Enzymatic Deinking and Alkaline Sizing for Recycled Fiber

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The use of de-inked pulp is essential from the Environment's point to conserve Forest and other resources. De-inking of Waste Paper is must to recycle the paper for producing quality Papers. Compared to the conventional chemical de-inking process, Bio de-inking is a novel concept through which impact on environment is a bare minimum, due to less amount of chemicals used, it also results in cost savings. The savings in cost with Enzymatic De-inking can vary from Rs 150 to Rs.300. per metric ton of fiber. When mills started making Writing and Printing Papers with de-inked Pulps with imported waste paper furnishes, the major problem encountered by mills was due to its inherent filler quality i.e. Calcium Carbonate. It caused several problems during sizing process i.e fluctuations in pH conditions, from mixing chest to Head box, as pH of the stock was widely varying. A temporary solace was to carry out size addition near to Head box and to use dispersed rosin size, which was not a permanent solution. AKD /ASA Sizing, is the only an ultimate solution to overcome these problems. Calcium carbonate filler used has a great impact upon sizing depending upon whether filler is Ground Calcium Carbonate or Precipitated Calcium Carbonate. Precipitated Calcium Carbonate results in more problems as compared to Ground Calcium Carbonate during sizing process..

INTRODUCTION

In a conventional de-inking process, Waste Paper is treated in a Hydra Pulper with Caustic, Sodium Silicate, Deinking chemical and H_2O_2. Action of these chemicals is as follows:

1. Caustic helps in swelling the pulp fiber, making it easier for slushing.
2. De-inking chemical either solvent based or fatty acid based helps separation of ink pigments by dislodging them from fiber surface due to chemical means.
3. Mechanical treatment helps for disintegration of ink pigments dislodged from fiber surface.
4. Sodium silicate acts to keep ink particles in suspension and do not allow further re-deposition by agglomeration.
5. H_2O_2 prevents the yellowing of the fiber which takes place in the alkaline media.

Removal of ink helps to improve brightness of the final de-inked pulp. The higher the ink removal, the better will be the improvement in brightness. The brightness improvement during deinking process is due to removal of ink, the final brightness after deinking can not be more than the brightness of unprinted paper prior to printing. If base paper used for printing is having a brightness of say 76%, virtually it will be difficult to go above 74-75% after thorough de-inking.

Bio-deinking deserves its merit over conventional de-inking due to the reason that it will not induce any alkaline yellowing as it is carried out in near neutral pH conditions.

In addition to alkaline yellowing, excessive usage of caustic results in generation of more BOD, COD, dissolved solids and alkalinity in the resulting effluentThus the resulting effluent will call for additional treatment costs. This is not the case with bio-deinking as pH adhered to is near neutral to slightly alkaline only.

The result obtained will depend upon the configuration of de-inking plant, as well as the type of printed waste used.

De-inking plant configuration and waste paper quality will govern the final filler content in the de-inked pulp. Presence of Calcium Carbonate in the de-inked pulp after de-inking, makes it difficult for paper sizing under acidic conditions. Calcium Carbonate reacts readily with the acidity in Paper making system and generates Carbon Dioxide which gives foam and scale forming

Calcium Sulphate. Surface area of filler particles is another problematic area The larger the surface area, the more will be the size consumption. The size consumption in general for Precipitated Calcium Carbonate filled papers is much higher as compared to GCC and other fillers as and Clay and Talcum.

Suppressing of foam with defoamer will result in further problem in that though the foam will be suppressed, use of excessive defoamer will result in much higher size consumption.

Under these conditions Switching over to Alkaline sizing is better as:

- Alkaline sizing with AKD Emulsion is an alum free system in which acidity factor doesn't arise and positive charge for size chemical fixation is managed by the reactive size of AKD itself or its supporting chemicals like fixing and retention aids.
- In alkaline sizing conditions, even further addition of Calcium Carbonate as filler is acceptable in addition to inherent quantity present in de-inked pulps.
- Basically alkaline sizing implies usage of Calcium Carbonate as a filler.

Application of Enzymatic De-inking Technology

Printing and de-inking technology both are closely inter-related subjects.

To implement Enzyme de-inking technology, it is required to understand Printing inks and technology, involved in Waste Paper being used.

Printing Inks

- Components of Printing inks are 1. Liquid medium called Vehicle and solid suspension called Pigment.
- For Gravure, Flexo, Inkjet, Electrographic, Electro Photographic methods of Printing, liquid inks are used, where as Paste type inks used for Lithographic and letter press printing.
- Second component in Ink, i.e. is solid part is Pigment of Carbon black or Color Pigment.

During any kind of Printing Process, print ink is lodged over fiber surface with the help of liquid part so called vehicle and once vehicle part reacts or evaporates, pigment part adheres to paper body.

Hence to dislodge the pigment part from Paper body, it is essential to understand liquid part i.e Vehicle and its chemical nature. This is because printing process is lodging of pigment, where as de-inking process is dis-lodging ink particles from fiber body.

Composition of Vehicle

- Vehicle is a medium for dissolving or dispersing of other ingredients in ink.
- Vehicle is made of fatty acid like Linseed Oil, Castor Oil, Vehicles carry Pigment on substrate (Paper body), bind pigment and evaporates later.

What is Pigment in Ink ?

- Pigments are generally Carbon Black, Organic, White Inorganic or Colored Inorganics.
- White Inorganics are TiO_2, $CaCO_3$, Clay etc.
- Colored Inorganics are Iron compounds like Ferric Ferro Cyanates (Iron Blue).
- Toners are Plasticized Carbon Particles.

Better understanding of Printing Technology and Print inks chemical nature and composition, will help to design proper de-inking system and de-inking chemical for suitable application and end use.

Reaction of De-Inking Enzyme with Pulp Fibers

Chemicals used for de-inking like caustic, fatty acid based de-inking chemicals react with binder by saponifying or solubilizing the same. Hence pigment de-bonds from fiber. This is because caustic saponifies fatty acid based Vehicle part of ink and solvent part of de-inking chemical dissolves it to remove pigment.

ENZYME DE-INKING

In case of enzymatic de-inking it is like of 'hair-cut' or trimming action.

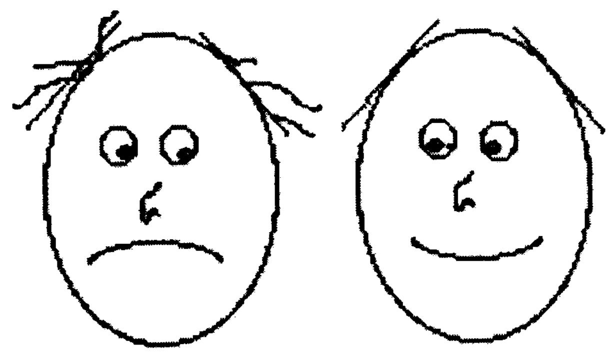


Figure 1 :

Recycled fiber is already once refined and processed pulp prior to paper-making. Slushing of the same in Hydrapulping doesn't loose original fiber characteristics much and it will have some fibrils on pulp fiber attached to which are ink pigments. Toner particles with fewer fibers are more likely to be carried to the surface during flotation. Figure 1, offers a cartoon notion of how air flotation works in removing ink particles from pulp fibers. The bubble on the left looks as though it is having a bad hair day.

He's got a lot of cellulose fibers still attached to the toner particles that he is carrying along, and they're going to fall off before he gets to the surface. The bubble on the right has picked up two particles that are free of fiber, and as a consequence they stick to the bubble much better and experience less drag from interaction with the water. If you can give the toner particles a clean shave, they'll get carried to the top much faster. Cellulases in bio-deinking enzyme along with Hemi-cellulase play a major part in detaching toner particles with little fibre/fibrils and trim them effectively. Toners are plastic polymers that are fused to fibers. Unlike dispersible inks that occur in newsprint or offset printing, laser and xerographic inks don't disperse. The residual ink decreases the brightness, and the toner particles create a conspicuous background. Only Enzymatic de-inking is the real solution for this kind of tough grade to de-ink efficiently.

Enzymatic de-inking is very effective for tougher grades of office records with laser, photographic printing etc (toners) also.

Typical Dosing Point in a Two Loop System

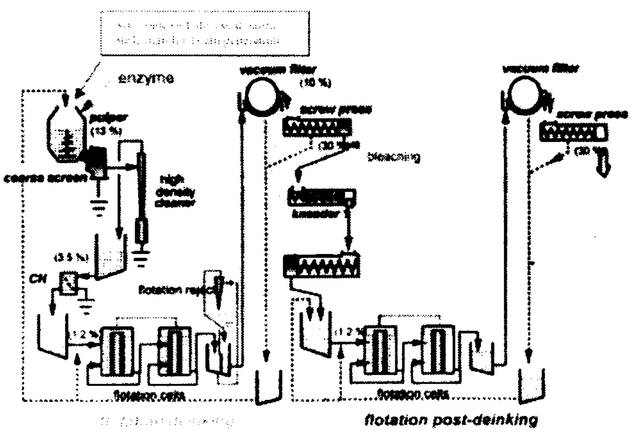


Figure 2 :

MECHANISM

Bio-deinking enzymes are likely to act on hydrodynamic forces to increasethe filtration and floatation rates. Thus they act in separation process of fiber and ink pigment.

They might also decrease the specific surface area of the fibers and thereby reduce interaction with contaminants. That is to say there might be microfibrils on the surface of these very frazzled, recycled fibers, which could be trapping the ink particles, and **by giving the fibers a "haircut", we reduce their adhesion.**

Most important factor with respect to toner/ink removal is by the increased flotation efficiencies imparted by cellulase activities. Regular usage of bio-deinking enzyme during plant trials had revealed that as per shown in Figure-2, if the sequence and application strategy is perfect, **it helped to eliminate the usage of following chemicals stage wise.**

- Absolutely no usage of caustic or bear minimum usage in case of mill water problems to maintain neutral to alkaline pH.
- This minimum usage may be due to back water recycling, if acid sizing is in practice.
- Absolutely no usage of Sodium Silicate, Fatty acid based/Solvent based de-inking chemical and Bleaching chemical in Hydra-pulper stage.

A Few Case Studies for Enzymatic Deinking

Mill A

Objective : The objective of the trial was to reduce the cost of production without adversely effecting quality of the final product.

Mill was carrying out Conventional Deinking in a High Consistency Pulper. The trial of Biodeink D was taken in our presence for a period of 3 days and the mill decided to continue its use. The following table gives the conditions employed under Conventional Deinking and Enzymatic Deinking.

Mill B

Objective : In Mill B The objective of the study was to improve the quality of the deinked pulp in terms of its various parameters such as reduction in stickies, improvement in brightness and cost reduction. Mill B trial was taken for a period of three days and the trial results were so impressive that they decided to use continuously the enzyme.

Here again the pulping is carried out in a High Consistency Pulper.

Mill C

A Mill manufacturing Writing & Printing Paper was

Table 1 : Chemicals Charged in The Pulper/M.T of O.D. Pulp

Chemicals	**Before Enzymatic Deinking(Kg)**	**During Enzymatic Deinking (Kg)**
Surfactant	1.0	1.0
Caustic Lye (100%)	14.0	4.0
Sodium Silicate	22.0	5.0
Hydrogen Peroxide	14.0	NIL
Biodeink-D	NIL	0.400

The mill had a saving of Rs. 300 P.M.T of Deinked Pulp.

Table 2 : Chemicals Charged in the Pulper/M.t. of Waste Paper

Chemicals	Before Enzymatic Deinking(Kg)	During Enzymatic Deinking (Kg)
Surfactant	2.0-3.0	2.0-3.0
Caustic Lye (100%)	6.0-7.0	Nil to 1.0
Sodium Silicate	7.0-8.0	1.5-2.0
Hydrogen Peroxide	5.0	NIL
Biodeink-D	NIL	0.3

At a slightly higher brightness of 0.5 to 1.0% the mill observed a cost saving of around Rs. 150 P.M.T of Deinked Pulp.

given a trial for about 7 days with Biodeink-D. The objective of the trial being reduction in cost while maintaining the brightness at the existing level. The trial was a successful one and mill decided to use the Biodeink-D on a regular basis.

Table 3 : Chemical Charged in the Pulper per Pulper

Chemicals	Before Enzymatic Deinking(Kg)	During Enzymatic Deinking (Kg)
Surfactant	8.0-10.0	8.0-10.0
Caustic Lye (100%)	25.0	6.0
Sodium Silicate	30.0	10.0
Hydrogen Peroxide	50.0	NIL
Biodeink-D	NIL	1.0

There was a cost saving of around Rs. 140-150 P.M.T of deinked pulp.

Operating Conditions for Enzymatic Deinking :

pH : 6.0-8.0
Temperature : 35-600C
Retention Time : 30-45 min.
Enzyme Dosage : 250-300 gms/ton of waste paper

ADVANTAGES OF ENZYME DE-INKING ARE

- Reduced chemical cost
- Reduced effluent toxicity
- Higher brightness
- Improved drainage properties
- Saving in energy
- Eco-friendly application
- No alkaline yellowing due to neutral pH conditions.
- Lower BOD/COD values due to neutral pH treatment. No alkaline hydrolysis of cellulose fibers.
- No side effects to pulp quality

Next step after enzymatic de-inking is processing the pulp suitably in alkaline sizing conditions.

Before switching over, the filler characteristics study is of paramount imporatance. Some case studies and technical observations are as follows:

ALKALINE SIZING OF DE-INKED PULPS

A FEW CASE STUDIES

1. In a few Paper Mills, We got frequent complaints about cobb variations and higher consumption of Size and Alum even though Mill water conditions were satisfactory.
2. After segregation and pH evaluation of slushed pulps it was revealed that the mill is using knowingly or unknowingly some waste paper filled with Calcium Carbonate.
3. Coated Papers and Window envelops are definite indication of Carbonate filled Papers. Paper pH and slushed pulp pH un-stability helped to understand its problem.
4. Depending on degree of Carbonate levels, various sizing methods were suggested. Some were recommended to switch over to Neutral sizing and forwarding / advancing dosages without giving much scope for alum / filler reaction.
5. In cases, where Carbonate filler was found to be higher than 5-8%, and furnish is beyond the scope for acid or neutral sizing, alkaline sizing was recommended.
6. We recommended to go for Alkaline sizing with

AKD due to the fact that its emulsion is much stable and easy to be used for even small mills. Only metering pumps are enough unlike emulsification system for ASA.

7. Some reported to us that they have size press also and would like to go for alkaline sizing in economic means. They use filler as locally available Ground Calcium Carbonate. We recommended them to start with trial initially at 70-80% size dosage in wet end and 10-20% in size press application. Slowly we have transferred/shifted AKD dosage to size press as high as 25-30%.
8. Partial usage of AKD Emulsion in size press had produced consistent cobb values, even consumption and reduced consumption compared to similar quality mills with size press.
9. In this experiment of size press application, we took the help of formulation expert to blend AKD emulsion with Cationic Starch solution and PVC solutions. The experiment had produced satisfactory and very economic results.
10. Another mill in the area, reported us that even though sizing efficacy was satisfactory with AKD emulsion, they are experiencing size reversion complaints occasionally, we have concentrated to find the relation between artificial curing and natural curing.

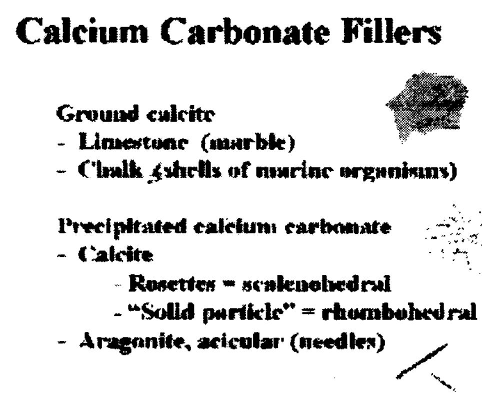
- For artificial curing, normal method of curing pope reel sample for 10 minutes in oven at 110 degrees centigrade was followed.
- This was compared with normal setting of 24-48 hours. We found that after 24-32 hours result is matching with Oven curing.
- However again complain has come after three months that reversion in sizing observed in certain lots.
- Careful study of furnish and its filler properties revealed that filler embedded in furnish is not of Ground Calcium Carbonate but of Precipitated Calcium Carbonate. Microscopic observation and evaluation in well equipped laboratories confirmed the facts.
- We also related the matter that Waste Paper imports from North America/Britain etc have GCC (Ground Calcium Carbonate), where as Waste Paper originated from European countries mostly have PCC (Precipitated Calcium Carbonate).
- As the Mill people cannot change their existing furnish, we advised them to increase size dosage and from our side we also increased cationic promoter level in AKD Emulsion.
- In addition to this we jointly discussed the problem with mill people and agreed that norms for artificial curing shall be reduced to 95 degrees temperature instead of 110 degrees centigrade to meet the after shocks of fugitive sizing.

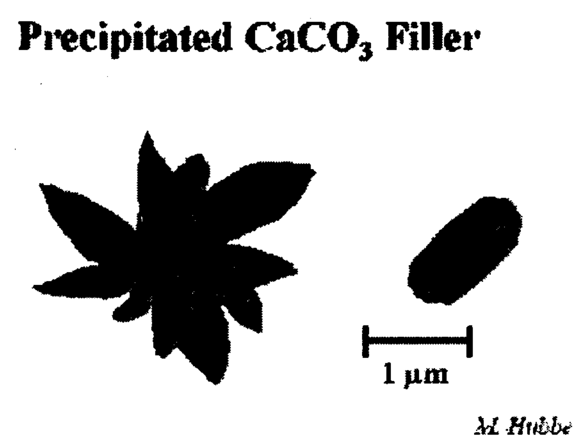
From this experience we came to the idea that fugitive sizing occasionally effecting the paper quality and giving size reversion after a few months is due to the presence of Precipitated Calcium Carbonate in excessive quantities in waste paper.

This forced us to understand the structure and surface area of Ground Calcium Carbonate vs Precipitated Calcium Carbonate. Precipitated Calcium Carbonate at the same percentage level of GCC can adsorb five to six time AKD emulsion but looses its sizing property after some time resulting in reverse sizing.

The below depicted structural variations of Ground

Papers filled with Precipitated Calcium Carbonate pose more problems in size consumption and size reversion. (fugitive sizing).





Another important phenomena is its pH turbulence.

In general either of the fillers impart more alkaline pH to stock (without any chemical addition slushed pulp alone). It is more in the case of Precipitated Calcium Carbonate due to its nature of origin (reprecipitation from Milk of lime). At the outset both the pulps will have pH higher that 8.0.

Calcium Carbonate vs Precipitated Calcium Carbonate throw more light on the subject and reasons for sizing problems.

Alkaline Sizing, The Ultimate Solution for Imported Waste Paper Furnish

ASA and AKD emulsions are synthetic sizes used for alkaline sizing with improved wet end chemistry and retention mechanism. In general Indian Mills opt for AKD Emulsion, compared to ASA emulsion as AKD Emulsion is stable, its shelf life is reasonably good for two months storage time and easy to handle with less capital investments. Where as in the case of ASA emulsification, it requires in-plant emulsifying unit which is expensive and shall be borne by either supplier or consumer. The only advantage with ASA size emulsion is its instant size effect unlike AKD emulsion, which requires longer time for size curing. Both ASA and AKD emulsions are cellulose reactive in nature and Anchoring Mechanism of both ASA and AKD are depicted in pictures. However ASA had small disadvantage as its emulsion is not stable and consumed at the earliest in five minutes time after production and hence in-plant production of the same near Paper Machine. Any frequent stoppages of Machine for runnability problems etc. likely to cause wastage of prepared emulsion, which do hydralyze and loose its property.

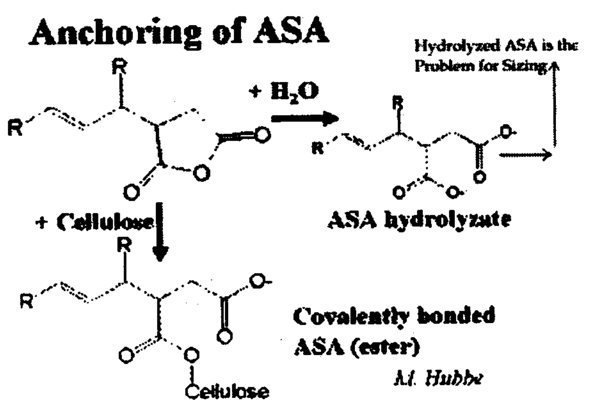
Salient features of Alkaline Paper Making with AKD Emulsion are as follows

- Alkaline Paper Making needs different approach compared to acid sizing.
- Switching over to Alkaine sizing from acid sizing requires thorough boil-out of system.
- Alkaline sizing requires Cationic promoters, Cationic Starch and Suitable Retinon aid.
- First Pass Retention shall be established well in alkaline sizing system. A minium of 75% F.P.R. is needed.

Major Differences Between AKD and ASA Sizing

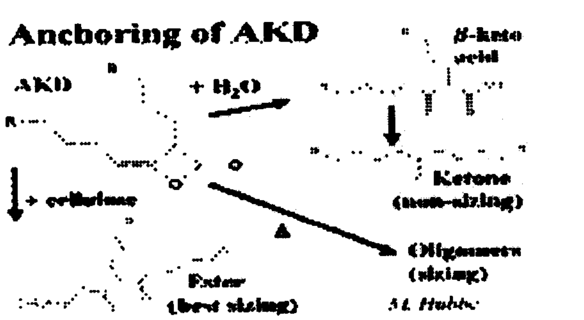
AKD Sizing	ASA Sizing
Completely Alum free system. Alum is harmful for the system.	A Small quantity of Alum (0.5%) do give better results.
Emulsion is stable for two to three months.	Emulsion is to be prepared at mill site only. It has to be consumed at the earliest time in five minutes.
Cationic Starch is generally used to produce emulsion.	Cationic Polymer or Cationic starch can be used.
On Machine cobb is not available. Curing is required.	On Machine cobb is available.

Anchoring Mechanism of ASA Size



Anchoring Mechanism of AKD Size

Ester Formation gives best Sizing, Where as Ketone and Keto acid are Problems



- Dye Selection is important and must as dye bleeding is possible.
- GCC is better selection than PCC due to its better surface area.
- PCC Surface area likely to be 5-6 times higher than GCC even at similar particle size due to its shape.
- AKD is available as ready to use emulsion, which can be stored for two months easily.
- Suitable deposit control program is must.
- Hence suitable biocide selection is considered for alkaline sizing conditions.

Cost Benefits

1. Lower fiber cost due to improved filler addition and improved first pass retention.
2. Increased pulp yield in Waste Paper use due to retention of Carbonate filler.
3. Increased Production due to better machine runnability and improved web strength.
4. Improvement in Paper brightness and Shade.
5. Reduction in shade variation and improvement in permanency.
6. Less usage of Optical Brightening agent, steam in drying etc.
7. Corrosion free back water system with better closure of system.
8. Considerable increase in yield of Waste Paper Processing as filler is within.