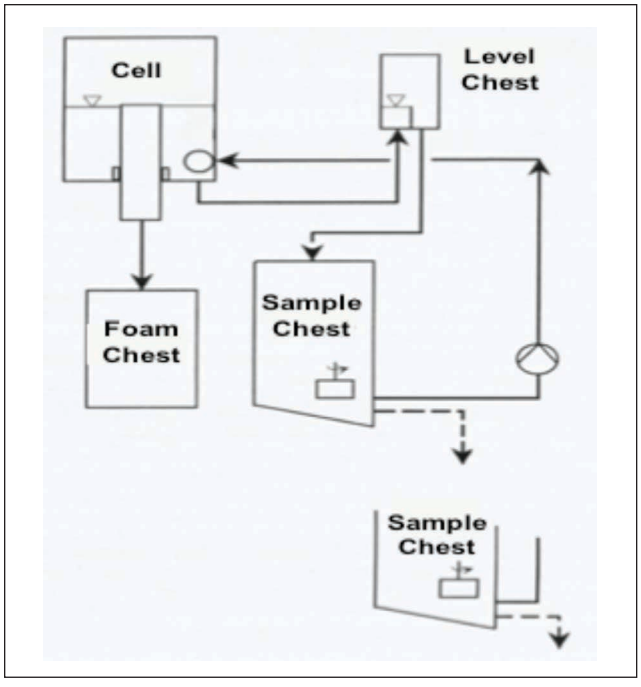
For the second part of the study, the influence of process water quality on the deinking process was investigated. For this, several deinkability tests with different process water qualities were performed. As a reference, tap water was used. For the other trials, process water was used as a substitute for tap water. The dilution water from loop I of several deinking mills was collected, analyzed, and used for deinkability tests (**Fig. 1**).

Process water was used for the disintegration step and for all further dilution steps during the laboratory trial. The procedure is based on the INGEDE Method 11 "Assessment of print product recyclability—deinkability test," but no aging and no pH-value correction were performed to cover all possible aspects caused only by the different process water samples.

As flotation devices, an IfP flotation cell [32] was used for a continuous trial at the Paper Technology and Mechanical Process Engineering (PMV) laboratory at the Technische Universität Darmstadt (Darmstadt, Germany) and a Voith Delta25 laboratory floatation cell (Voith; Heidenheim an der Brenz, Germany) was used for the trials performed by Papiertechnische Stiftung (PTS) Munich. **Figure 2** shows the IfP cell set up. All trials had certain time set points to monitor the DIP quality over flotation time. For the IfP



1. Laboratory procedure.



2. IfP flotation cell.

flotation cell, it is possible to get several samples at different flotation times from one trial, whereas for the Voith Delta25 cell, several different trials with various flotation times had to be performed. For all trials, a standard flotation recipe with deinking chemicals according to Fig. 1 was used (based on bone dry solids), as described in INGEDE Method 11.

To cover all influences, the process water quality was characterized by several parameters. After the trials, the DIP quality parameters were measured and compared in relation to the process water parameters. As a benchmark, average values were used, which were theoretically calculated by using the INGEDE database for a mixture of 50% offset newsprint, 30% offset-lightweight coated (LWC), and 20% rotogravure-LWC.

The following water samples were used for the tests:

- Darmstadt and Munich tap water, respectively
- Newsprint mill A
- Newsprint mill B/DIP 2 plant
- Newsprint mill B/DIP 1 plant
- Newsprint mill C
- Newsprint mill D
- Tissue mill before (cloudy) and after dissolved air flotation

The water samples were characterized regarding:

- pH-value
- Water hardness
- Solid content
- Residual ink
- Surface tension
- Annealing residue (DIN 38409-2:1987-03 "German standard methods for the examination of water, waste water and sludge; parameters characterizing effects and substances (group H); determination of filterable matter and the residue on ignition [H 2]")
- Cationic demand
- Foaming behavior

For the optical properties of the water samples, 15 mL of each sample were filtered over a membrane filter with 0.45 µm pore size. Afterwards, optical parameters were measured on the surface of the membrane filter using INGEDE Method 2 "Measurement of optical characteristics of pulps and filtrates from deinking processes." The foaming behavior was measured according to our own laboratory method, in which the sample is aerated for a certain time using a jet pump and afterwards the ratio between foam and liquid phase is described as foaming factor [33].

In a third step, a closer look on selected process water parameters was performed to screen relevant parameters and to cover possible solutions for improving the process water quality by changing the following parameters in a standard mixture, as well as in a mixture with 30% flexo newsprint (flexo-NP 30):

- Solid content (for a tissue mill by using filtrate before and after dissolved air flotation; for newsprint mill C solid content was reduced by a filtration process)
- Surface tension (by adding non-ionic surfactant)
- Water hardness (by adding calcium chloride)
- pH-value (by increasing sodium hydroxide during pulping)
- Special water flotation as a cleaning measure

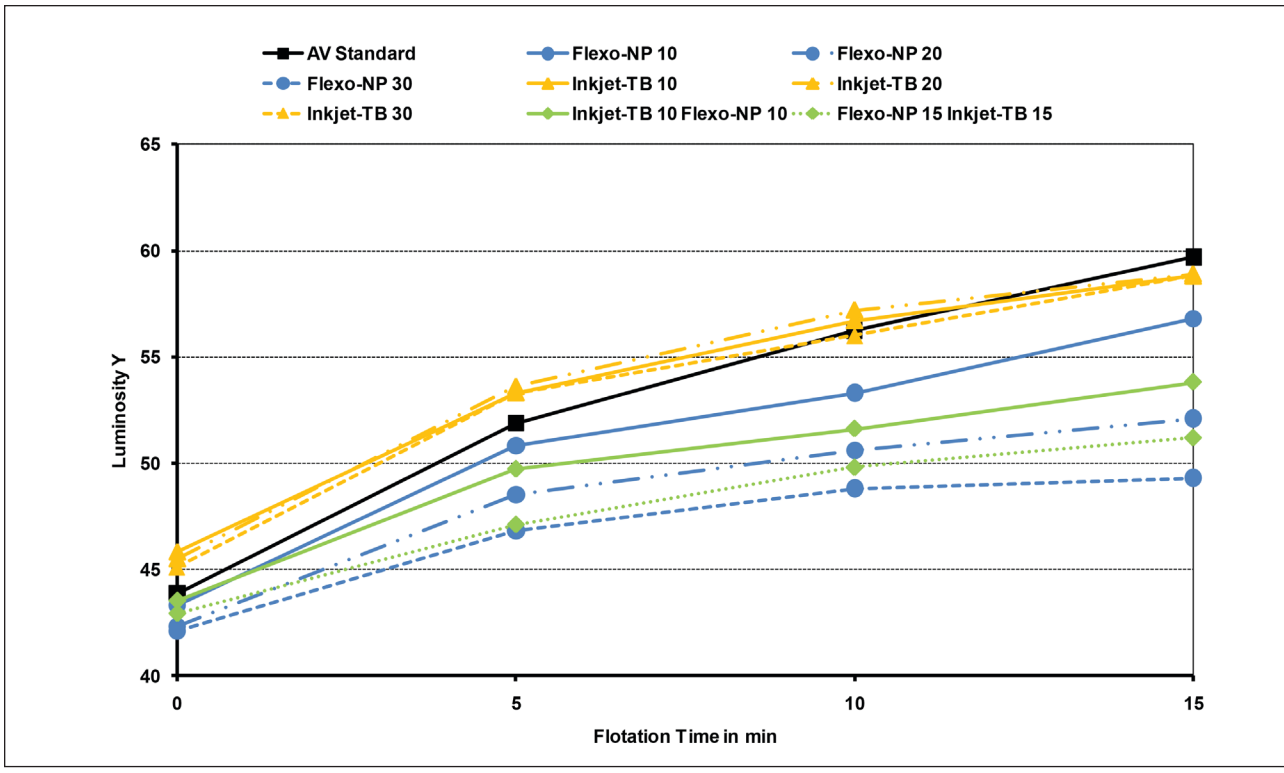
For this final treatment, process water was floated in a Voith Delta25 cell for softening and a reduction of surface tension. During the trial, 0.1% (by volume) sodium carbonate was added and the pH-value was adjusted to 8.5. The flotation was performed for 7 min with an aeration of 6-7 L/min resulting in a water loss of 30% [34].

RESULTS AND INTERPRETATION

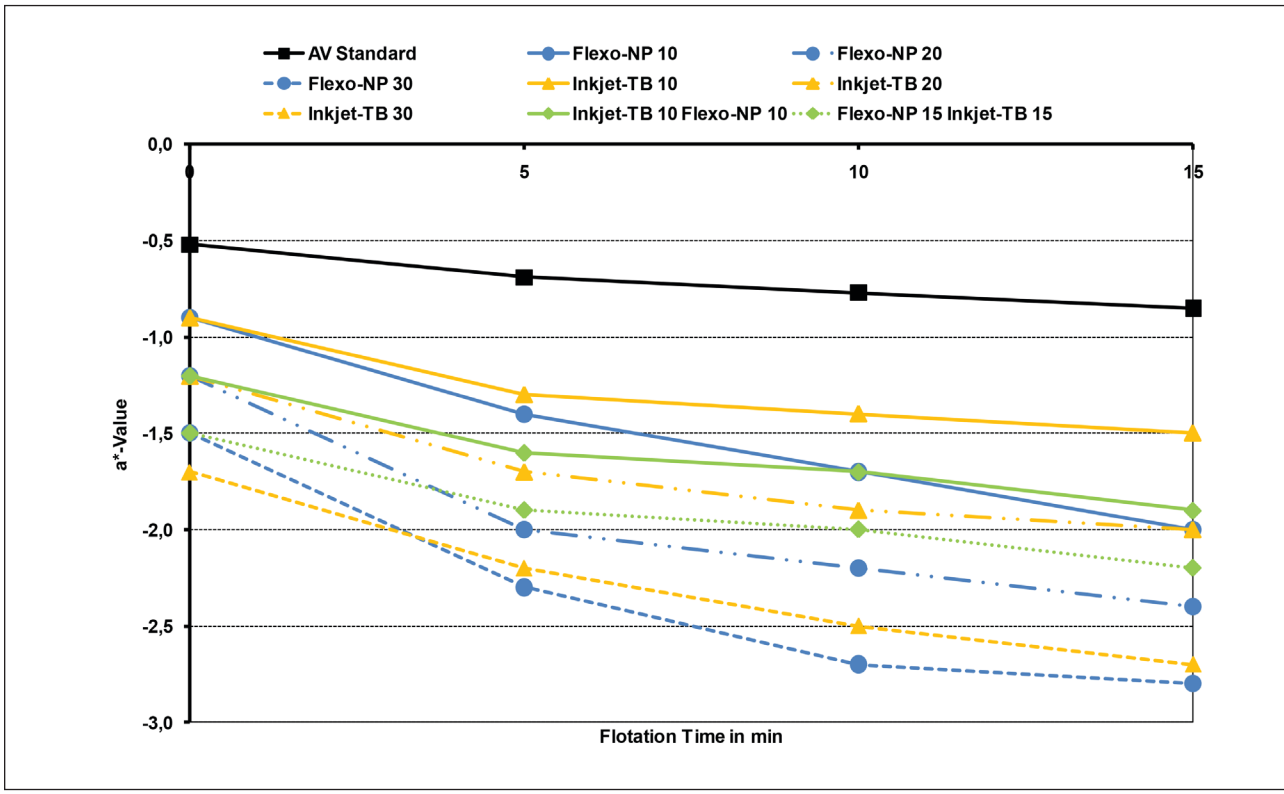
In this section, the influences of various proportions of water-based printing inks on the deinking results are considered for a better understanding of the process. After that, the results of the water sample analysis are discussed to prepare the examination of the influence of those water samples on the deinking results.

Influences of proportion of water-based print products on deinking results

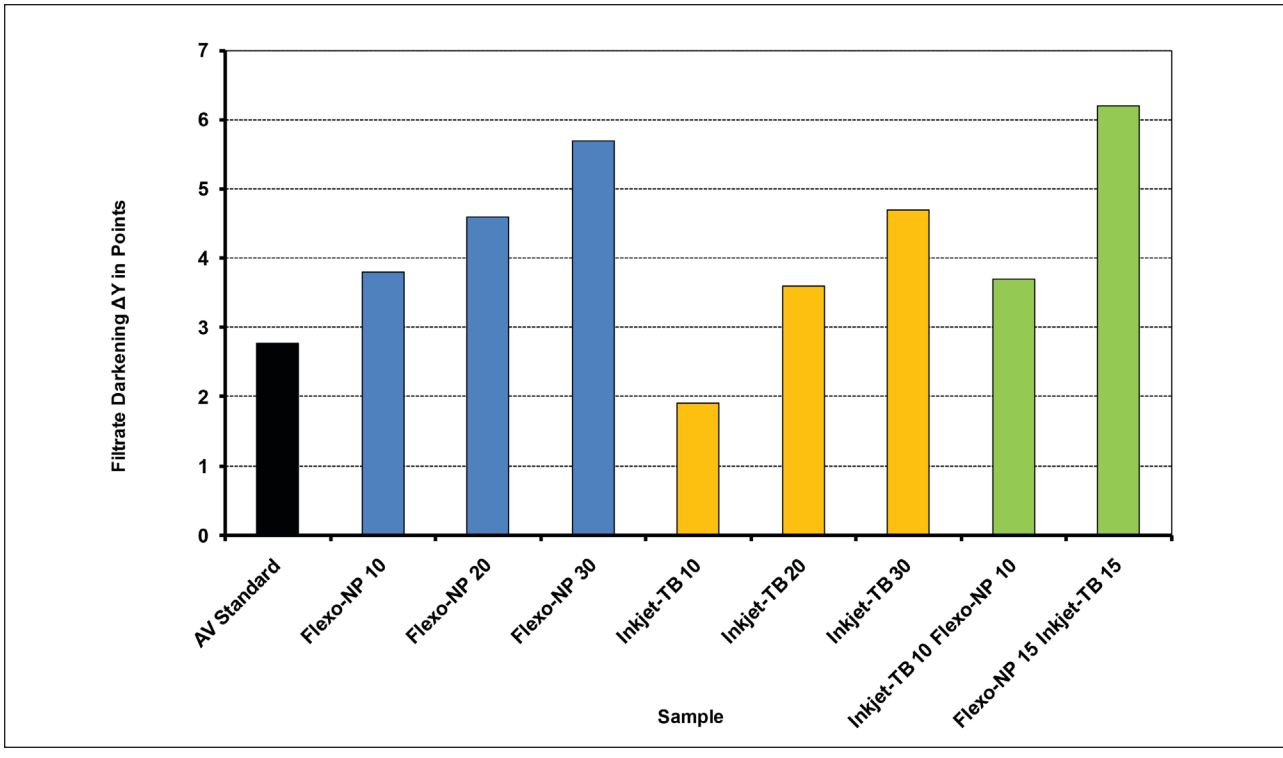
Figure 3 presents the deinking results in terms of luminosity over flotation time for the analyzed recovered paper mixtures using Darmstadt tap water with 18°dH (German hardness: 1°dH = 0.1786 mmol/L calcium [Ca^{2+}]) as a standard for pulping and all following dilution steps. **Figures 4** and **5** show the results of the same mixtures for the parameters



3. Luminosity Y depending on flotation time and recovered paper mixture (tap water).



4. Color value a depending on flotation time and recovered paper mixture (tap water).*

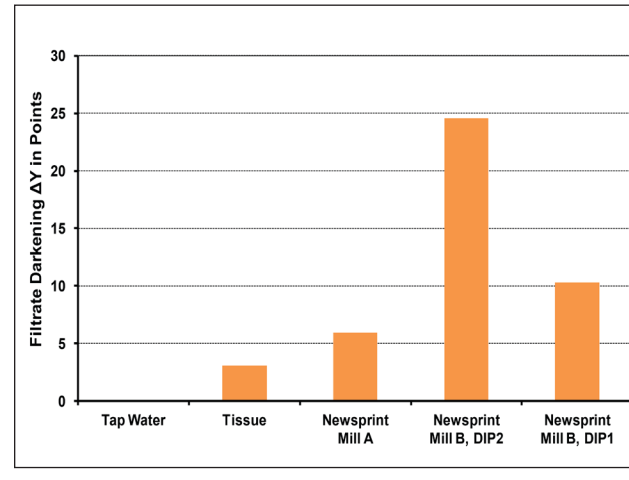


5. Filtrate darkening ΔY after 15 min flotation for various recovered paper mixtures (tap water).

color value a* and filtrate darkening ΔY. It becomes evident that after 15 min flotation time, the standard furnish without any flexo and ink jet proportion has the highest luminosity (Fig. 3) and the lowest discoloration in terms of the color value a* (Fig. 4) of the DIP. The filtrate darkening gives an indication of how much the filtrate of the DIP is affected by very small or soluble ink particles. The higher the ΔY figure, the larger the effect of the ink in the filtrate. Summarizing all results, it becomes obvious that the inkjet textbook had less effect than the flexo newspaper. This is related to the print products used during this investigation, because the textbook had a much lower ink coverage [34].

Results of water samples analysis

Figure 6 shows the optical results of the process water samples analysis. It can be seen that the substances in the tap water create no filtrate darkening. In contrast, the process water from all paper mills contain substances leading to reduction of approximately 3-25 luminosity points of the used membrane filter. **Table II** shows selected results of the process water samples. It is apparent that any process water has a special characteristic, leading to a wide range of results when comparing one parameter of all process water samples. Therefore, the comparison of results in direct relationship to the deinking results is not an easy issue because the different deinking results might be caused by several water parameters. For this reason, a further investigation was set up to affect single water parameters and obtain a better understanding of their influence on the deinking results.



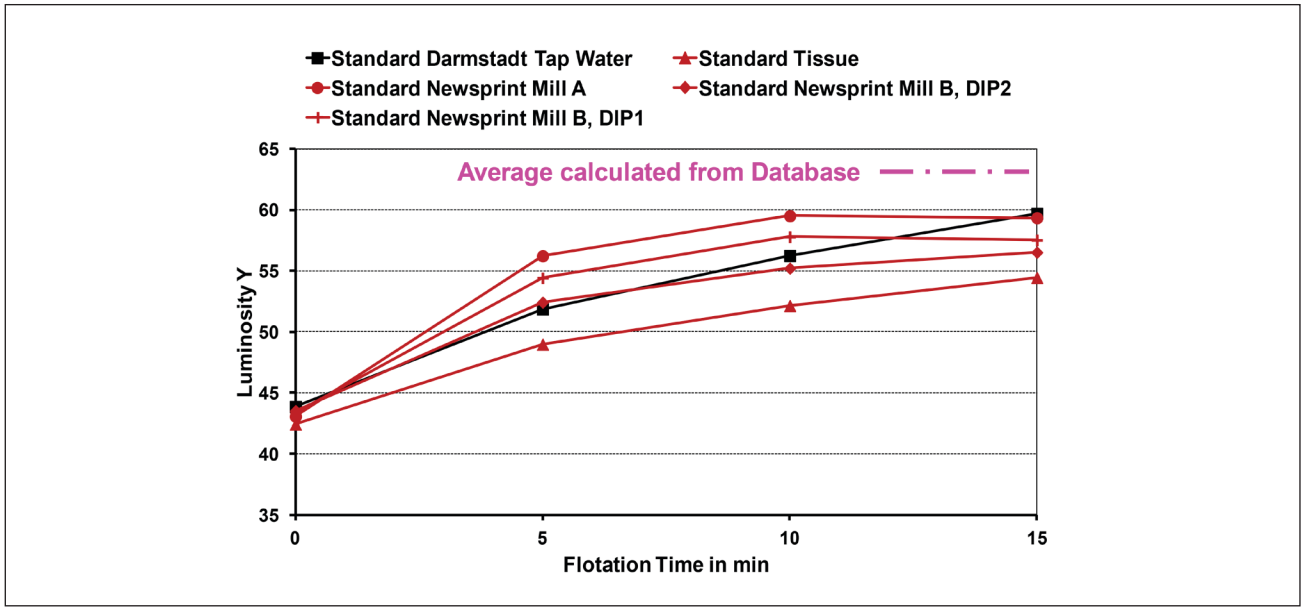
6. Optical results (filtrate darkening) of different process water samples.

Influence of different process water samples on deinking results

As visible in **Fig. 7**, the deinking results for the standard mixture vary with the different process water samples. The luminosity over flotation time is plotted for selected samples. The laboratory conditions are not directly transferable to industrial processes; therefore, yield and overall luminosity might be different for industrial processes. The interpretation is only

Name	pH	Hardness (centrifuged)	Solid Content 105 °C	Annealing Residue 550 °C	COD	Conductivity	Surface Tension
	-	°dH	g/l	g/l	mg/l	mS/cm	mN/m
Darmstadt Tap Water	7.2	19	0.00	0.36	0	0.68	n.a.
Newsprint Mill A	7.6	11	0.60	2.57	2840	2.92	50.5
Newsprint Mill B, DIP 2	6.5	33	0.30	3.03	4068	4.13	n.a.
Newsprint Mill B, DIP 1	7.2	21	0.04	1.92	1603	2.54	n.a.
Newsprint Mill C	7.3	12	0.04	n.a.	2210	2.54	49.7
Newsprint Mill D	8.0	12	0.14	n.a.	1080	2.42	44.4
Tissue	6.7	49	0.10	2.64	2800	3.54	50.9
Tissue after softeneing	8.1	17	0.20	3.31	2910	4.37	41.2
Tissue (cloudy filtrate)	6.9	54	2.40	4.31	3990	3.60	40.1

II. Results of water sample analysis.

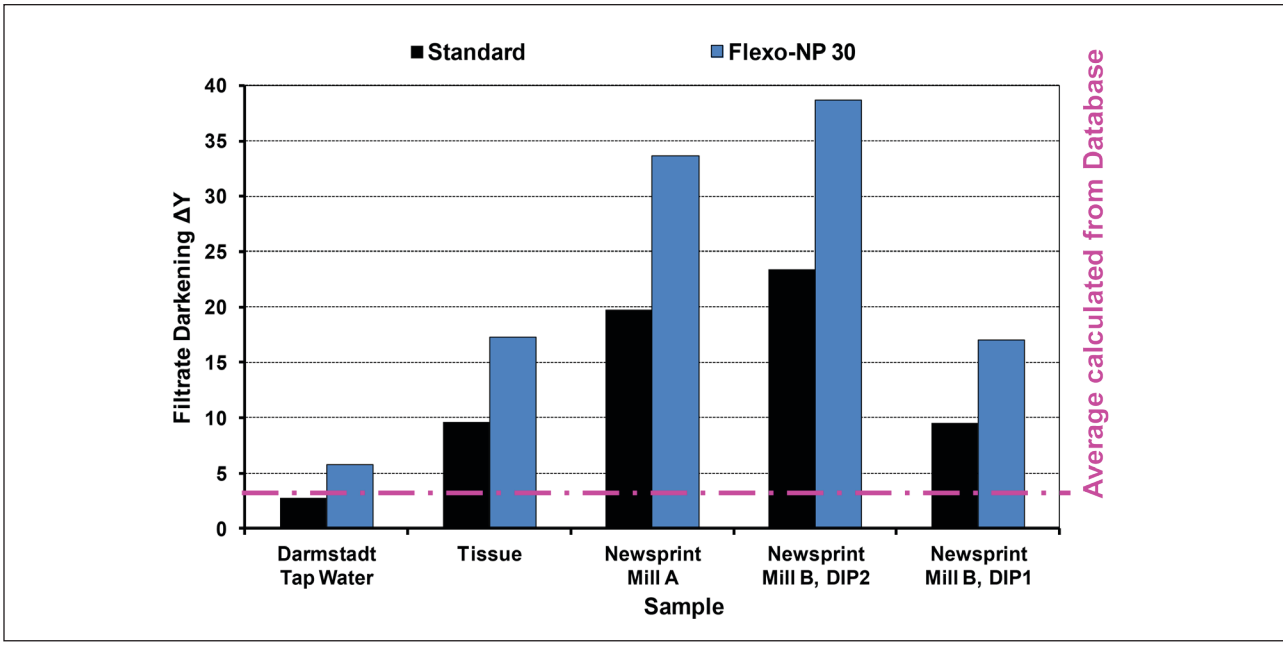


7. Luminosity Y of standard mixture during flotation with different process waters.

based on this specific setting. Even for the undeinked sample directly after the disintegration step, differences in the luminosity are visible, which have to be traced back to the used process waters. The highest luminosity after flotation was possible with the Darmstadt tap water sample and with the process water from newsprint mill A. The lowest results were obtained with the process water from the tissue mill. The indicated average (dotted and dashed purple line) is a theoretical value calculated on basis of the INGEDE database for the used print products in the furnish mixture. Any of these results do not reach the average of the database regarding luminosity, but the process conditions might be a bit different.

The overall observations during the trials with several different process water samples showed that a decrease of DIP luminosity after flotation can occur. The process water led to an increase in filtrate darkening ΔY (**Fig. 8**). This might be related to the general optical properties of process waters (Fig. 6). It also becomes clear that filtrate darkening of the recovered paper mixture with flexo newspapers is always higher than for the standard mixture as a result of the fine hydrophilic dispersed ink particles.

Although not shown in the figures, we also observed a lower ink elimination during the trials. The yield of all trials was in a range between 70% to 85%, which is typical for



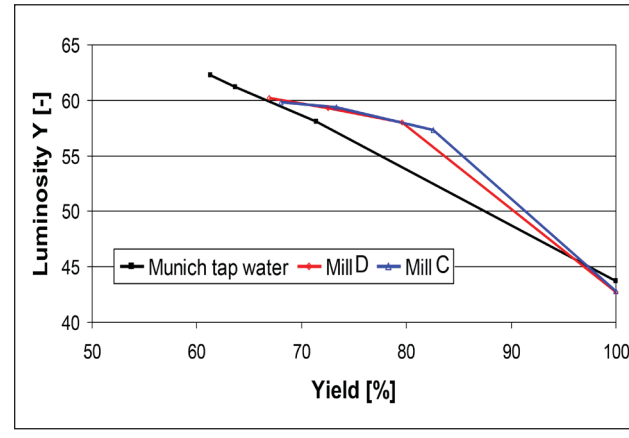
8. Filtrate darkening ΔY after flotation with different process waters of a standard mixture and one with flexo newspapers.

such laboratory flotation tests. The different process water samples have only a minor influence on the ash content of the DIP after the flotation process, but influences the yield of the process, leading to a yield reduction in the majority of cases.

In some trials, as seen in Fig. 7 and in **Fig. 9**, a higher increase in luminosity or ink elimination was possible, even with lower losses or lower flotation times. Considering the water parameters shown in **Table III** for the trials displayed in Fig. 9, this effect is related to a lower surface tension, and thus higher air content during flotation, leading to increased ink removal. In contrast, the final results for luminosity were higher with the respective tap water, probably because of the effects of higher solid content of the process water samples, which induces a higher flotation consistency and additional impurities introduced with the process water.

Because of the interaction of several process water parameters influencing the deinking potential, a closer look was necessary to identify the important ones. In a first trial, the water hardness of the newsprint mill A water sample was increased from 11°dH to 50°dH by adding calcium chloride, leading to a final luminosity of 54 instead of 57.

Figure 10 shows the results of differently treated tissue

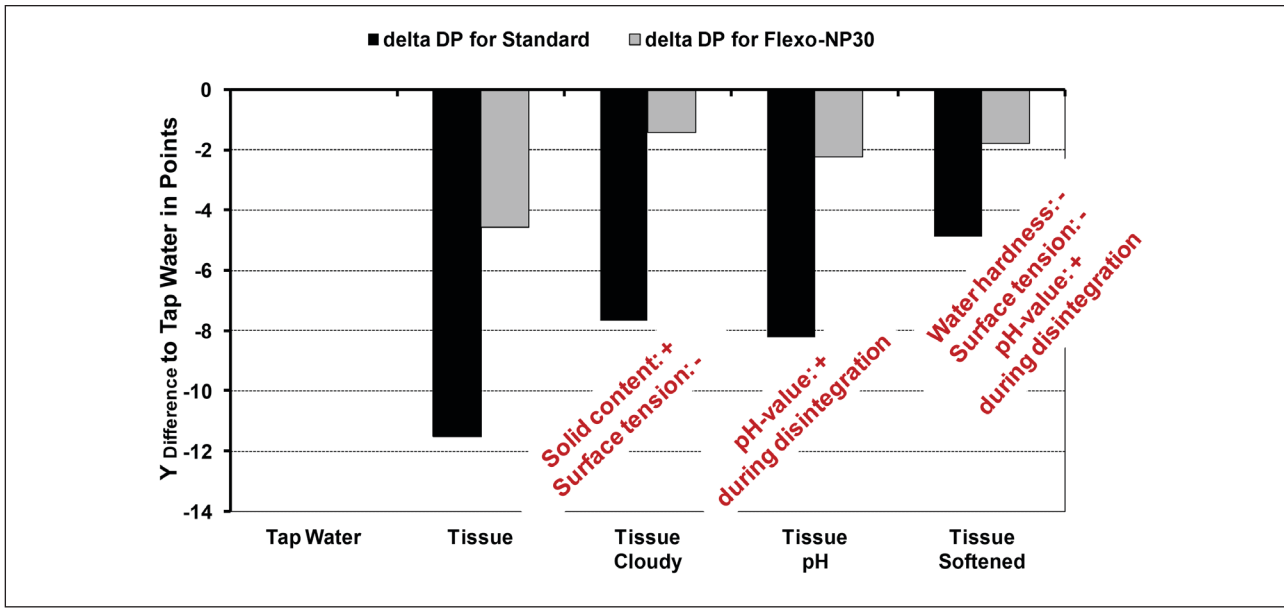


9. Luminosity Y over flotation yield for flotation trials with Munich tap water and different process waters.

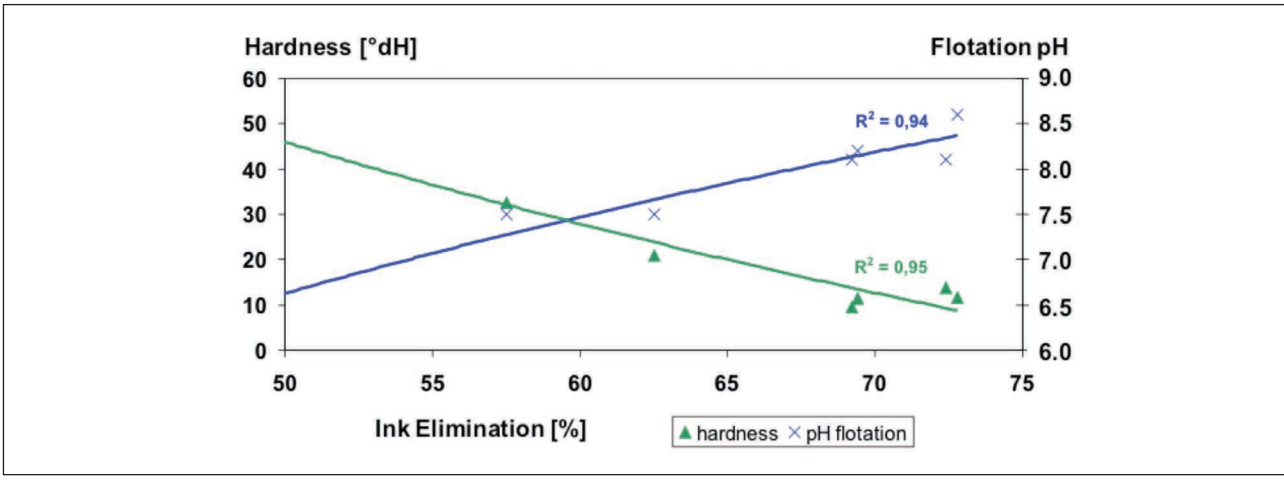
process water samples and the respective influence on the deinking behavior displayed as luminosity difference ($Y_{Difference}$), which is the calculated difference between $Y_{Process\ Water}$ and $Y_{Tap\ Water}$. Negative results in this case mean that a higher luminosity was possible for tap water than for process water. Although more than one parameter is changed

Name	Solids Content (%)	Surface Tension (mN/m)	Luminosity Y of Membrane Filter after Filtrating 15 mL of Sample (-)
Tap water	0.00	72.0	96.0
Newsprint mill C	0.04	49.7	77.3
Newsprint mill D	0.14	44.4	78.4

III. Sample characteristics for flotation trials with Munich tap water and different process waters.



10. Luminosity difference for deinking trials with standard and flexo newspaper mixtures and differently treated process water of a tissue mill.



11. Correlation between ink elimination and flotation pH-value as well as water hardness for a standard recovered paper mixture after analyzing the statistical design of experiments.

during the treatment of the process water, the trials demonstrate the relevance of suitable process water conditions for good deinking results. With improved treatment of the process water, from changing it from left to right in Fig. 10, it becomes obvious that the luminosity between tap and process water gets smaller.

To cover the influences of each parameter, a statistical design of experiments was set up for the standard mixture and the flexo-NP 30 mixture with process water of newsprint mill C. Following a statistical design scheme, several parameters were varied on a higher and lower level to cover their influence. For this, the pH value was varied between 7.5 and 8.5, the solid content between 0.04% (by filtration) and 0.09%, the water hardness between 13°dH and 30°dH, and the surface tension between 42 mN/m and 48 mN/m (measured at 25°C). Other measured water parameters were also used for the investigation, but were not varied. Following this setting, nine different deinking trials were performed. After analyzing the statistical effects, no correlation between the deinking results and solids content, chemical oxygen demand, and cationic demand of the process water were visible. A clear correlation between ink elimination, flotation pH-value, and water hardness could be observed for a standard recovered paper mixture (**Fig. 11**). Higher water hardness and a lower flotation pH-value leads to lower ink elimination [36].

The results of the statistical design of experiments were also used to examine the effect of several process parameters on the luminosity and selectivity of a deinking process with standard recovered paper mixture. Selectivity was defined

as the ratio between ink elimination and fiber loss. Therefore, for higher luminosity, the process water should show the following characteristics:

- Low solid content
- Low calcium concentration (water hardness)
- Low surface tension

The results show no influence of the flotation pH-value.

Considering the selectivity of such a process, a higher selectivity is possible with increasing flotation pH-value, and a decrease is visible for increasing water hardness. As there are interaction effects, the effect of calcium concentration and surface tension turns out to be higher at lower pH-values of the process water.

The picture is a bit different if considering the flexo-NP 30 mixture which requires the following modifications for higher luminosity:

- Low flotation pH-value
- Low calcium concentration (water hardness)
- Low surface tension

These characteristics seem to be beneficial, meaning that the suitable settings for a standard recovered paper mixture do not match the requirements for successful deinking of a flexo-NP 30 mixture.

CONCLUSION

The results of this study clearly show that process water properties of different deinking plants vary significantly. Furthermore, process water properties have a significant effect on the deinking potential of recovered paper. In general, higher contents of water-based inks influence the deinking results and the process water quality in a negative way.

After analyzing several water parameters, no general recommendation for optimum results are possible, because process solutions must be adapted on process water conditions or on the subsequent recovered paper mixture used.

However, after this investigation, it became clear that water hardness, pH-value, and surface tension are important process water parameters, which have to be monitored and optimized. For this, general trends are visible, leading to certain recommendations for a successful deinking process. On this account, a negative effect of increased water hardness is visible; therefore, only a minimum of calcium concentrations is necessary for a successful flotation result. Furthermore, a higher selectivity for a standard recovered paper mixture is possible with increased flotation pH-value. Hence, good results for a standard recovered paper mixture are possible with low water hardness, low surface tension, and higher flotation pH-value. In the special case of a recovered paper mixture with 30% flexo newspaper, slightly improved results are obtained with low water hardness and low surface tension, but low flotation pH-value. **TJ**

ACKNOWLEDGMENTS

With especially thank Elisabeth Hanecker and Abhijeet Virdhe from PTS Munich for their contribution. The research project (INGEDE 13210) was funded by the International Association of the Deinking Industry (INGEDE e. V.) in Bietigheim-Bissingen, Germany.

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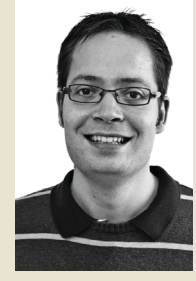
ABOUT THE AUTHORS

We have excellent knowledge from laboratory deinking of various print products, based on the use of tap water. The next step of consequence was to study the impact of process water on deinking results.

The most difficult aspect of this research was the selection of process water. We tried to cover representative samples from the market. We found that process water has a huge impact on deinking results.

Mills should realize that process water can greatly affect their deinking results. The larger the difference of deinking tests with process and tap water, the bigger the potential to improve the industrial deinking process by additional cleaning steps of the process water.



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