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Recovery Process for the Recycling of Waste Carbon Black

Sungoh Lee[1)], Nampyo Kook[2)], Tam Tran[3)], Bangsup Shin[4)] and Myongjun Kim[5)]

1),3) Chem. Eng. and Ind. Chem., Univ. of New South Wales, Sydney, 2052, Australia.
2) Civil and Environmental Engineering, Hanlyo University, Korea.
4) Kwangju Woman's University
5) Resources and Energy Engineering, Chonnam National University, Korea

Impurities removal from waste carbon black was carried out to produce high-grade carbon black. A lot of hydrophilic carbon black is produced as a byproduct of the hydrogen production process by flame decomposition of water. Due to its impurity content such as sulphur, iron, ash and etc., it can only be used as low-grade carbon or burnt out. High-grade hydrophilic carbon black is 3-5 times more expensive than oil-based carbon black because of its process difficulties and requires pollutant treatment. Hydrophilic carbon is normally used for conductive materials for batteries, pigment for plastics, electric wire covering, additives for rubber, etc.. In these applications, hydrophilic carbon must maintain its high purity. In this study magnetic separation, froth flotation and ultrasonic treatment were employed to remove impurities from the low-grade hydrophilic carbon black. As results, the ash, iron and sulphur content of product decreased to less than 0.01wt.%, 0.01wt.% and 0.3wt% respectively, and the surface area of product was about 930㎡/g.
Key words: Waste carbon sludge, Hydrophilic carbon, Magnetic separation, Ultrasonic processing, Froth flotation

Introduction

Total world production of carbon black is about 6 million tones per year [1]. Most of this is used in the rubber industry as a reinforcing filler. The rubber industry is by far the largest consumer of carbon black, accounting for approximately 90% of total carbon black sales and the remaining 10% is used to the non-rubber industry. Their uses as pigment blacks in printing inks and plastic industry are the most important. Carbon blacks has unique properties such as high chemical and electrical resistance, high strength, thermal and chemical stability and therefore is widely used in tyres, paints and coatings, electrodes in primary and secondary batteries and fuel cells, and in the production of electrically conductive plastics and inks for printing [1-3]. The product quality varies according to the carbon structure, its particle size distribution and surface functionality. Hydrophilic carbon is the raw material from which all types carbon black are made, either via incomplete combustion or thermal decomposition depending on the presence or absence of oxygen during processing [4].

In most synthesis gas manufacturing processes used in Korea, water and fuel oil are used to produce hydrogen gas by thermal decomposition (according to the reaction $C_nH_m \quad nH_2O \quad ^{Heat}o \; nCO_2 \quad \frac{m}{2}H_2 \quad nC$) [5]. Incomplete combustion at a high pressure and temperature will yield carbon black as a byproduct that is very fine and has a high surface area. However, the produced carbon black contains many impurities such as iron and ash, which are harmful to most applications. The carbon black produced in this process is therefore burnt or used in applications where high purity is not required [6,7]. Synthesis gas manufacturers in Korea have to treat carbon black sludge, which is produced at around 30,000 tones/year, at a high cost. Burning of this carbon black sludge also produces sulphur dioxide gas that is even harder to deal with as discharge regulations in Korea have become much stricter.

In this study, mineral processing techniques have been extensively used for purification of minerals and by-products. Raghvanan et al [8] used floc-flotation to remove ultrafine graphitic impurities from china clay and Kim et al [9] investigated the removal of unburned carbon from coal fly ash by froth floatation. High-intensity magnetic separation was also adopted by Shin [10] to remove iron from coal fly ash.

This study was therefore conducted to recover high purity carbon black by froth flotation, ultrasonic treatment and magnetic separation to remove impurities such as sulphur, iron and ash. The study was conducted on both laboratory scale and pilot plant.

Experiment

All chemicals and reagents used in this study were of analytical grade. All solutions were prepared using distilled water. For froth flotation tests, kerosene was used as collector. Aero Froth 73 (from Cyanamid), MIBC (from Cyanamid) and fine oil (from Nippon Koryo Yakuhin Co. Ltd) were used as frothers. NaOH and HCl were also used to adjust the pH.

The metal concentrations were analysed using ICP (Inductively Coupled Plasma). Thermal gravimetric and thermal differential analyses were conducted using TMA-1500 equipment. The morphology of the products and feed samples were also evaluated using scanning electron microscopy (JSM-5400). Iodine adsorption tests and N_2SA(㎡/g) were used to determine the surface area and DBP absorption method was used to analysis the structure of carbon black using dibutyl phthalate (ASTM D-2414-

79). The analysis of the tinting strength and toluene discoloration of carbon blacks were used for quality control and assessment of particle size (ASTM D-3265-80) [6].

The batch tests were conducted for each unit operation as shown in figure 1. Figure 1 shows the flow sheet for the recycling of the waste carbon sludge. In this unit operation process, the pulverization process was conducted to disperse the caked carbon sludge, using attrition mill (koryo ceramic co, kmd-1b) and ball mill (ceramic mill) with alumina ball or ultra sonification (shinhwa tech. Co., ultrasonic generator-1000 (40khz)) and mechanical stirring. A ranking was determined based on the average percents of carbon left on 275 mesh after dispersing and sieving. Flotation (denver flotator, joy manufacturing co., model: d1) and magnetic separation (boxing co. Hims) processing were conducted to remove impurities from the carbon sludge.

Waste carbon sludge
↓
Pulverization
↓
Flotation
↓
Ultrasonic treatment
↓
Magnetic separation
↓
Precipitation
↓
Dewatering
↓
Pelletization

Figure 1. Flow sheet for the recycling of the waste carbon sludge.

Results and Discussion

Characteristic of carbon sludge

The carbon black sludge usually contains 80% water and was within the range of pH 4.3 – 5.5. Dehydration of this sludge would yield a product containing 0.5-1% ash, 0.3-0.6% iron and 0.1-0.5% sulphur, as dry basis. Most of the carbon black is very fine (99.2% less than 400 mesh). The rest (0.8%) is coarse (200-400 mesh) and contains around 41% of the ash component. Table 2 shows the particle size distribution of the slurry and dried samples.paper here.

For the dry sample, the distribution of ash is almost same to the size distribution of all particles and therefore, it is very difficult to remove ash from the dry carbon. Around 41.5% of ash is under 400 mesh which is 99% of the material, but only 1% of carbon black that is larger than 400 mesh, which contains 58.5% of ash. Most of impurities in the carbon black feed are Fe, V, Ca, Na, Mg and Si.

Scanning Electron Microscopic photo of feed materials show that all fine particles are well distributed in Figure 2.

Table 2. Particle size distribution of carbon and ash in slurry and dried samples

Particle size (mesh)	Dry sample (100θC, 24hrs)		Slurry sample	
	Dist. (wt%)	Ash Dist. (wt%)	Dist. (wt%)	Ash Dist. (wt%)
+4	28.16	27.45	-	
-4/+8	19.30	20.22	-	
-8/+20	29.80	31.35	-	
-20/+50	19.25	17.24	-	
-50/+100	3.03	1.88	-	
-100/+200	0.29	1.85	-	
-200/+400	0.07	0.01	0.78	58.50
-400	-	-	99.22	41.50
Total	99.90	100	100	100

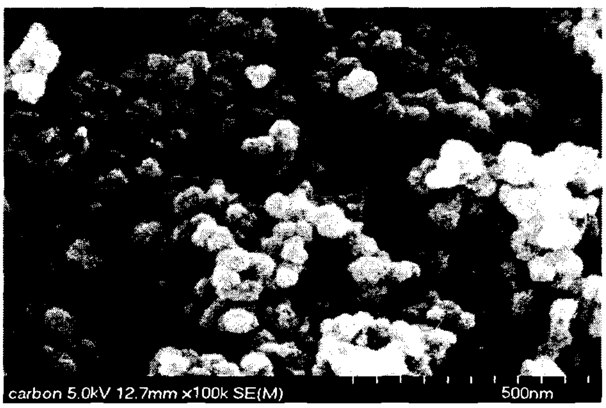

Figure 2. Scanning electron micrographs showing carbon particles.

Particle dispersion tests

It is very difficult to disperse agglomerated carbon particles in water due to attraction of particles and the oil component in the feed. The dispersion and separation tests were conducted over the range of 5 to 30 minutes at room temperature. The best time was 15 minutes, which was then fixed for all dispersion tests as shown in Table 3. The dispersion characteristics were then tested at same conditions (15 minutes, room temperature), using grinding (attrition mill and ball mill) or ultrasonification and mechanical stirring. A ranking was determined based on the average percents of carbon left on 275 mesh after dispersing and sieving.

Table 3. Dispersion of particles (% retainer by 275 mesh screening) by different techniques after 15.

Test methods	US+MS	US	AM	BM	MS
Dispersion(%)	72	24	96	90	58

About 90% of dispersion was achieved using ball mill and attrition mill after 15 minutes. However, impurities existing as large particles were also finely milled which make it harder to separate from fine carbon particles. Also, less than 60% of dispersion was achieved with mechanical stirring but more than 70% dispersion was achieved by combining stirring and ultrasonification.

Settling characteristics

The settling tests were conducted at different pulp density after mixing of pulp for 10minute. The settling point was fixed at 200ml measuring line on 2L of mass cylinder. The settling efficiency as a function of pulp density at pH 6.5 is shown in Figure 3. As most impurity and ash components are larger in size and heavier than carbon particles, their settling rate was expected to be faster than of carbon particles. More than 90% of the material tested (carbon and ash components) was well settled within 2 hours at less than 4% pulp density. However, settling % dropped as the pulp density was increased. Therefore, the slurry density should be less than 4% to settle the carbon particles. Table 4 shows the viscosity of carbon sludge. It shows that the viscosity at 4% of pulp density was sharply increased compare with 3% of pulp density. This result was shown in Figure 3.

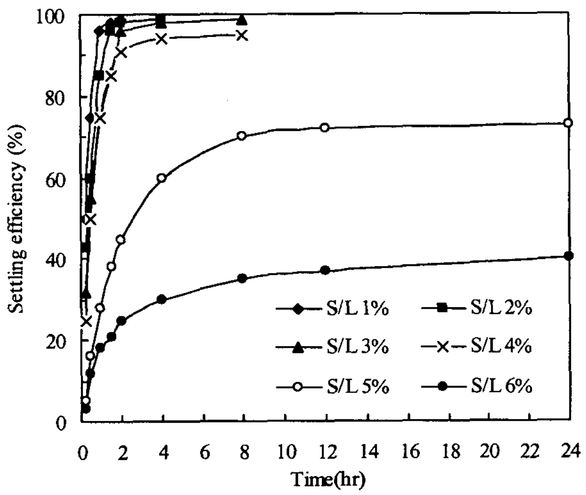

Figure 3. The settling efficiency as a function of pulp density at pH 6.5.

Table 4. The viscosity of carbon sludge

	Carbon particle ratios in water				
	1%	2%	3%	4%	5%
Viscosity (unit: cp)	60	228	336	2400	12,000

Carbon recovery by flotation

The flotation method was conducted to remove the impurities on the dispersed carbon sludge. In the flotation test, the pulp density was fixed at 3%. The amount of frothers were changed with various pH conditions. The collector used for carbon floatation is Kerosene (Kanto, Chem. Co. Inc.) and the frothers tested are Aero Froth 73 (Cyanamid Co.), MIBC (Cyanamid Co.) and Fine Oil (The Nippon Koryo Yakuhin Co., LTD). Of the frothers tested, Aero-Floth AF 73 was the most efficient at 5.5-6.5kg/t as shown in Figure 4 for flotation at 4.5 kg/t kerosene and pH 6.0. For AF73, the maximum recovery was achieved at around pH 6.0 as shown in Figure 5.

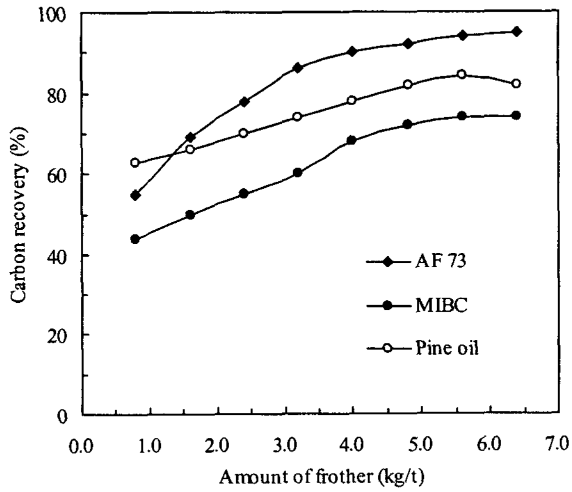

Figure 4. Carbon recovery using different frothers (Conditions: kerosene: 4.5kg/t, pH 6.0, air flow rate: 8l/min)

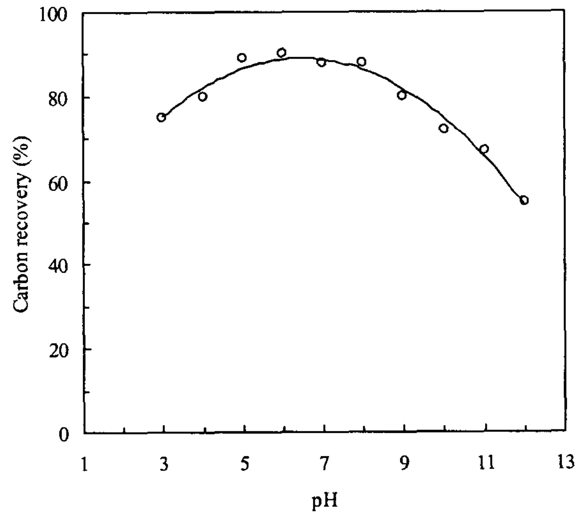

Figure 5. Carbon recovery as a function of pH values using AF73 frother (Conditions: kerosene: 4.5g/t, AF73: 4.0kg/t, air flow rate: 8l/min)

When only $Na(PO_4)_6$ of dispersant was used from 0.1-3.5kg/t without frother, carbon was well dispersed and floated. However, carbon and ash were floated together more than 3.5kg/t of $Na(PO_4)_6$. At the same condition, an aeration increased the carbon recovery. In the flotation process, the carbon recovery was 90% contained 0.1% assay of ash and the removal rate of ash was 85%.

The characteristics of impurity with magnetic separation

Magnetic materials removed by high intensity magnetic separation (HIMS) were mainly Fe, Fe_2O_3, FeOOH, and

FeO as analyzed by Electron Spectrometer for Chemical Analysis (ESCA, SSX-100). Some FeS was also detected. About 90% of metal impurities were removed at 5,000gauss, and 100% at 7,000gauss as seen in Figure 6. The pulp density also affected the magnetic separation, as magnetic materials were well removed at less than 4% pulp density but hardly at more than 4% as seen in Figure 7. The reason why S/L ratio affects magnetic separation is that too much solid concentration in water causes to protect the movement of slurry..

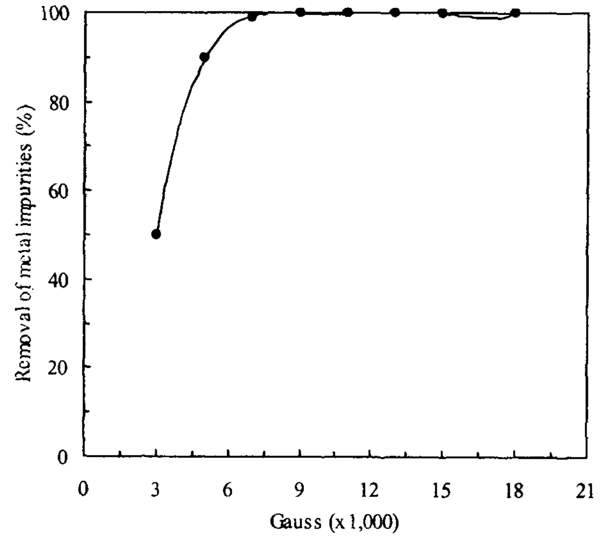

Figure 6. The percentage removal of metals using by HIMS at 3.5% pulp density

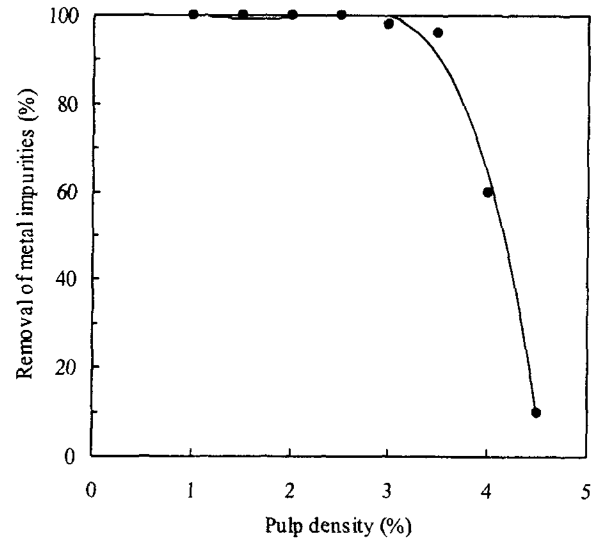

Figure 7. The percentage removal of metals using by HIMS in various pulp density. (7,000gauss)

Ultrasonification treatment

Ultrasonification was found to improve the separation of ash component from carbon. Table 5 shows the characteristic of impurities and the dispersion of each particle at 3% of slurry concentration as time and ultrasonification are increased. As shown in table 5, the recovery of carbon and the removal of impurity are increased by increasing ultrasonification and time.

Table 5. Removal of ash as a function of ultrasonic power and time

	Time	10min.	20min.
200W	Precipitated carbon (wt.%)	6.50	5.25
	Removal rate of ash (%)	45.71	55.70
600W	Precipitated carbon (wt.%)	4.86	3.58
	Removal rate of ash (%)	71.43	92.85
1200W	Precipitated carbon (wt.%)	4.34	2.85
	Removal rate of ash (%)	84.29	94.20

Product quality

A pilot plant was designed and built on the basis of the flowsheet presented in Figure 8 where high purity carbon black was produced using optimized conditions determined in batch tests. The pilot plant test was carried out at 10times with 0.5tonnes of carbon sludge contained 75% water for one hours as shown in Figure 9. After tests, the carbon recovery was about 84% (105.0kg/hr of dried carbon black) with about 0.01% assay of ash and 700-900m^2/g of surface area and pH 5-6.

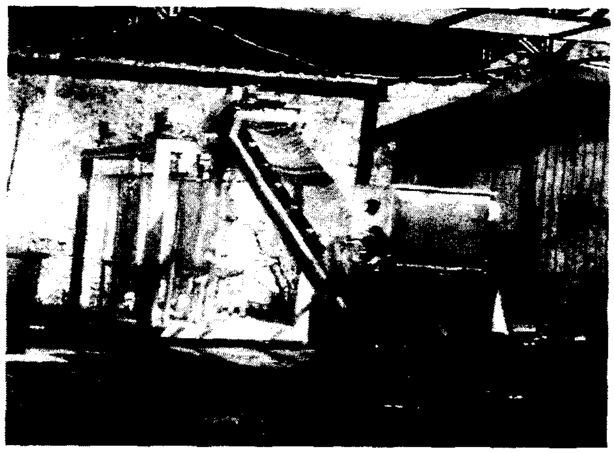

Figure 8. Flow sheet for the recycling of the waste carbon sludge

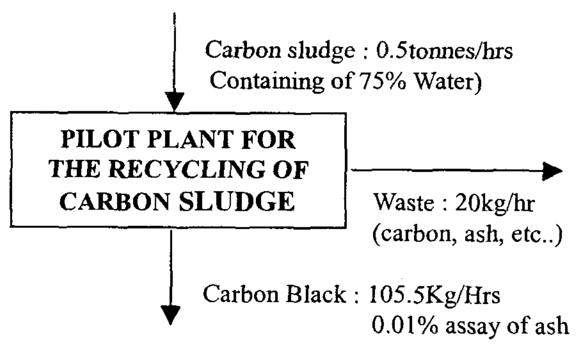

Figure 9. Mass balance for the recycling of the waste carbon sludge

The EDXS(Energy Dispersive X-ray Spectrometry) study also confirmed that most metal ion impurities found in the feed such as V, Fe, Ca, Na, Mg and Si were removed using the developed process.

Conclusion

1) The waste carbon black sludge usually contains 80% water and was within the range of pH 4.3 – 5.5. Dehydration of this sludge would yield a product containing 0.5-1% ash, 0.3-0.6% iron and 0.1-0.5% sulphur. Most of the waste carbon black is very fine (99.2% less than 400 mesh). The rest (0.8%) is coarse (200-400 mesh) and contains around 41% of the ash component.
2) Less than 60% of dispersion was achieved with mechanical stirring but more than 70% dispersion was achieved by combining stirring and ultrasonification.
3) More than 90% of the material tested (carbon and ash components) were well settled within 2 hours at less than 4% pulp density. However, settling % dropped as the pulp density was increased.
4) Of the frothers tested, Aero-Floth AF 73 was the most efficient at 5.5-6.5kg/t for flotation, at 4.5 kg/t kerosene and pH 6.0. A dispersants and aeration affected the carbon recovery and the carbon recovery was 90% containing 0.1% assay of ash and the removal rate of ash was 85% in flotation tests.
5) Ultrasonification was found to improve the separation of ash component from carbon. The characteristic of impurities and the dispersion of each particle at 3% of slurry concentration as time and ultrasonification are increased.
6) Magnetic materials removed by high intensity magnetic separation (HIMS) were mainly Fe, Fe_2O_3, FeOOH, and FeO. About 90% of metal impurities were removed at 5,000gauss, and 100% at 7,000gauss at less than 4% pulp density.
7) From the result of pilot plant tests, the carbon recovery was about 84% (105.0kg/m of dried carbon black) with about 0.01% assay of ash and 700-900m^2/g of surface area as pilot tests was campaigned at 10times with 0.5tonnes of carbon sludge contained 75% water for one hours.

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