신문지 탈묵공정의 pH에 따른 수율 변화 및 그 최적화 방안

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ABSTRACT

재생 신문지 생산공정의 탈묵처리는 공정의 pH에 따라 그 수율이 달라진다. 기존의 알칼리 탈묵처리 조건으로부터 의사 중성 혹은 중성으로 pH가 중화됨에 따라 과도한 탈묵 리젝트가 발생하고 수율이 저하되는 문제점이 있다. 본 연구에서는 탈묵 pH에 따른 수율 변화를 실험실 평가를 바탕으로 분석하고 리젝트를 절감하는 방안을 탐색하여 수율을 최적화하고자 하였다.

Introduction

Excessive reject from froth flotation deinking

Due to the increased demand in developing countries, international trade of recovered paper has been growing every year[1, 2]. To confirm the sustainable development of the paper industry in the future, sufficient supply of raw material, in particular high quality recovered paper is inevitably required. Increasing the collection rate can be a solution for the shortage of recovered paper but increasing recycling yield is also important. Recycling yield of recovered paper is mainly influenced by two major factors: the amount of contaminants and the removal efficiency of contaminants during the stock preparation process. Old newspaper gives relatively low recycling yield, in particular compared with packaging grade due to losses in the deinking process.

Deinking processes for recovered paper can be classified as washing and flotation. These days, selective segregation of ink by froth flotation is preferred due to reduced contamination and consumption of process water. Ink separation by froth flotation is based on the differences in surface properties between hydrophobic ink and hydrophilic fibers. Hydrophobic ink particles show a strong tendency to adhere on air bubbles. After attachment, they are to be segregated from hydrophilic components including hydrated cellulose fibers, fines and inorganic fillers. The efficiency of flotation deinking process depends upon the surface physico-chemical properties and the hydraulic movement of suspended solids in flotation cell. Ink particles are more efficiently removed when the hydrophobic ink particles are completely detached from hydrophilic fiber surfaces and when the detached ink particles collide with air bubbles in flotation cell and are floated to the surface.

Based on organic solvent extraction data, the amount of ink in deinking stock was estimated as below 2% (dry basis). However, the total reject loss during flotation deinking of ONP is usually higher than 10%. In addition to the hydrophobic ink particles, pulp fines and inorganic pigments are also floated and discharged during flotation. Although virgin pulp fines and unused inorganic pigments or fillers have hydrophilic surfaces, during the deinking process they have hydrophobic surfaces due to the adsorption of hydrophobic materials including sticky contaminants or other chemicals intentionally added at wet end. Here the stickies means various polymeric contaminants including styrene-butadiene latex, polyvinyl acetate (PVAc), vinyl acetate (VA), polystyrene (PS), polyisoprene, hot melts (EVA, polyethylene, waxes). Wet end chemicals include sizing agents, which adsorb mainly on fines due to their large specific surface area. These fines could be floated easily in deinking cells because of their physical size and surface hydrophobicity.

Fragmented stickies also adsorb on the surface of suspended solids, again, preferentially on the fines due to their higher specific surface area3). Most of the inorganic pigment particles originate from coating layers of OMG. Surfaces of inorganic pigments in deinking stock are usually covered by insoluble hydrophobic synthetic binder, SB latex. As a result, small particles including fiber fines and inorganic pigments are lost by rejection in the froth flotation step. The flotation loss means not only simple lossof raw materials but also waste of energy for stock preparation including pulping, cleaning and coarse screening. The flotation loss also results in unnecessary contamination of process water. For these reasons it is urgently required to optimize the flotation efficiency and to reduce the flotation loss. If we can control the flotation selectivity by modifying the hydrophobicity of fine materials in deinking stock, reduction of production cost could be achieved along with environmental impact.

Deinking pH vs. froth flotation loss

Reduction of the surface hydrophobicity of fine materials could be easily done by increasing alkali chemicals in the pulping stage, to increase alkaline hydrolysis of certain types of chemical linkages. That is, if a sufficient amount of alkali is added to pulping stage, wetting or hydration of hydrophobic suspended solids is promoted and loss of fines and minerals can be reduced. However, higher alkali dosage in pulping and deinking may indiscriminately dissolve or fragment inks and stickies. Therefore, a special method for the selective modification of valuable hydrophobic particles is required.

Reducing alkali in deinking process of ONP has been considered. Currently suggested neutral deinking of ONP has the primary benefits of significantly reduced chemical costs by the elimination of caustic, peroxide, chelant, biocide for catalase control and all or part of the sodium silicate from the pulper. There are other related advantages as well, since several of these eliminated chemicals have serious safety and environmental implications4). However one of the original purposes behind the development of neutral deinking technology was to reduce the breakup of stickies containing alkali-soluble lattices and adhesives that are readily dispersed when recovered paper is pulped with high alkali levels5). Although cleaner and cheaper deinking of ONP could be achieved at the neutral or low alkaline conditions, an excessive loss from flotation is unavoidable due to less wetting of fines6,7). The focus of this work is how to overcome this contradictory relation, getting the best of both.

Experimental

The lipase was added after concentrating the hydrophobic materials and prior to separating and discharging the concentrated materials. The main components in primary froth-flotation rejects are ink and paper components with adsorbed hydrophobic materials on their surfaces. In the deinking method used in this study, the primary stage flotation rejects are treated with the lipase to make the fiber fines and mineral particles more hydrophilic, followed by the normal secondary flotation stage to reduce the amount of the final flotation rejects. While lipase could be added to whole stock, for example at the drum pulper inlet or the feed of primary flotation stage, the amount of lipase added can be reduced by more than 70% by the selective application of lipase on only the rejects of the primary flotation stage. In addition to economic gains, the application of lipase on the entire stock causes less efficient segregation of ink particles in the primary flotation stage due to the excessive reduction of froth generation and reduced froth stability. The lipase can change the hydrophobic surface of small particles which is the key in the stabilization of froth, so the amount of froth or reject from the primary flotation stage could be reduced significantly. An excessive decrease of flotation reject could be the reason for deficientsegregation of ink particles in flotation. This will be further explored in next Part of this series.

The flotation process of ONP with lipase applied on the secondary froth flotation is illustrated in Fig. 1. In order to apply the lipase to the secondary stage in lab scale flotation, reject material from the primary flotation stage at Norske Skog Korea Co., Ltd. in JeonJu, Republic of Korea, was obtained.

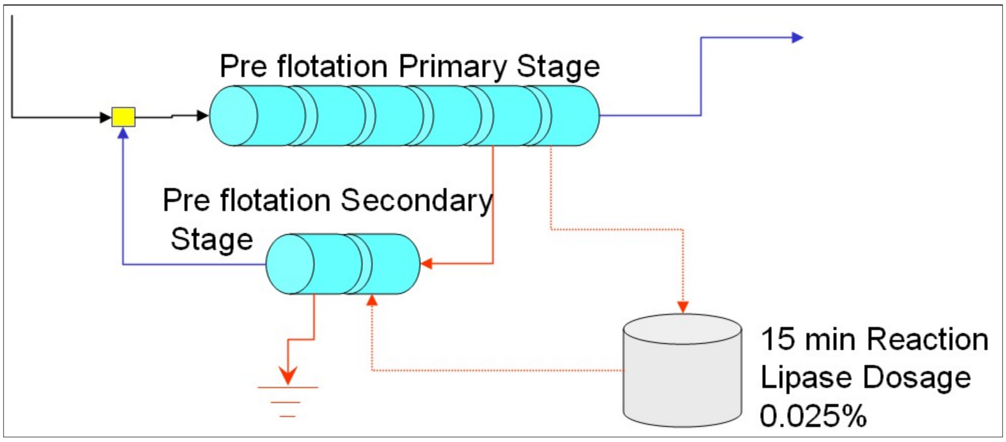


Fig. 1. Flotation process for ONP, and schematic for lipase application to the second stage flotation feed.

Table 1 shows the pulping conditions in the drum pulper in the JeonJu mill. Since the addition level of caustic soda was relatively low, hydrogen peroxide was not added to drum and the pulping pH was low compared with the conventional conditions [5)].

The primary froth-flotation rejects corresponding to about 30% of the paper components were treated with the secondary froth flotation. The primary froth-flotation rejects consist of about 66% ash (inorganic fillers), about 30% organic fines, and less than 1% fibers. Water drop contact angle of three pads was measured with a Goniometer to check the hydrophobicity of the secondary flotation feed (primary flotation reject), accept and reject, as shown in Fig. 2.

Table 1. Pulping conditions of the drum pulper

Stock composition	
Korean ONP (%)	60
American ONP (%)	20
European ONP (%)	10
American OMG (%)	10

Pulping Conditions	
Temperature(°C)	47
Consistency (%)	17
H_2O_2 (%)	-
NaOH (%)	0.5
Silicate (%)	0.6
DTPA or Other chelating agent	-
Other Additives (%)	Scale inhibitor 600cc
Dump Chest Consistency(%), pH	3.5%, 9.5
Ash Content (%)	21.5
Yield (%)	98.2

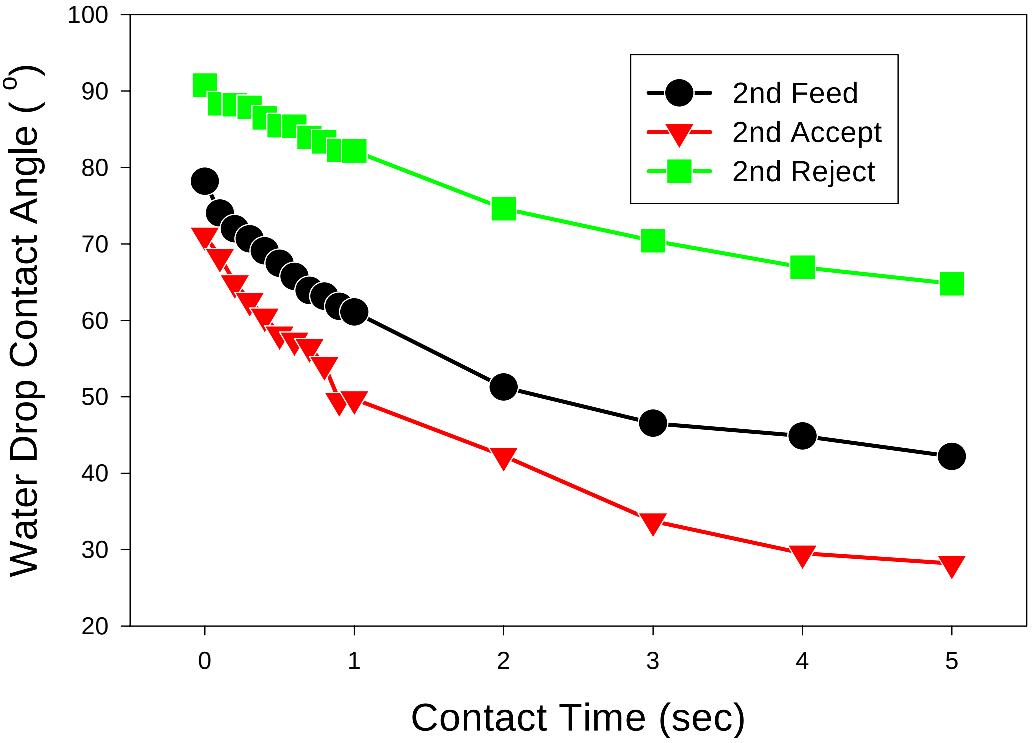


Fig. 2. Water drop contact angle of secondary flotation feed, accept and reject pads.

The lipase (ResinaseA2X, Novozymes, from *Thermomyces Lanuginosus*)was added at 0.025%(w/w) based on the total dry weight of stock to degrade hydrophobic additives and contaminants adsorbed on fines. The mixture was stirred in a Labor Flotation Cell Delta25 (Voith, Germany) for 15 minutes at 45℃ without air introduction. After agitation the treated rejects were subjected to froth flotation using a Labor Flotation Cell Delta25 (Voith, Germany) to separate rejects. The froth flotation was carried out under the following conditions: consistency: 1.3%, volume: 25 L, total dry mass: 325 g, temperature: 45℃, mixing rotor speed: 1,500 rpm, and air flow rate: 7 L/min without any additional deinking agents.
Flotation accepts and rejects were analyzed to evaluate the lipase effectiveness in terms of reject reduction and ink removal. The block diagram of the whole test procedure is shown in Fig. 3.

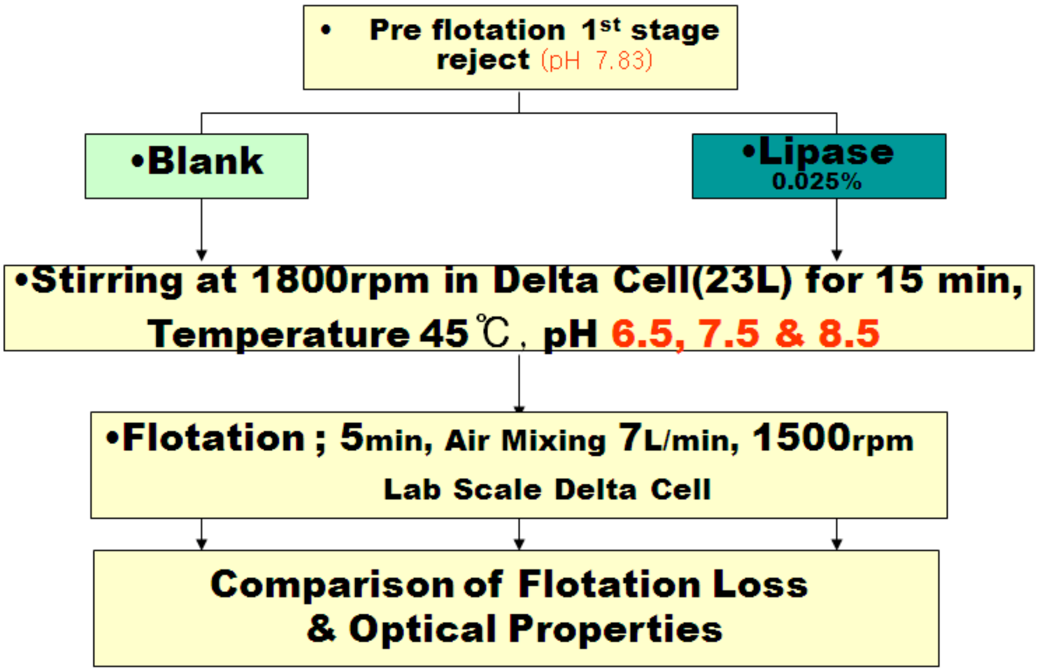


Fig. 3. Block diagram for froth flotation of primary reject of ONP with and without the application of lipase.

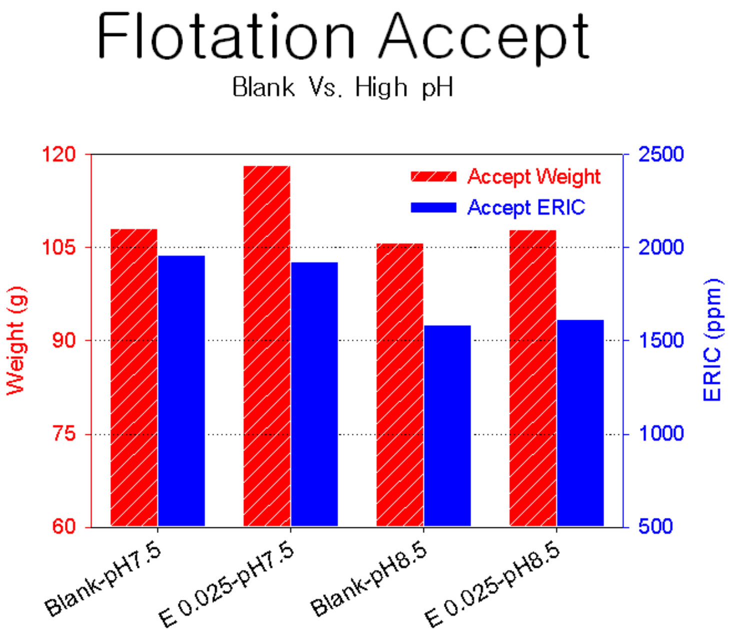
The mass of secondary froth-flotation rejects and accepts were measured and then thefroth flotation yield was calculated. Ash content was measured in a muffle furnace at 400℃.

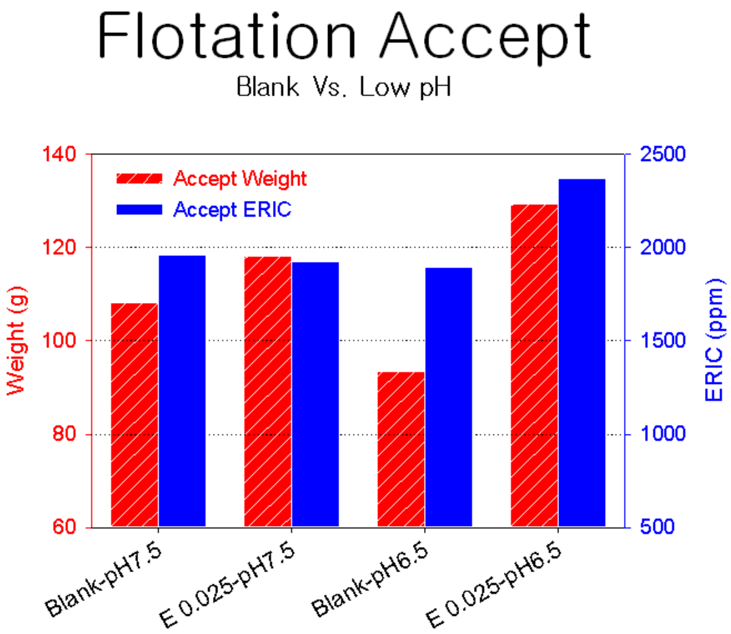
In accordance with ISO 3688:1999, the flotation accepts and rejects were molded into pads in a funnel and the basis weight of the pads was more than 200 g/m^2. Pursuant to ISO 2470:1999, ISO brightness of the pads was analyzed by measuring the reflectance of light at a wavelength of 457 nm using a spectrometer (Color Touch 2, Technidyne, U.S.A.) and the ERIC values of the pads were analyzed by measuring the reflectance of light at a wavelength of 950 nm using the same spectrometer.

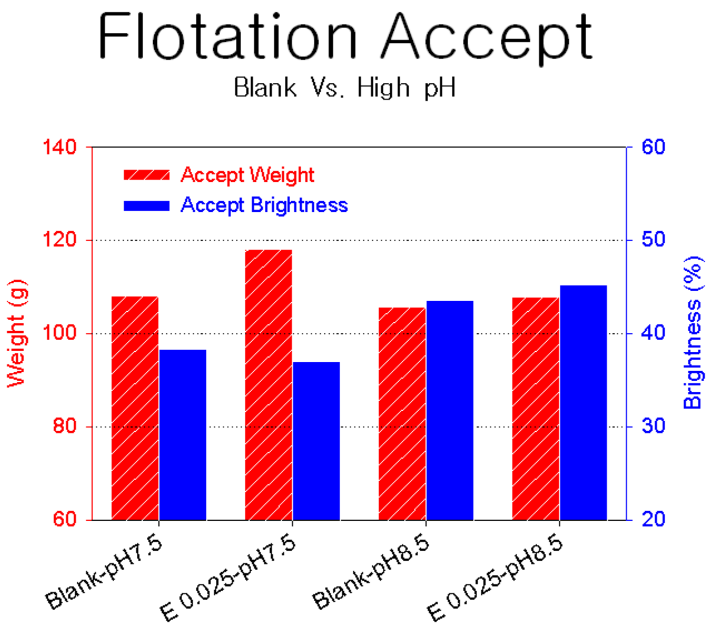
Results and Discussion

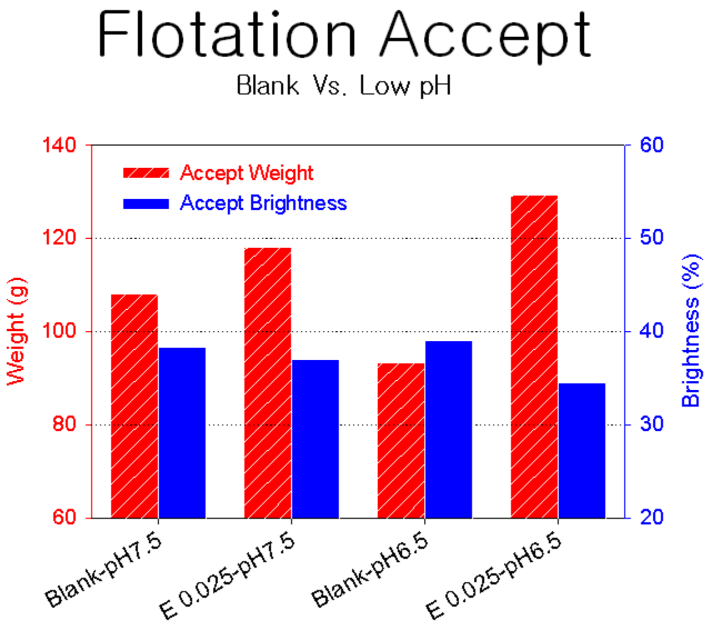
At low pH the hydration of hydrophobic surface is relatively difficult compared with the case of high pH stock and so the increase of flotation loss is unavoidable. Stock introduced to unsuccessful flotation showed low pH, froth stability, ERIC, reject consistency and high dewatering tendency compared with the case of successful flotation.

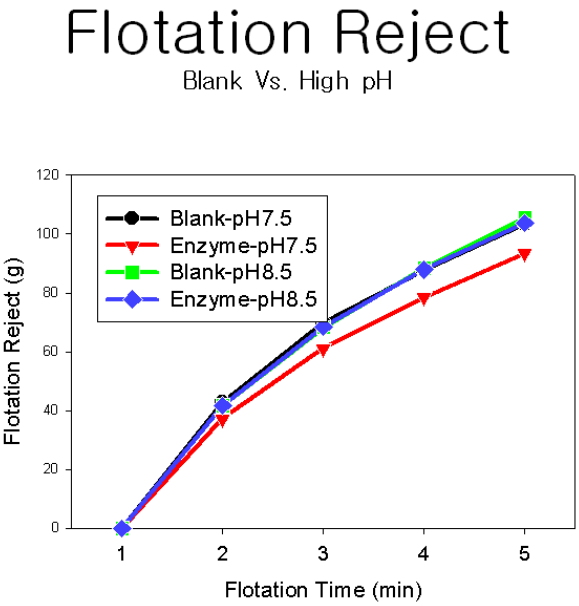
Stock showing weak froth stability contains lots of fiber or big size suspended solids according to the raise of flotation cell level and easy overflow of stock. Enzymatic hydrolysis promotes the hydration of suspended solids and the froth stability is destined to decrease for the worse. Therefore ink particles loose their chance to be accumulated in froth layer of flotation cell surface and the efficiency of ink removal goes down although flotation loss could be reduced.

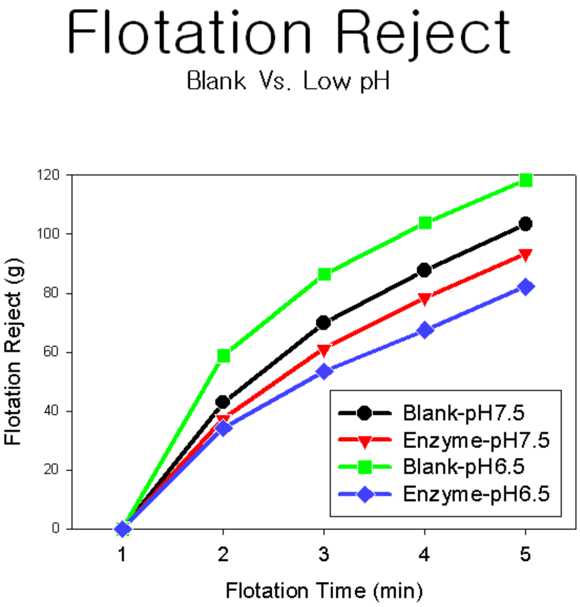

Flotation Accept
Blank Vs. High pH
Accept Weight
Accept ERIC
Weight (g)
ERIC (ppm)
120
105
90
75
60
2500
2000
1500
1000
500
Blank-pH7.5
E 0.025-pH7.5
Blank-pH8.5
E 0.025-pH8.5

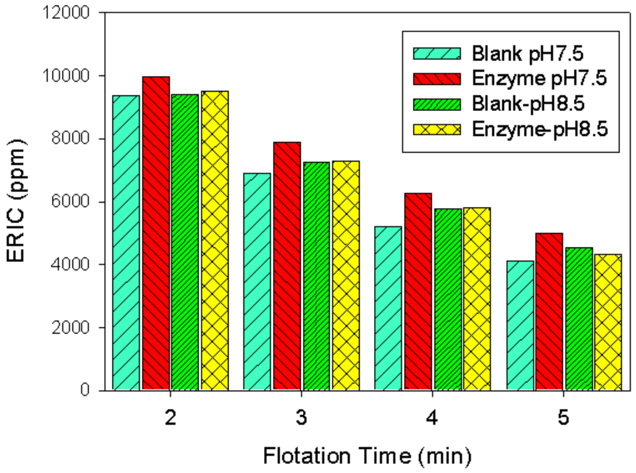

Flotation Accept
Blank Vs. Low pH
Accept Weight
Accept ERIC
Weight (g)
ERIC (ppm)
140
120
100
80
60
2500
2000
1500
1000
500
Blank-pH7.5
E 0.025-pH7.5
Blank-pH6.5
E 0.025-pH6.5


Flotation Accept
Blank Vs. High pH
Accept Weight
Accept Brightness
Weight (g)
Brightness (%)
140
120
100
80
60
60
50
40
30
20
Blank-pH7.5
E 0.025-pH7.5
Blank-pH8.5
E 0.025-pH8.5


Flotation Accept
Blank Vs. Low pH
Accept Weight
Accept Brightness
Weight (g)
Brightness (%)
140
120
100
80
60
60
50
40
30
20
Blank-pH7.5
E 0.025-pH7.5
Blank-pH6.5
E 0.025-pH6.5

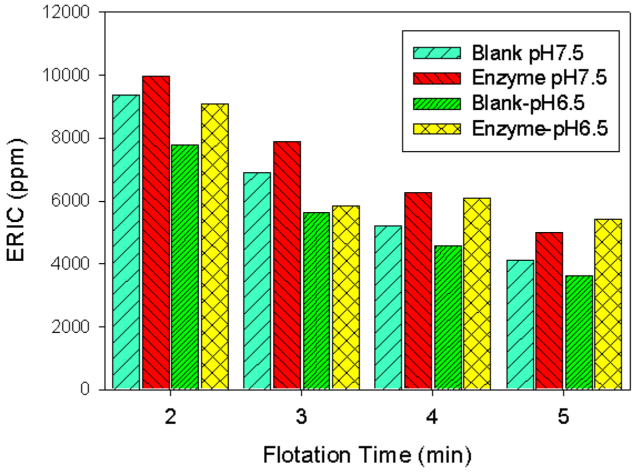

Flotation Reject
Blank Vs. High pH


Flotation Reject
Blank Vs. Low pH



Flotation Reject ERIC

Blank Vs. High pH

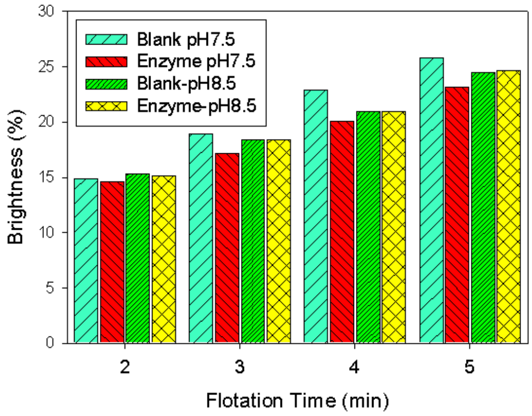


Flotation Reject ERIC

Blank Vs. Low pH

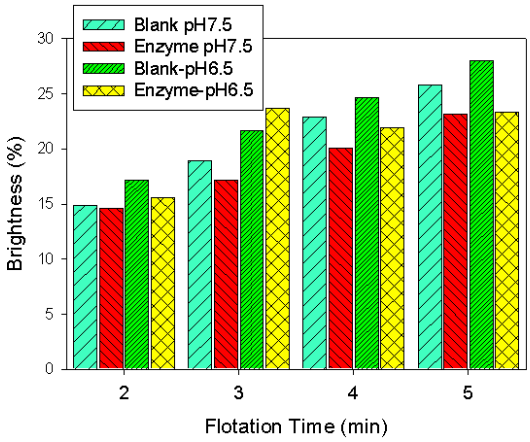
Flotation Reject Brightness

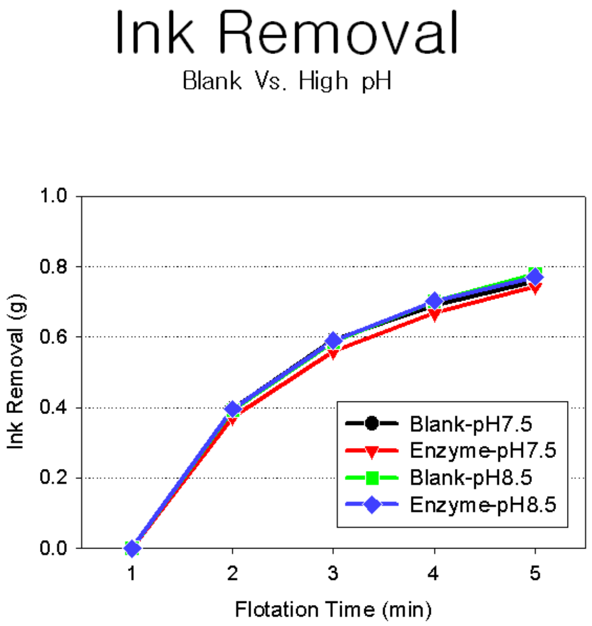
Blank Vs. High pH

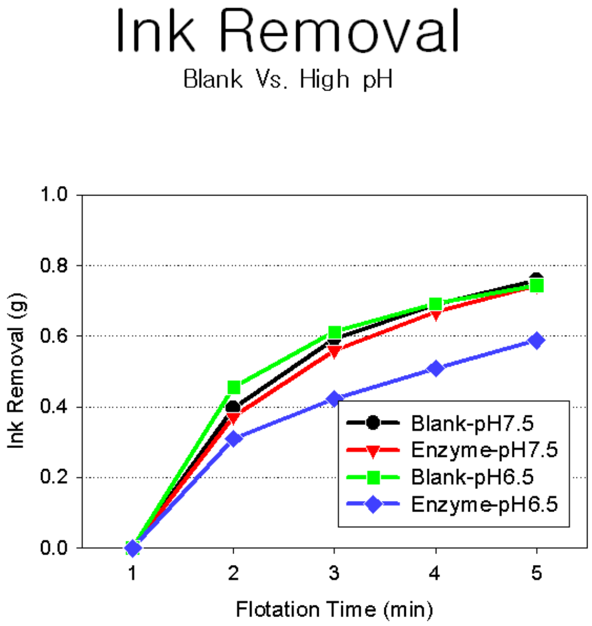


Flotation Reject Brightness

Blank Vs. Low pH

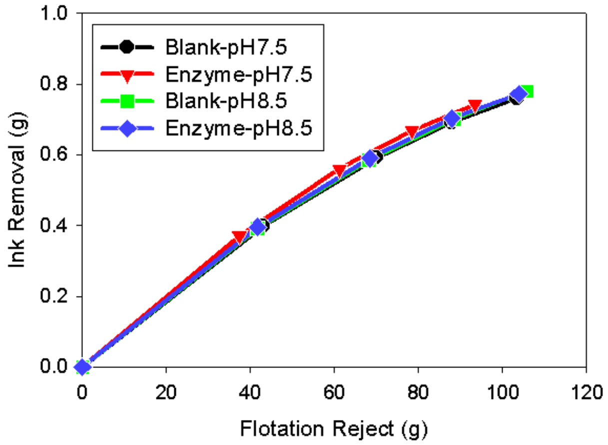



Ink Removal
Blank Vs. High pH
Ink Removal (g)
1.0
0.8
0.6
0.4
0.2
0.0
1
2
3
4
5
Flotation Time (min)
Blank-pH7.5
Enzyme-pH7.5
Blank-pH8.5
Enzyme-pH8.5


Ink Removal
Blank Vs. High pH
Ink Removal (g)
1.0
0.8
0.6
0.4
0.2
0.0
1
2
3
4
5
Flotation Time (min)
Blank-pH7.5
Enzyme-pH7.5
Blank-pH6.5
Enzyme-pH6.5

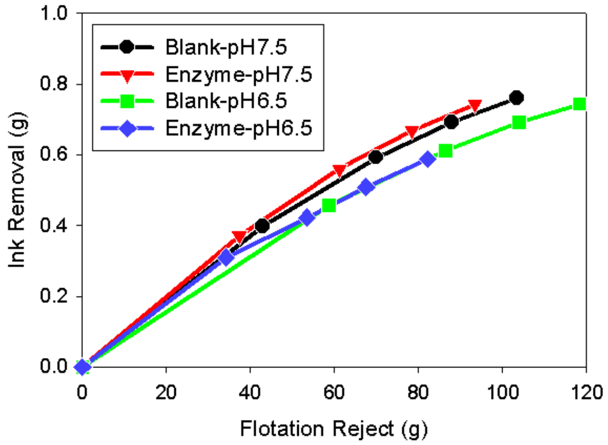
Reject Vs. Ink Removal

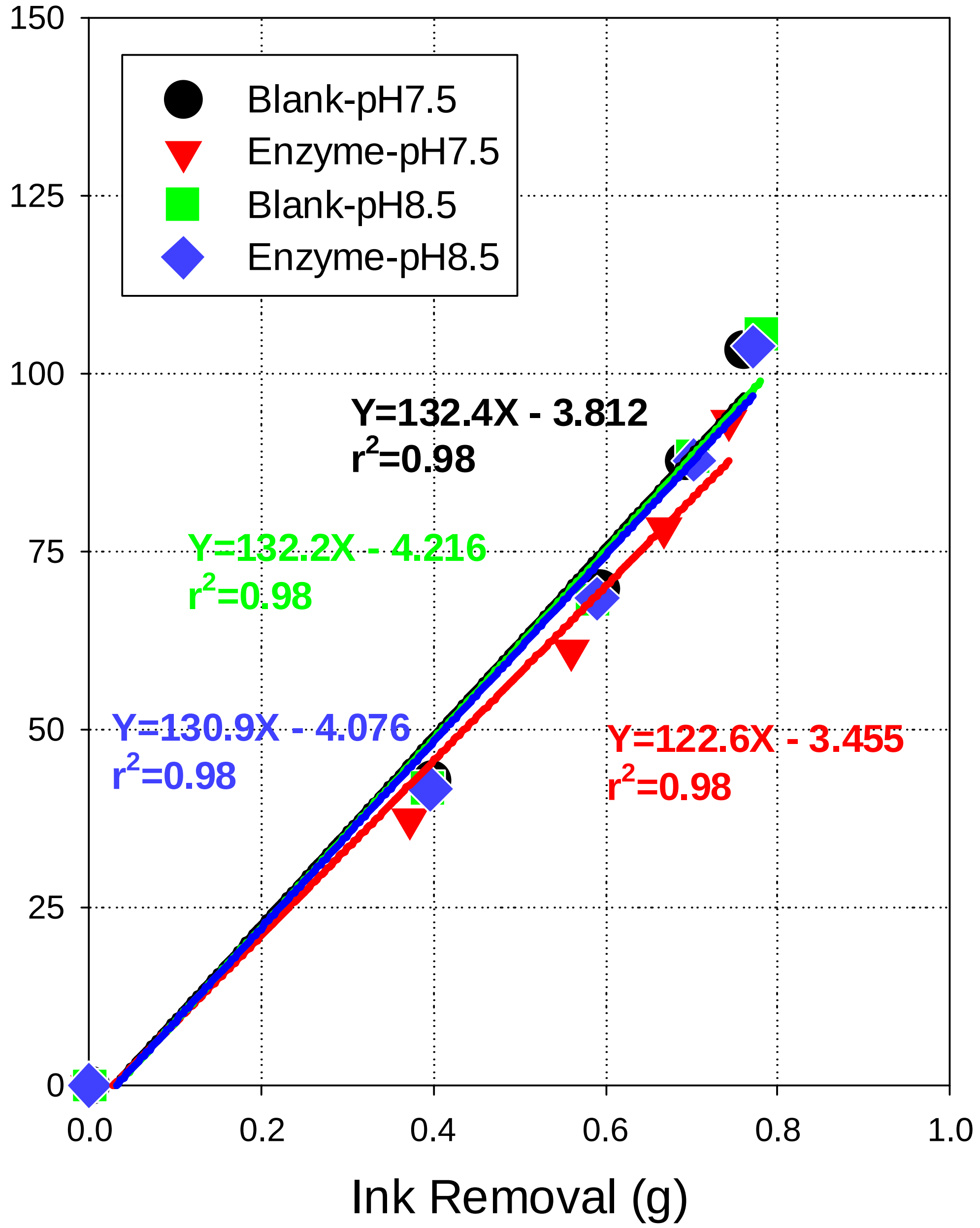
Blank Vs. High pH

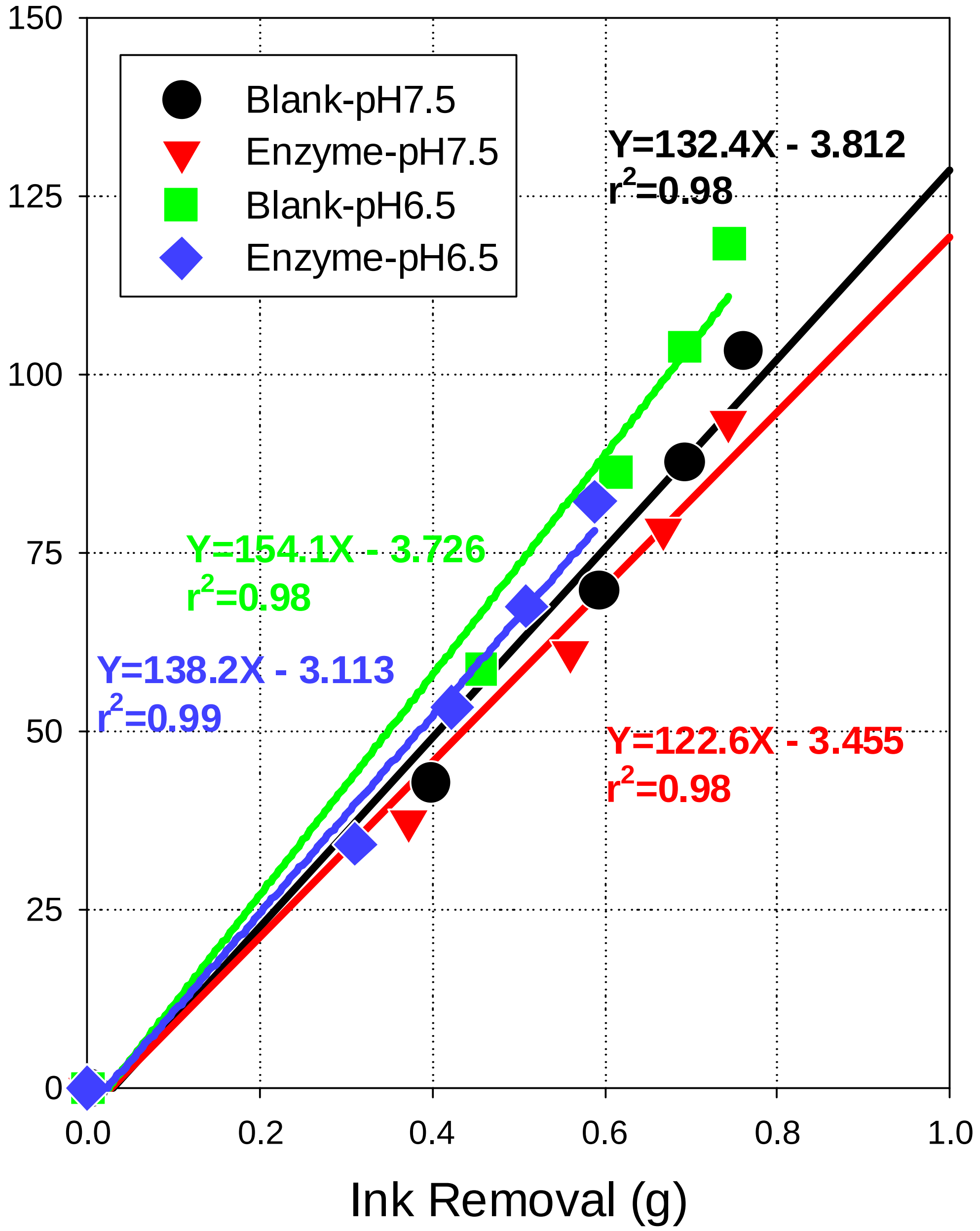


Reject Vs. Ink Removal

Blank Vs. Low pH




150
125
100
75
50
25
0
0.0
0.2
0.4
0.6
0.8
1.0
Ink Removal (g)
● Blank-pH7.5
▼ Enzyme-pH7.5
■ Blank-pH8.5
◆ Enzyme-pH8.5
Y=132.4X - 3.812
r²=0.98
Y=132.2X - 4.216
r²=0.98
Y=130.9X - 4.076
r²=0.98
Y=122.6X - 3.455
r²=0.98


150
125
100
75
50
25
0
0.0
0.2
0.4
0.6
0.8
1.0
Ink Removal (g)
Blank-pH7.5
Enzyme-pH7.5
Blank-pH6.5
Enzyme-pH6.5
Y=132.4X - 3.812
r^2=0.98
Y=154.1X - 3.726
r^2=0.98
Y=138.2X - 3.113
r^2=0.99
Y=122.6X - 3.455
r^2=0.98

Conclusions

Although cleaner and cheaper deinking of ONP could be accomplished at the neutral or low alkaline condition, excessive reject from froth-flotation is unavoidable under these conditions. Hence reduction of alkali dosage sacrifices the yield of ONP recycling. We suggest that lipase is a better choice to change the hydrophobicity of ONP than conventional inorganic alkali. The lipase hydrolysis of ester linkages on the surface of hydrophobic fines was suggested in a previous paper as a new method to promote hydration of the fines and to prevent the unwanted loss of these fines during froth flotation. Lipase was added before the secondary flotation stage of ONP such that concentrated hydrophobic fine components were subjected to selective lipase hydrolysis. As a result, secondary flotation rejects were reduced while the brightness and the effective residual ink concentration (ERIC) of secondary flotation accepts were maintained at the same level with the non-treated case.

Reference

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