Removal of mineral oil during recovered paper processing

CHRISTIAN EWALD, ANTJE KERSTEN, AND SAMUEL SCHABEL

ABSTRACT: A flotation process and two different heat treatment processes prior to pulping were investigated according to their ability to remove mineral oils. For flotation, a correlation between removal of mineral oils and inorganic particles could be found for all process chemicals used in this study. By optimization of chemical concentration and dosing sequence, up to 80% of mineral oils could be removed while keeping the total losses smaller than 15%. The heat treatment processes achieved mineral oil removal rates that were in some cases even higher than those for flotation. For these processes, the most important parameters appeared to be the specific energy applied, the temperature, and the particle size distribution of recovered paper components. However, the specific energy consumption was quite high.

Application: This study shows the possibilities for removing mineral oil in recovered paper processing at laboratory scale. Besides conventional processes, treatments with hot air and steam were used with success.

Today, recovered paper for recycling is the most important raw material fiber for the paper industry worldwide [1]. It represents high economic and ecologic benefits, including an important cost reduction as well as a better use of paper resources, which are reused instead of landfilling or incineration. The 2010 global paper recycling rate of over 58%, corresponding to approximately 230 million metric tons, was the highest rate ever achieved. Of all paper products, the highest recycling rates can be reported for corrugated packaging materials and newspaper, which are more than 90% in Europe [2]. Also, the recovered paper utilization for folding boxboards is very high—twice as high as that for the production of graphic papers and roughly 8 times higher than for the production of sanitary and special paper grades.

Nevertheless, these recycled paper and cardboard products, which are also used as food packaging for a large variety of products, can contain harmful substances typically not removed by the recycling process [3,4]. In this context, their possible migration into foodstuffs has to be considered. During the last two years, an intensive discussion between representatives from authorities, paper manufacturers, and researchers about mineral oil in foodstuff and packaging material has taken place. The fact that recycled board products contain mineral oils between 300 to 1000 mg/kg with a relative low mass (C18–C22) and an aromatic proportion of 15% to 20% [5,6] cannot be ignored and has been well known by experts as mineral oil hump for a long time.

The mineral oil components consist of saturated, open chained, mostly branched, and cyclic hydrocarbons (mineral oil saturated hydrocarbons–MOSH), as well as aromatic hydrocarbons (mineral oil aromatic hydrocarbons–MOAH), often with alkylated side chains [7]. Due to their small chain length, below 24 carbon atoms, they may migrate from the board via the gas phase into foodstuffs. Inner bags from paper or polyethylene are not effective barriers in food packaging, also resulting in a general mineral oil migration from transport packages (e.g., corrugated boxes) into foodstuff, referred to as cross-contamination. This is true not only for foodstuff in board packaging but also for foodstuff in other packaging materials, such as plastic bags that are stored and/or transported in secondary packaging made from corrugated board, for example [8,9].

The major source of mineral oil contaminants are offset coldset inks present on newspapers, which contain on average 3000 mg/kg of these substances [4,10]. However, mineral oil components can also be found in smaller amounts in virgin fiber-based products and can be derived from other sources, such as retention aids, defoamers, and sizing agents, for example, that are also present in recovered paper. In order to protect consumers health, the German Federal Institute for Risk Assessment (BfR) proposed five potential solutions against migration in 2009 [6]:

1. Use of virgin fiber-based board and packaging
2. Separation of recovered paper loops by modified collection and sorting systems and the utilization of selected recovered paper grades for recycled board production
3. Use of barrier coatings or plastic bags
4. Use of mineral oil free inks and process chemicals
5. Removal of mineral oils and other contaminants from recovered paper and board

The European Food Safety Authority (EFSA) is even thinking about proposing a mandatory limiting value for migration based on further toxicological evaluations [11]. As a consequence, a series of research projects has been initiated to find new economic and ecologic ways to inhibit migration.

The aim of this study is to investigate both heat treatment processes for mineral oil removal from dry recovered paper with steam and hot air and the influence of flotation parameters and chemical additives during recycled pulp processing on the mineral oil removal efficiency. Another objective was to determine the influence of raw material composition by correlating the mineral oil removal with other paper characteristics like raw material composition and ash content. Finally, the three processes were compared in terms of mineral oil removal and cost efficiency to determine whether they are economically viable to be used in industrial processes.

MATERIALS AND METHODS

For the optimization of both mineral oil removal treatments, three different raw materials were chosen and compared to each other in terms of mineral oil reduction during treatment and raw material composition. These materials are listed in **Table I**. Deviations from the mean mineral oil values can be attributed to calibration of the analytical apparatus and sampling of test material that was stored in pails packed in aluminum foil to prevent mineral oil losses.

Furthermore, three different chemicals were used for removing mineral oils from fibers and for stabilization of contaminants in the aqueous phase. The first chemical was an oleic acid normally used for deinking trials according to INGEDE Method 11 "Assessment of print product recyclability–Deinkability test" (2012). This surfactant (Chemical 1) had been used in earlier research work connected with mineral oils and was therefore used as a benchmark.

The second chemical was a strongly emulsifying surfactant based on fatty acid esters (mainly oleic acid ester) dissolved in ethanol (Chemical 2), which becomes surface active after reaction with sodium hydroxide. Furthermore, it reacts with calcium ions present in process water by forming stable flocks easy to remove during flotation. Moreover, this chemical helps to reduce the average air bubble size during flotation. These characteristics made it highly effective in removing mineral oils from pulp suspensions.

The third substance was an anionic emulsifier for mineral oil emulsions composed of sulfated fish oil and sodium salt (Chemical 3). According to manufacturer's data, this chemical foams just weakly, which is why it was combined with oleic acid (Chemical 1) for some of the trials. Both emulsifying chemicals were food grade products so that no further contamination of pulp was caused. For initial dosage, manufacturer recommendations were used. For trials with Chemical 1 (oleic acid), 0.8% substance related to oven dry pulp was used. The dosage of Chemical 2 was twice the dosage of Chemical 1, and for Chemical 3, a dosage of 0.5 % substance related to oven dry pulp was added to the raw material.

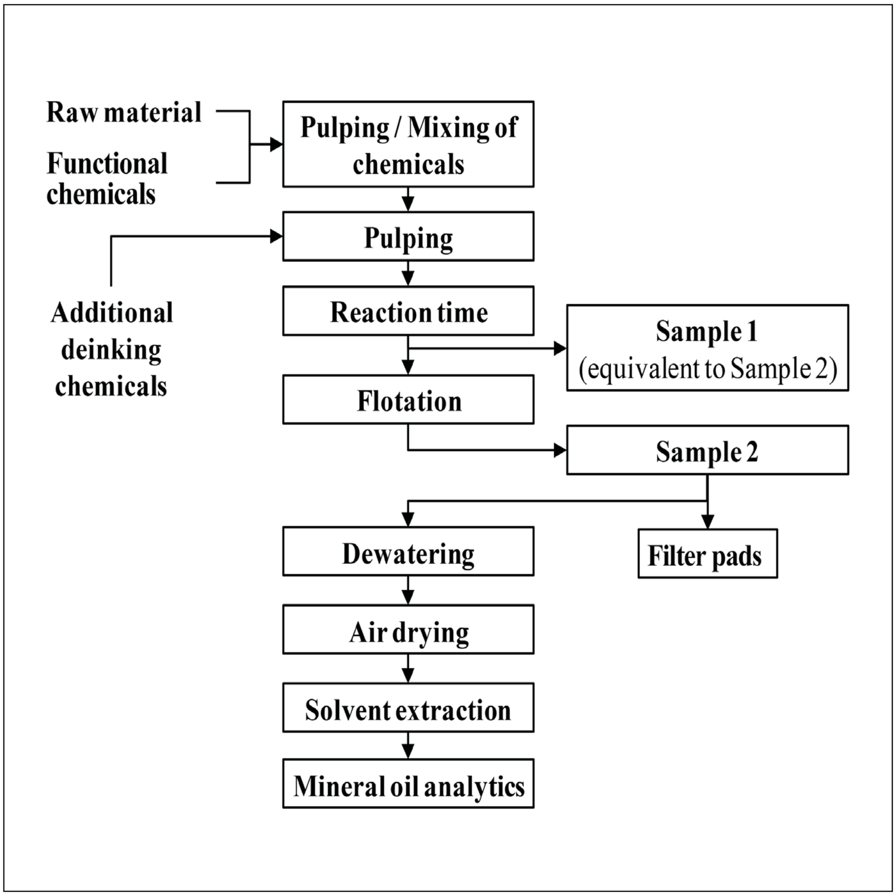
To achieve results which are transferable to industrial processes, flotation trials were made according to INGEDE Method 11, whereas a high consistency pulping stage at 24% consistency for 10 min was applied prior to standardized pulping, at 15% consistency. Before high consistency pulping, only functional chemicals dissolved in deionized water (Chemical 1, 2, or 3) were added to the paper samples to guarantee a better emulsification of mineral oils inside the aqueous phase. The remaining deinking chemicals were added prior to the second pulping stage in quantities defined in INGEDE Method 11 and diluted with water at 18° of German hardness (°dH). The only exceptions were trials with Chemical 1 where sodium hydroxide was added to the first pulping stage for dissolution reasons. After the second pulping, the stock was diluted to 5% consistency with prepared water at 18°dH and stored at 45°C for 1 h.

Besides optimization of flotation chemistry, the process parameters' flotation time, air volume, consistency, and temperature were also varied in two different steps to determine their influence on mineral oil removal. Before and after flotation, pulp samples were taken, according to **Fig. 1**, to form filter pads for brightness and ink elimination measurements. Furthermore, 4 g o.d. pulp was dewatered by centrifuging the pulp for 17 min at approximately 5000 g and removing the supernatant. The thickened samples were then dried to a constant weight in a climatic chamber at standard climate (23°C and 50% relative humidity). According to BfR method [12], the mineral oils were then extracted with an n-hexane-ethanol (1:1) solution for 2 h and analyzed by gas chromatography equipped with a flame ionization detector (GC-FID).

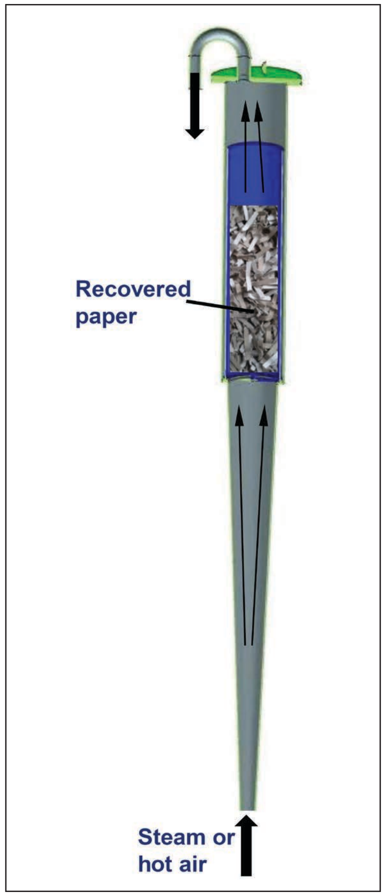
The heat treatment processes for mineral oil removal were performed with dry paper samples in shredded (0.5 cm²) form

Material	Ash Content, %	Mineral Oil Content, mg/kg
German coldset printed newspaper (ONP)	19.6	6000
Coated unprinted boxboard with a grammage of 320 g/m²	26.6	500
Unprinted double face corrugated board with C flute	15.6	500

I. Composition and type of raw materials used for the study



1. Flow chart test procedure for assessment of mineral oil removability during flotation.



2. Experimental setup for steam and hot air treatment.

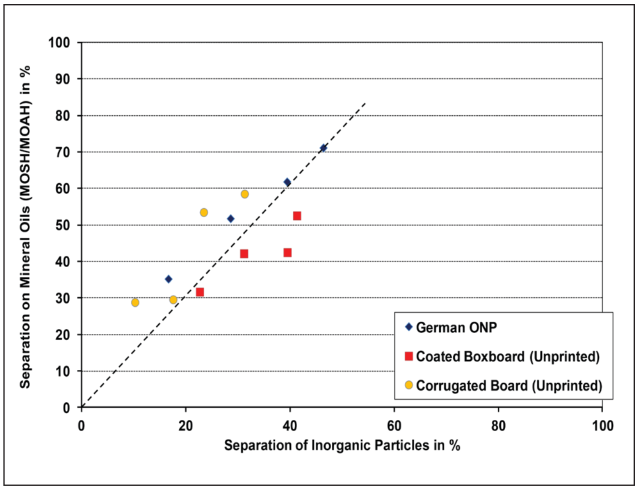
that were placed in a cylindrical body with 100 mm diameter. On top and bottom of that cylinder, perforated plates with a hole diameter of 0.5 mm were installed so that air from a hot air gun (500 l/min) or a transportable steam generator (70 l/min) could be passed through (**Fig. 2**). Different process parameters such as the air temperature, steam pressure, and treatment time were analyzed. For some trials, paper samples were cut into squares of 4, 16, and 64 cm² to determine the influence of particle size on mineral oil removal. To evaluate the mineral oil removal during these processes, paper samples were analyzed according to BfR method [12] already described for the flotation process. In case of steam treatment, the processed samples were air dried for few hours at standard climate prior to solvent extraction.

RESULTS AND INTERPRETATION

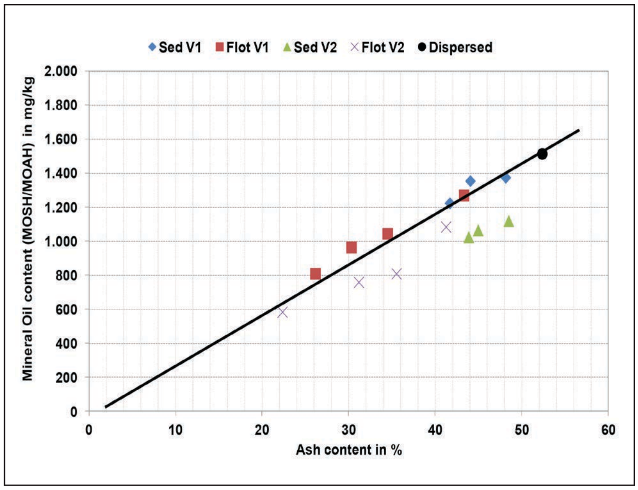
Flotation trials

The evaluation of flotation process parameters showed that a higher temperature and a lower air ratio did not influence the removal efficiency for mineral oils at all, whereas a higher flotation time increased the mineral oil removal in cases of Chemical 3 and Chemical 1. Also, the pulp consistency had an influence on mineral oil reduction. A higher consistency caused a lower solids air ratio and decreased the mineral oil reduction as expected. Furthermore, higher losses were caused at high consistencies. However, these effects were only minor compared to those achieved for the alternative flotation chemistry that is discussed in more detail in the following paragraphs. To achieve appropriate correlations between the separation of inorganic particles and mineral oils, mass balances of both parameters were used for calculation. By doing so, variations on flotation yield could also be discounted.

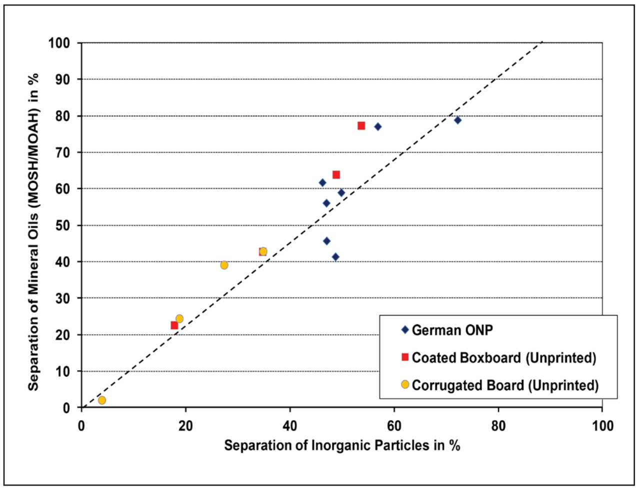
As demonstrated in **Fig. 3**, a standard deinking chemistry with Chemical 1 achieved a maximum mineral oil separation of 70% for ONP, whereas the separation for board products was much lower (60%). For the addition of Chemical 3, the mineral oil separation of both ONP and coated boxboard could be increased significantly. Separation rates for both products were almost at 80% (**Fig. 4**), whereas the separation rate for corrugated board could not be increased, which might be explained by its low inorganic content as Chemical 3 seemed to improve the selectivity of the flotation process for inorganic particles by forming smaller air bubbles and a very stable flotation froth. As opposed to Chemical 1, a good



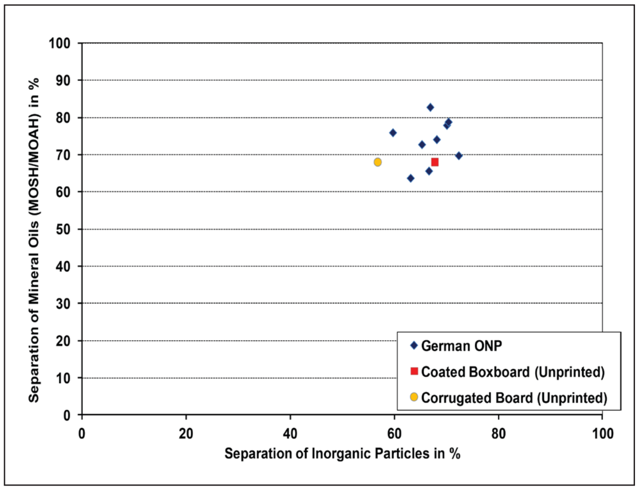
3. Correlation between separation of mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH) and inorganic particles from three different paper samples for the use of Chemical 1 (oleic acid) as functional chemical at different process parameters.



5. Correlation between mineral oil (MOSH/MOAH) and ash content for fines suspensions after flotation (Flot) and counter flow sedimentation (Sed) treatment [13].



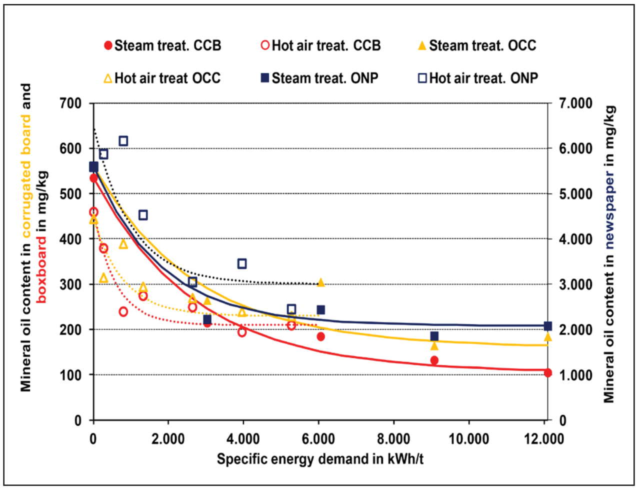
4. Correlation between separation of MOSH and MOAH and inorganic particles from three different paper samples at three different process parameters for a combination of Chemicals 1 and 3 as functional chemical.



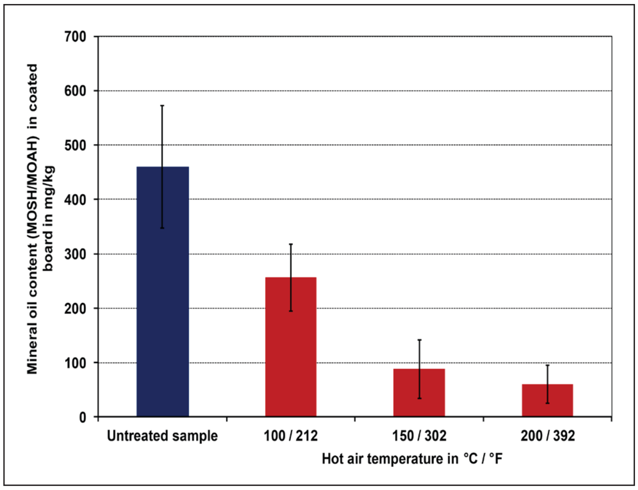
6. Correlation between separation of MOSH and MOAH and inorganic particles from three different paper samples for the use of Chemical 2 as functional chemical at different process parameters.

correlation between mineral oil (MOSH and MOAH) separation and the removal of inorganic particles was determined for the combination of Chemicals 1 and 3. The reason for this lies in the fact that Chemical 1 has a good selectivity for hydrophobic ink particles while the ash removal rate is quite small. Those hydrophobic particles can mainly be found in printed newspapers (printing dots), which had the highest mineral oil removal in combination with Chemical 1 since most of the mineral oils are still attached to those hydrophobic printing dots. In board products, mineral oils are well distributed in the sheet and preferably adsorb to inorganic particles with a large surface area, which could be shown in earlier studies where a fines fraction was removed from a recovered paper suspension and separated into inorganic and organic enriched fractions [13]. In order to separate inorganic and organic fines, flotation and counter flow sedimentation were applied after a dispersing treatment that was applied to split up bonds between both compounds. The results are demonstrated in **Fig. 5**. Furthermore, specific surface area measurements of the untreated and treated fines fractions were performed and the results were correlated with mineral oil measurements of the same samples. It could be shown that the mineral oil content in the fines fraction decreases with a decreasing specific surface area of the fines fraction. To that end, a separation of small, mainly inorganic particles is needed to achieve a good mineral oil removal, which is impossible for the use of Chemical 1.

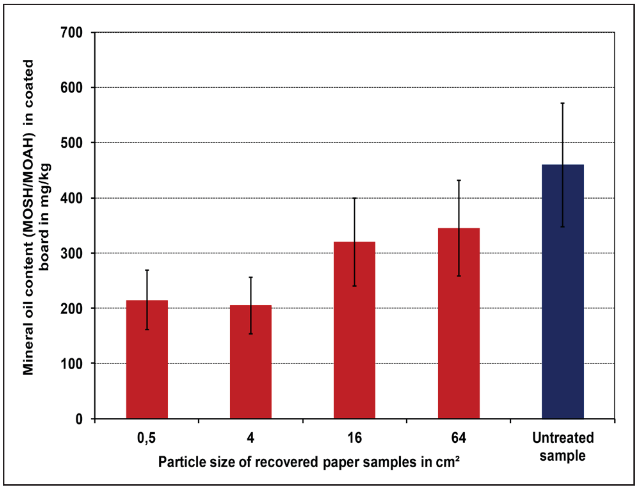
Of all tested chemicals, Chemical 2 achieved the best



7. Specific energy demand for mineral oil removal during hot air and steam treatment of newspapers (ONP), coated cardboard (CCB), and corrugated board (OCC) at 100°C (212°F).



8. Influence of hot air temperature on mineral oil removal after 10 min (shredded samples).



9. Influence of particle size on mineral oil removal from coated board during hot air treatment at 100°C (212°F).

mineral oil removal efficiencies. For Chemical 2, no differences between various paper grades could be found, and almost similar removal rates were achieved for all flotation parameters tested (**Fig. 6**). In fact, a mineral oil removal rate of about 60% was already achieved after 5 min flotation. As opposed to other functional chemicals tested, a shift to lower inorganic removal rates could be achieved by dosing Chemical 2 in combination with a 50% increased amount of sodium hydroxide and dilution water of 18°dH. In this way, a mineral oil removal of 80% and total losses of only 13% were possible for ONP.

However, none of the chemicals may achieve complete mineral oil removal from recovered paper suspensions since mineral oils do not only adhere to inorganic particles; those that are attached to fibers cannot be removed because a detachment does not take place. In fact, only particles with a high concentration of contaminants are removed during flotation, resulting in smaller losses compared to washing processes.

Heat treatment prior to pulping

The two approaches for heat treatment showed that, despite their similarity in process conditions, different influencing parameters could be discerned. As with all investigated mineral oil removal processes, both followed an exponential decay function. However, for steam treatment at 100°C, a mineral oil removal of 70% for ONP and of 81% for coated boxboard was possible, whereas the removal rate for hot air treatment was significantly lower at the same temperature, as shown in **Fig. 7**. Moreover, the hot air treatment had a significantly lower specific energy demand and a greater initial removal rate than the steam treatment. Another disadvantage of the steam treatment was found to be the condensation. During recovered paper treatment, samples were moistened at border areas to metal surfaces in the upper layer of the sample, which reduced the mineral oil removal rate in these areas. An increase in steam pressure followed by a higher temperature did not result in further improvements.

In contrast to steam treatment, a better mineral oil removal rate could be achieved when using hot air treatment at temperatures higher than 100°C. As demonstrated in **Fig. 8**, an equivalent mineral oil removal of 81% could be achieved for coated boxboard at 150°C. At that temperature, the specific energy consumption was about 4300 kWh/t and still less than half of the energy necessary for steam treatment.

The explanation for the improved mineral oil reduction at higher temperatures can be found in the composition of the mineral oil mixtures. Those with low molecular weight contribute to a high removal speed at the beginning of the process, while those with large molecular weight evaporate very slowly and incompletely, resulting in a saturation concentration for each temperature. To that end, the mineral oil removal is independent of the initial concentration.

Further investigations showed that the mineral oil removal rate decreases with increasing particle size due to unfavorable flow conditions. This means that recovered paper samples need to be shredded prior to treatment. As illustrated in **Fig. 9**, the best results were achieved for particles smaller than 4 cm².

CONCLUSIONS

All processes examined here have a high potential to remove mineral oils from recovered paper to more than 80%. However, the final mineral oil content in recycled paper will still be too high to meet mandatory limits that might be posed by the European legislation in the near future. However, in the short term, these processes could make a big contribution in removing mineral oils from the recovered paper cycle and would help to steadily decrease the mineral oil content in foodstuffs.

Of the three different investigated processes, flotation is most favorable in terms of energy demand. It was shown that a very fast mineral oil removal in a single loop flotation process is possible when choosing the right flotation chemistry. However, it was found that a correlation between mineral oil removal and the removal of inorganic particles exists, which causes significant losses that need to be replaced by virgin fiber products. Moreover, the residues needed to be landfilled or incinerated, which would increase the cost of the final product. Nevertheless, a removal of inorganic particles would contribute to better strength properties of recycled papers, and it might be possible that new valuable products will soon be found that could be produced from these residues.

A solution without any residues, but with a higher specific energy demand, would be the heat treatment process. Here, the hot air treatment would be preferred, as its specific energy demand is significantly lower than that for steam treatment. Moreover, no problems with condensation can appear. The only disadvantage of this process would be the requirement for prior size reduction of recovered paper samples to improve flow conditions. **TJ**

ACKNOWLEDGMENTS

The authors thank the VDP-Forschungsrat for financing the research project INFOR 155. Special thanks go also to the Federal Ministry of Economic Affairs and Technology (BMWi) that finances the AIF research project 17272 N of the research association Kuratorium für Forschung und Technik der Zellstoff- und Papierindustrie im VDP e.V. via the AiF within the funding program Industrielle Gemeinschaftsforschung und -entwicklung (IGF) due to a decision of the German Bundestag.

LITERATURE CITED

1. Ringman-Beck, J., "The paper industry experience: from pioneering in recycling to industrial ecology," *Sustainable Industry Forum 2013*, European Commisison, Brussels, 2013, p. 17. Available [Online] http://ec.europa.eu/DocsRoom/documents/11843/attachments/7/translations/en/renditions/pdf <16Dec2015>.

ABOUT THE AUTHORS

Mineral oil in paper products is a hot topic in Germany, and we are experts in the required mineral oil analytics. Therefore, it was a logical next step to evaluate possibilities for removal of mineral oil during recovered paper processing. We are working on mineral oil analytics and the migration of mineral oil from packaging material into foodstuff. Investigations as to the deinkability of mineral oil- free printing inks are also part of previous and still ongoing research projects.

The development of a good usable test rig that allows reproducible results was a challenge. A good solution was found in collaboration with our workshop at the institute. Our most interesting finding in this research was the very fast and good results of the hot air treatment on mineral oil reduction in paper.

With this study, mills and suppliers are now aware of these processes for mineral oil removal and can determine their usefulness and how such a treatment should be implemented at mill scale. Our next step is to finalize a publicly funded research project that combines various treatments to achieve a maximized mineral oil-free reduction during recovered paper processing. We also have to make some cost estimations for the various treatments.

Ewald

Kersten

Schabel

Ewald is product segment engineer, Surface Treatment, for Freudenberg Filtration Technologies, Weinheim, Germany. Kersten is senior researcher, and Schabel is head of department, Chair of Paper Technology and Mechanical Process Engineering (PMV), Technische Universität Darmstadt, Darmstadt, Germany. Email Kersten at kersten@papier.tu-darmstadt.de for more information.

2. CEPI, "CEPI Sustainability Report 2011," Confederation of European Paper Industries, Brussels, 2011, p. 74.
3. Demel, I., Kappen, J., Kersten, A., et al., "Bewertung von Maßnahmen zur Problemlösung von Mineralöl in Verpackungspapieren und Karton," Abschlussbericht zum INFOR-Forschungsprojekt Nr. 155, Technische Universität Darmstadt, Fachgebiet Papierfabrikation und Mechanische Verfahrensechnik (PMV), Papiertechnische Stiftung (PTS), Darmstadt / München, 2012.
4. Kersten, A., Putz, H.-J., and Schabel, S., "Volatile organic compounds in printed papers and measures for removal in recovered paper processing," *Res. Forum Recycl., 9th*, TAPPI PRESS, Atlanta, GA, USA, 2010.
5. Lorenzini, R., Fiselier, K., and Biedermann, M., et al., *Food Addit. Contam.* 27(12): 1765(2010).
6. BfR, "Übergänge von Mineralöl aus Verpackungsmaterialien auf Lebensmittel," Stellungnahme Nr. 008/2010, Bundesinstitut für Risikobewertung (German Federal Institute for Risk Assessment), Berlin, 2009, p. 6.
7. Vollmer, A., Altkofer, W., and Biedermann, M., et al., "Mineralölmigration aus Kartonschachteln: EH-119-Proben-Studie und neuere Daten," *BMELV Conf.*, Bundesministerium für Ernährung, Landwirtschaft und Verbraucherschutz (German Federal Ministry of Food, Agriculture and Consumer Protection), Bonn, 25 August 2010.
8. Biedermann, M., Ingenhoff, J.-E., Dima, G., et al., *Eur. Food Res. Technol.* 236(3): 459(2013).
9. Biedermann, M., Ingenhoff, J.-E., Barbanera, M., et al., *Packag. Technol. Sci.* 24(5): 281(2011).
10. Biedermann, M. and Grob, K., *Eur. Food Res. Technol.* 230(5): 785(2010).
11. European Food Safety Authority,"Scientific opinion on the use of high viscosity white mineral oils as a food additive," *EFSA J.* 7(11): 1387(2009). Available [Online] http://www.efsa.europa.eu/sites/default/files/scientific_output/files/main_documents/1387.pdf <15Dec2015>.
12. BfR, "Determination of hydrocarbons from mineral oil (MOSH & MOAH) or plastics (POSH & PAO) in packaging materials and dry foodstuffs by solid phase extraction and GC-FID," Bundesinstitut für Risikobewertung (German Federal Institute for Risk Assessment), Berlin, 2012.
13. Mohr, J., "Möglichkeiten der Mineralölentfrachtung durch gezielte Feinstoffbehandlung," Bachelor's thesis, Technische Universität Darmstadt, FG Papierfabrikation u. Mech. Verfahrenstechnik, 2012, p. 41.