ENZYMATIC DEINKING OF MIXED OFFICE WASTE: PROCESS CONDITION OPTIMIZATION

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ENZYMATIC DEINKING CAN BE SUCCESSFULLY APPLIED TO MIXED OFFICE WASTE FURNISH UNDER NEUTRAL pH CONDITIONS.

THIS ARTICLE PROVIDES GUIDELINES FOR THE USE OF enzyme/surfactant combinations in deinking mixed office waste furnishes. Preliminary indications were presented earlier *(1, 2)* that one class of cellulytic enzymes could enhance toner removal from xerographic and laser printed papers at the elevated pH these papers can generate when repulped. This elevated pH is caused by calcium carbonate, which is present in many of the neutral and alkaline papers available today. The results with toner-based inks are in stark contrast to recent reports that describe enzyme-enhanced deinking of old newspapers (ONP) *(3, 4)*. In both of the latter reports, an acidic cellulase mixture was chosen to assist in the deinking process, and few advantages were observed.

Rhône-Poulenc has developed novel chemistry for deinking mixed office waste under neutral pH conditions in a closed-loop process. Specifically designed enzyme/surfactant combinations provide a synergistic effect to afford enhanced deinking performance. Successful lab and pilot-scale evaluations have been conducted to compare the newly developed enzymatic approach to a conventional alkaline one *(5)*. Some of the benefits realized include:

- Improved dirt removal efficiency (DRE)
- Increased brightness
- Reduced COD
- Enhanced physical properties
- Increased ash removal
- Reduced chemical cost
- Use of lower grade, less-sorted recovered paper.

While lab and pilot scale evaluations have shown good results, mill-scale data are difficult to obtain simply because of the limited understanding of the effects of enzyme/surfactant chemistries in a deinking system. Prior to industrial trials, most mills require a high comfort level about the impact of new chemistry to their existing process.

The objective of this work is to increase the awareness and understanding of how enzyme/surfactant technology can be successfully applied in deinking realistic, mill-affordable MOW furnishes to produce products such as fine printing and writing grade paper and/or tissue.

DEINKING PROCESS OPTIMIZATION

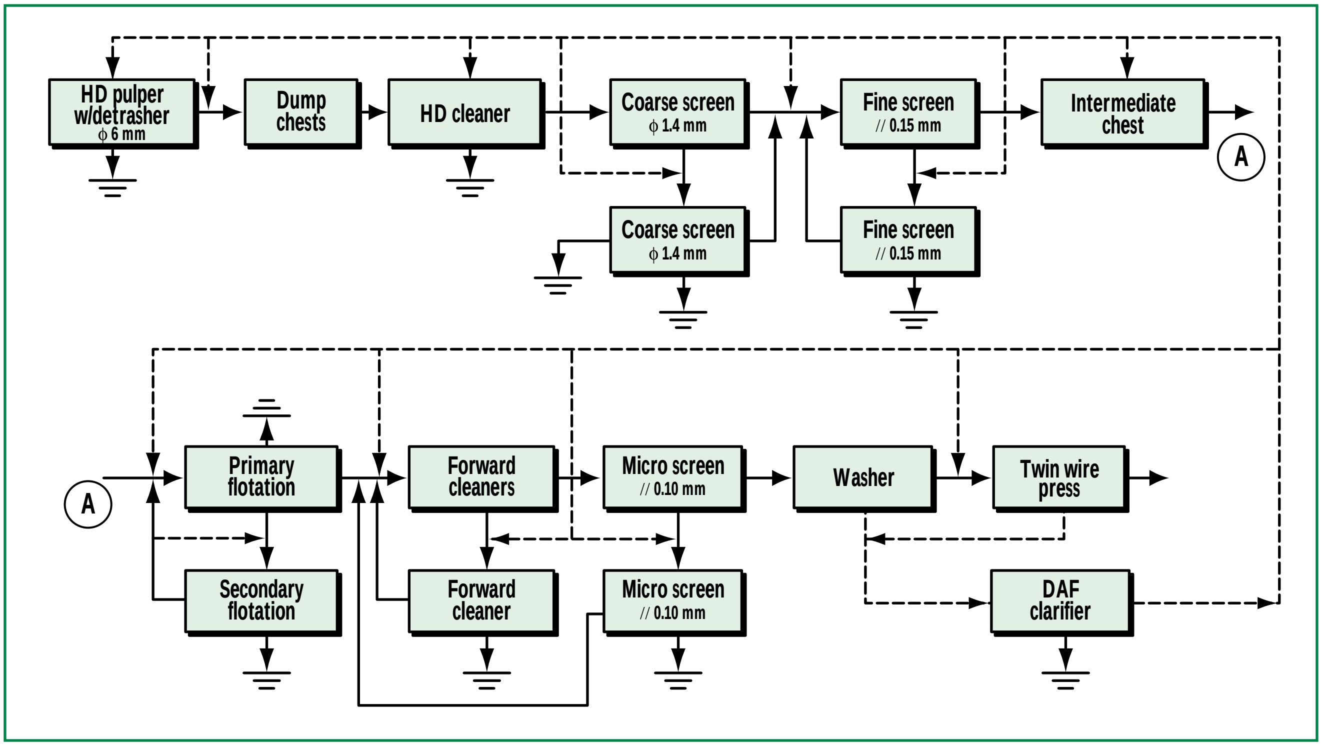
Process

Most experience with enzyme/surfactant chemistry in deinking MOW has been gained in hybrid deinking systems complete with screening, flotation, washing, and whitewater clarification. The hybrid process used for semi-industrial scale testing *(5)* discussed in this report is depicted in **Fig. 1**.

Recovered paper

Newly developed enzyme/surfactant combinations have been successfully applied on a variety of recovered papers. Specifically, we have been successful deinking furnishes containing the following components in varying proportions:

- Mixed office wastepaper (MOW)
- Sorted white ledger (SWL)
- Sorted colored ledger (SCL)
- Computer printout (CPO)
- Coated book sections (CBS)
- Sulfate bleached sections (SBS)
- Groundwood sections (<10%) (GWS)
- Ultraviolet printed (<5%) (UV).



1. Deinking process

Test scale	Mill product target	FURNISH COMPONENTS, %								PULPER CONDITIONS			
		MOW	SWL	SCL	CPO	CBS	SBS	GWS	UV	Csty, %	Temp, °C	pH	Time, min
Pilot	P&W		65	25				10		16	54	7.2	40
Pilot	Tissue	70				25			5	18	49	7.3	40
Pilot	P&W		100							14	55	7.9	30
Lab	P&W	38	30		32					14.4-18.1	53-59	7.6-8.2	45
Lab	Tissue	50	25				25			16	55	7.5	40

I. Application of RP enzyme/surfactant chemistries

A summary of specific examples of recovered papers can be found in **Table I**.

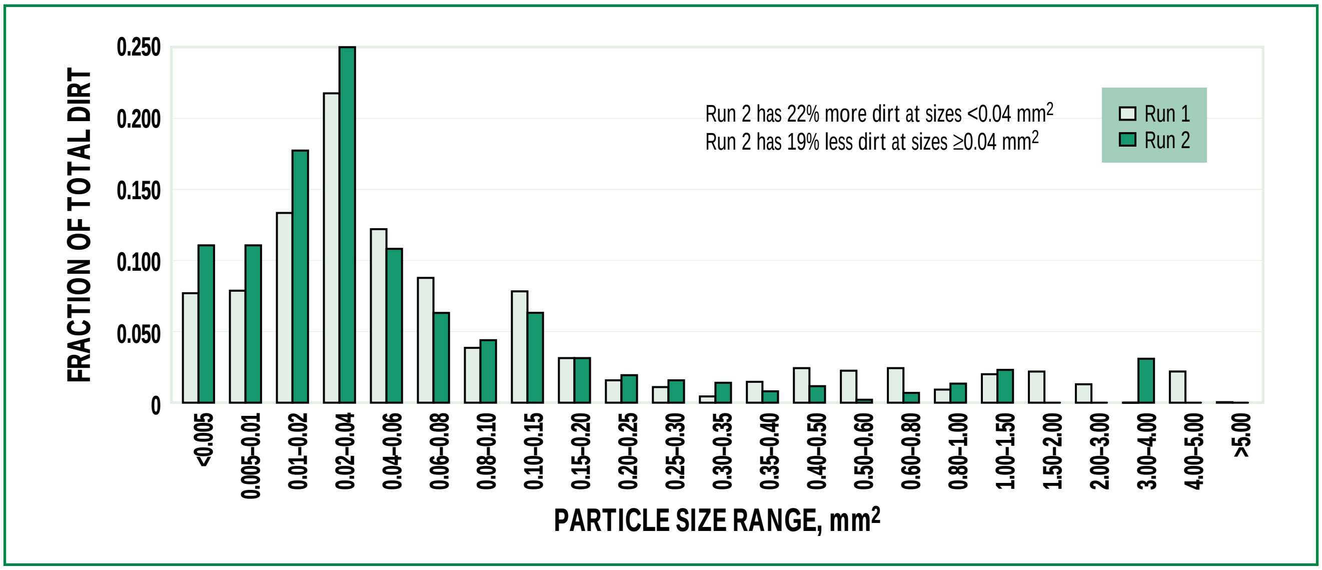
Point of chemical addition

Experience has shown that chemical application is best done in the pulper near the beginning of the repulping process. This allows for chemical reaction with the recovered paper furnish at higher consistency while undergoing optimum mechanical agitation. In cases where the components are added downstream from the pulper, the results have not been as uniform or as good. There is evidence from other industries, where cellulases play an important processing role, that increased mechanical agitation can improve the efficiency of the process. Zyer, et al. *(6)* demonstrated on a lab scale that the removal of offset ink from a cellulosic matrix using a cellulase can be enhanced by increasing the mechanical energy input. Although the nature of offset and toner-based inks is different, there is no reason to suspect that the role of mechanical energy would be different in these two systems.

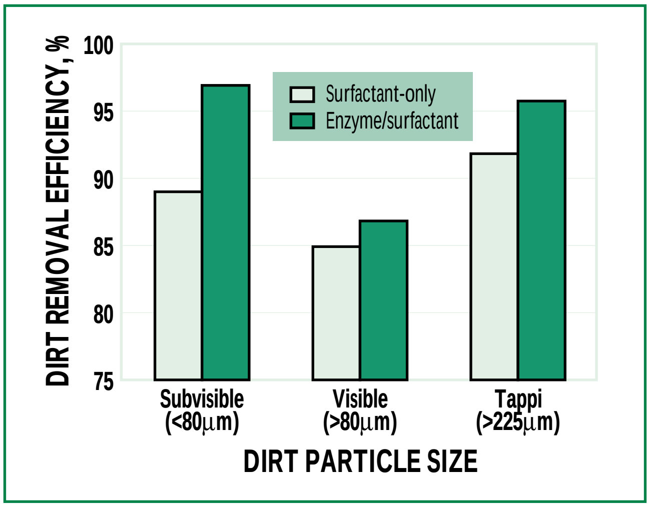
Pulper conditions

Chemistry. Toner inks, found in typical MOW furnishes, are traditionally difficult to remove by hybrid and/or wash-only processing due to the large size and flat profile of the dirt particle. Interesting photomicrography depicting the nature of these particles has been previously reported *(7)*. Specifically designed enzyme/surfactant combinations have demonstrated a positive influence on deinking performance. Recently developed formulations are mainly comprised of non-ionic surfactants and alkaline cellulase/hemicellulase mixtures. Use of enzyme/surfactant chemistry obviates the need for conventional alkaline pulper chemistry, including sodium hydroxide, hydrogen peroxide, sodium silicate, chelants, and fatty acids.

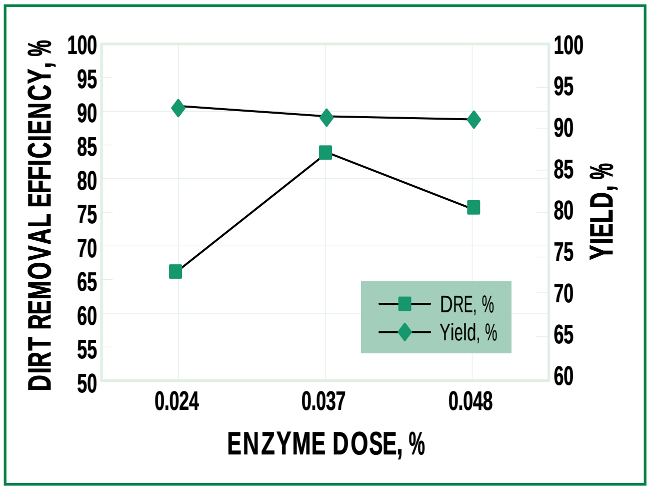
Deinking performance is often assessed by studying dirt removal across flotation. One criterion for effective



2. Dirt particle size comparison of repulped MOW following the pulping stage



3. Dirt removal efficiency across flotation using enzyme/surfactant vs. surfactant-only chemistry

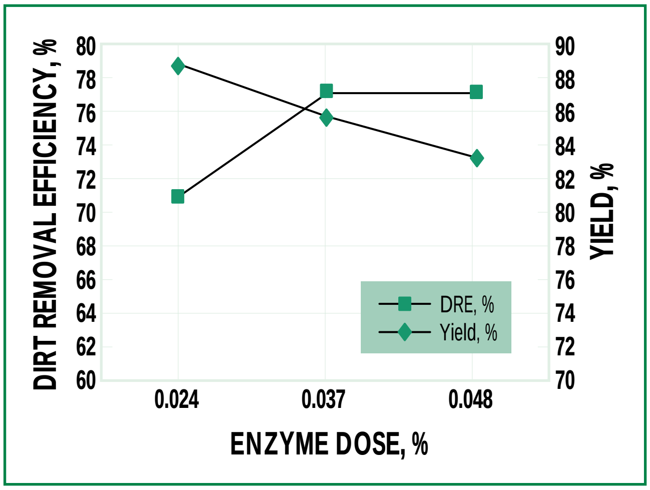


4. Influence of enzyme concentration on dirt removal efficiency and yield for furnish containing 50% MOW

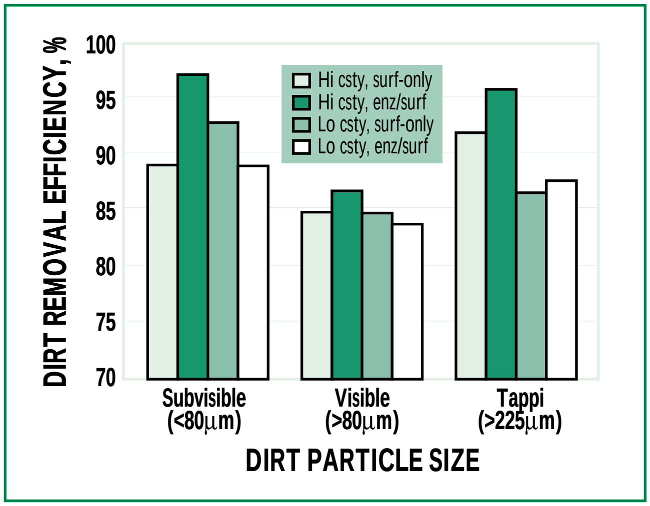
dirt removal by flotation is particle size. A comparison of particle size profiles from two semi-industrial scale pulping experiments is illustrated in **Fig. 2**. Both experiments were conducted on recovered paper containing 65% white laser ledger, 25% colored mixed office waste, and 10% groundwood sections, under neutral conditions, and at 16% repulping consistency. A surfactant alone was used in Run 1, whereas an enzyme/surfactant system was used in Run 2. When the particle size profiles following the pulping stage are compared, it can be seen that Run 2 has more dirt at particle sizes <0.04 mm^2 (or <225 µm). The two pulps were then subjected to flotation according to the process described in Fig. 1. Flotation consisted of six stages of primary flotation with reject froth vacuum followed by two stages of secondary flotation. Dirt removal across flotation is shown in **Fig. 3**. More efficient dirt removal occurred with the enzyme/surfactant combination than with the surfactant alone. Increased dirt removal efficiency is due to the significant reduction in the dirt particle size.

Chemical dose. The optimum enzyme/surfactant dose ratio depends on the quality of the recovered paper processed, the quality of the whitewater used in the pulping stage, and the ability to achieve acceptable system runnability. The concentration of surfactant must be selected to achieve good system runnability and careful foam control. Our experience indicates that an acceptable range of surfactant concentration is from about 0.04% to 0.2% (based on fiber). In addition, we have observed an optimum response in dirt removal efficiency vs. enzyme dose.

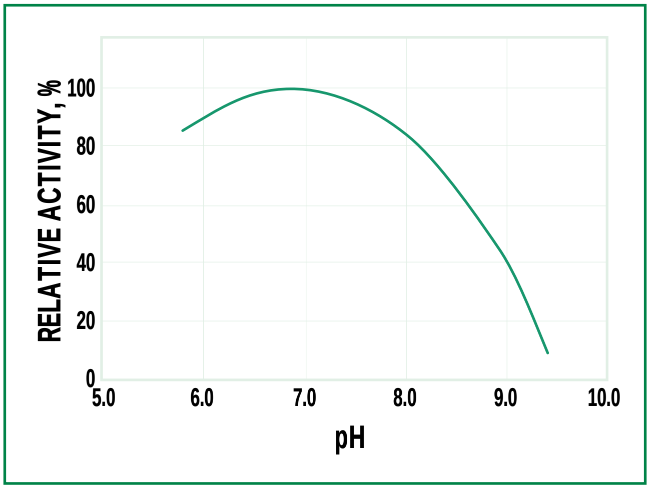
Experiments to define this optimum were done under the following conditions. The furnish was a mixture of 50% MOW, 25% SWL, and 25% SBS. Pulping was completed at 7.5 pH, 16% consistency, and 55°C. The surfactant used in this system was maintained at 0.06%. **Fig-**



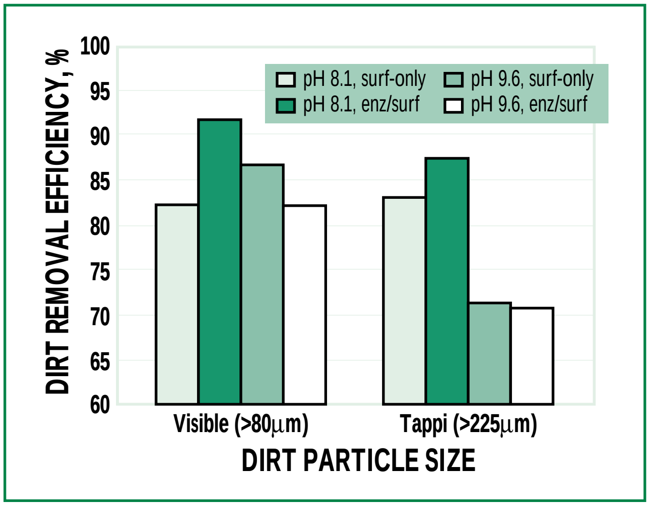
5. Influence of enzyme concentration on dirt removal efficiency and yield for furnish containing 38% MOW



6. Influence of pulper consistency on deinking efficiency



7. Influence of pH on enzyme activity



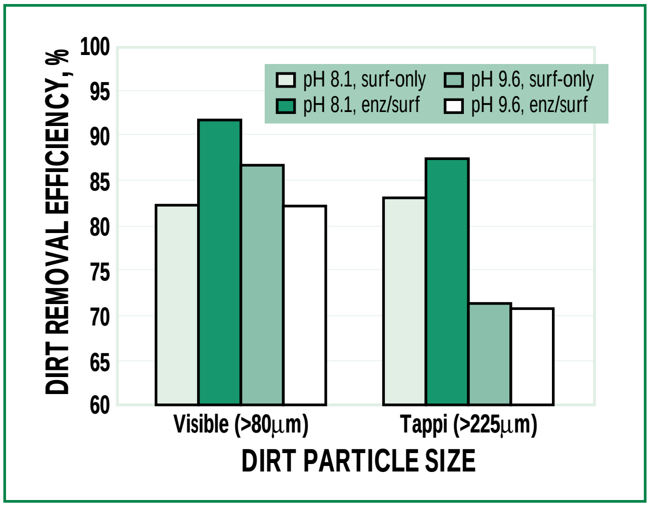
8. Influence of pH on deinking efficiency

ure 4 shows yield and dirt removal efficiency across flotation vs. enzyme dose. Optimum dirt removal efficiency was achieved at 0.037% enzyme concentration. Yield did not vary significantly over the enzyme concentration range studied. This observation is consistent with enzyme dose response results previously reported *(2)*.

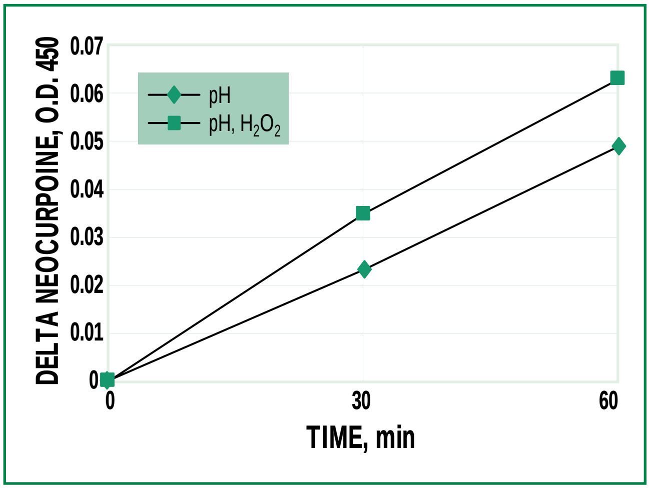
Figure 5 shows the influence of enzyme concentration on yield and dirt removal efficiency across flotation for another deinking condition. In this case, the furnish was 38% MOW, 32% CPO, and 30% SWL. Pulping was completed at 7.8 pH, 16% consistency, and 58°C. The surfactant was maintained at 0.075%. While we did not observe an optimum dirt removal efficiency, it can be seen that increasing the enzyme dose reduces the yield. For this reason, it is important to utilize surfactants which work synergistically with the enzyme. The goal is to achieve optimum deinking efficiency without stabilizing foam and thereby sacrificing yield.

The quality of the whitewater used in the pulper can have an influence on the deinking efficiency of a system utilizing enzyme/surfactant chemistry. If a large amount of cellulosic fines are returned from the DAF clarifier, the surface area of the pulp mass will increase due to the relatively high surface area of fines. This can cause an uneven distribution of the chemicals in the pulp mass and may result in inefficient chemical usage, thereby requiring a greater concentration of additives to reach optimum dirt removal.

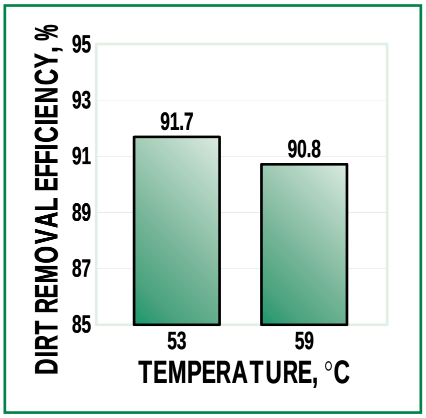
Consistency. Both laboratory and semi-industrial scale experience indicates that use of enzyme/surfactant chemistry at high pulper consistencies provides a beneficial effect on dirt removal efficiency. A comparison of enzyme/surfactant and surfactant-only performance at both high consistency (16%) and low consistency (4%) is shown in **Fig. 6**. The experiments were completed on a semi-industrial scale having a process sequence described in Fig. 1. The furnish used contained 65% white laser ledger, 25% colored mixed office waste, and



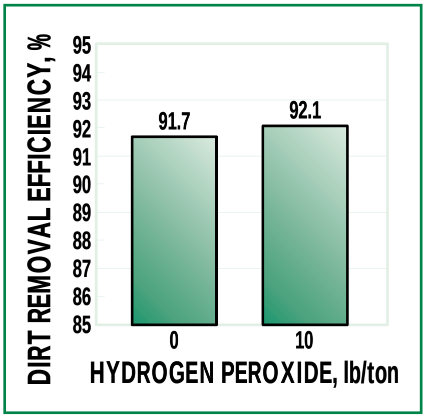
9. Influence of temperature on enzyme activity



11. Influence of hydrogen peroxide on enzyme hydrolysis, H_2O_2 at 13 lb/ton



10. Influence of temperature on deinking efficiency



12. Influence of hydrogen peroxide on deinking efficiency

10% ground wood sections. The high consistency test was done by adding the chemistry directly to the pulper having a 16% consistency furnish. Low consistency conditions were done by adding the chemistry to the dump chest which followed high consistency repulping. The highest dirt removal efficiency was achieved with enzyme/surfactant added to the pulper at 16% consistency. Results show 97% removal for subvisible specs (<80 µm), 87% removal for visible specs (>80 µm), and 96% dirt removal for laser specs (>225 µm). Addition of enzyme/surfactant to the dump chest at 4% consistency did not show an advantage in dirt removal when compared to the surfactant-only chemistry.

pH. Use of enzyme/surfactant technology requires a pulping pH which is suitable to ensure optimum enzyme activity. Experimental pH activity curves are available for specific enzymes. One such example can be found in **Fig. 7**. This cellulase enzyme has activity in the pH 6-9 range. The optimum activity is from about pH 6.5-7.5. In many cases with mixed furnishes, such as combinations of MOW, SWL, and SBS or MOW, CPO, and SWL, the natural pH of the furnish is about 7.2 to 8.1. Good results have been obtained when operating at the natural pH of the starting furnish or by adjusting the pulper pH to about 7.5 with either sulfuric or phosphoric acid. **Figure 8** shows a comparison of enzyme/surfactant and surfactant-only performance at ambient furnish pH (8.1) and at alkaline pH (9.6). The furnish consisted of 38% MOW, 32% CPO, and 30% SWL, and the stock was repulped at 16% consistency and 53°C. The results indicate that a significant increase in dirt removal efficiency is apparent when enzyme/surfactant is used vs. surfactant-only at pH 8.1. Also, dirt removal efficiency is generally greater when pulping is accomplished at neutral pH vs. alkaline pH. Finally, it is observed that use of enzyme/surfactant systems at alkaline pH 9.6 offers no advantage when compared to surfactant-only chemistry. These data are consistent with the experimental pH activity curve. One would not expect enzyme activity at pH 9.6.

Temperature. The operating temperature range of a cellulase enzyme using northern bleached softwood kraft as the substrate is shown in **Fig. 9**. Highest activity is found between 45-55°C. Results from deinking experiments completed on a furnish of 38% MOW, 32% CPO, and 30% SWL and at pulping conditions of 16% consistency and 8.1 pH are shown in **Fig. 10**. Here, we have illustrated a comparison of dirt removal performance of enzyme/surfactant chemistry at two temperatures. These results show only a slight decrease in the dirt removal performance at the elevated temperature. While it may be possible to operate at temperatures slightly greater than 60°C, it is not recommended due to the rapid decline in enzyme activity at elevated temperatures.

Higher enzyme concentrations would be required to compensate for the lower activity. In addition, pulper temperatures greater than 60°C can also adversely impact other contaminants in the deinking process, such as stickies.

Additives. While the use of enzyme/surfactant chemistry does not require any additional chemical additives in the pulping stage, other chemicals may be present in the pulper or in the pulper feed circuit. As water loops become more closed, chemical carryover into whitewater circuits becomes a concern. Also, some mills feel that the presence of certain levels of hydrogen peroxide in the pulper will help control microbial growth in the rest of the system *(8)*. Therefore, experiments have been conducted to determine tolerance levels of additives such as hydrogen peroxide on enzyme/surfactant activity in the pulping stage and the resulting effect on dirt removal performance across flotation. **Figure 11** shows the effect of hydrogen peroxide on enzyme hydrolysis. The data were obtained by measuring hydrolytic changes of enzyme-only and enzyme plus peroxide additives on a bleached northern kraft pulp at 10% consistency and 8.0 pH. The measure of reducing carbohydrate production by the Neocuproine method is compared to the base level contained in the pulp defibered in mill whitewater. While there is a difference in the hydrolysis values, the difference is not considered large enough to detract from the fact that the cellulase does remain active in the presence of this amount of peroxide.

Deinking studies were then completed with hydrogen peroxide added to the pulper. The recovered paper deinked was a mixture of 38% MOW, 32% CPO, and 30% SWL. Pulper conditions were maintained at 16% consistency, 53°C, 8.1 pH, and constant enzyme/surfactant addition rates. The first experiment had no added peroxide in the pulper, and a comparative run was completed with 10 lb/ton peroxide. Deinking efficiency was measured following flotation, and the results are illustrated in **Fig. 12**. These data suggest that the presence of peroxide at 10 lb/ton does not adversely affect enzyme/surfactant performance in deinking.

Active chlorine is known to be very effective for inactivating enzymes. For this reason, 2 ppm active chlorine in the process water that comes in contact with enzymes is considered a safe upper limit. If necessary, most antichlors would be compatible with enzymes and could be employed if there is a question about chlorine levels.

Residence time. We have tested pulping residence times ranging between 30 and 45 min. In general, a minimum of 30 min is required for complete defibering of the recovered paper mixtures reported in this paper. Mill processes will require varying pulping times to achieve complete defibering. This variance is dependent on both the type of mill equipment and the composition of the recovered paper processed.

Applicability of enzyme/surfactant chemistry

Table I is a summary of actual lab and pilot examples where Rhône-Poulenc enzyme/surfactant combinations have been successfully applied. Actual furnish type and pulper conditions are listed, along with the mill product targeted. The goal in each case was to improve dirt removal efficiency over that commonly achieved with a traditional alkaline approach, without causing any adverse effects. In addition to improving dirt removal efficiency, we also positively influenced final product brightness, final product physical properties, whitewater COD levels, and ash removal across flotation.

SUMMARY

Neutral deinking of complex recovered paper mixtures to produce products such as fine printing and writing grade paper and/or tissue can be successfully accomplished using enzyme/surfactant technology. The data presented offer a guideline for optimizing process conditions to ultimately achieve the desired deinking performance above and beyond what is capable with a traditional alkaline approach. Specific conditions with regard to the deinking process, recovered paper, and detailed pulper conditions are indicated. An applicability summary of actual pilot and lab-scale examples that resulted in successful deinking performance is also provided. **TJ**

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