Carbon Decontamination of Activated Sludge From Plastics Processing

Y. El-Shoubary and D. E. Woodmansee
General Electric Research and Development Center, Schenectady, NY 12301

INTRODUCTION

This paper is concerned with the site treatment of wastes generated at a plastic manufacturing plant. Most of the waste produced in the plastic manufacture process is transferred to an onsite treatment facility. Figure 1 shows a flow diagram of the sludge process. The waste, containing approximately 400 ppm COD, is first mixed with powder-activated carbon to enhance bioreaction and then goes through a two-stage operation. The first stage, known as thickening, is physiochemical and involves the conversion of discrete, unflocculated particles of the suspension into a thickened underflow with a clear overflow, which is accomplished by the addition of a coagulant or a flocculent. This process is of vital importance in terms of establishing the conditions required for the biodegradation (biomass) which will start on the carbon substrates. The second stage is to reduce the remaining water content of the thickened underflow by a suitable solid liquid separation process, thereby transforming it into a compact rigid solid containing only smaller quantities of water (sludge).

The objective of this work is to try to break the biocell mass and separate the fine carbon from the sludge using hydroclones and/or flotation equipment. The carbon will be regenerated for reuse.

LITERATURE SURVEY

The art of separation using flotation techniques is well known. The flotation techniques are used to separate minerals from their raw materials, coal, from its gangue and contaminant from soils (1:4, 18:24). No attempts to separate the processed sludge carbon were found in the published literature. However, several books and publications were found on sludge process control, kinetics, microbial theory, factors affecting the process and sludge activation methods (5:17). This literature was studied to find a method to break the carbon biocell mass and liberate the carbon. Once the cell mass is broken, techniques to float the carbon away from the rest of the sludge components could be developed.

EQUIPMENT

The equipment used in this study is a hydroclone and a flotation cell. Figure 2 shows a schematic diagram of a hydroclone and a flotation cell. The hydroclone used in this study was supplied by Mozley Corporation located in the United Kingdom.

The flotation cell used in this study was a 4-cell flotation device model #5-DR float supplied by Denver Equipment Company, Colorado Springs, Colorado. Air is pumped through a vein-type rotor revolving within a fixed stator.

In addition, Perkin Elmer Thermogravimetric Analyzer 7, thermal analyzer controller (TAC/PC), IBM personal system 2 and Perkin Elmer graphics plotter 8 were used to estimate the carbon separation performance.

The materials used were Fine Activated Charcoal (400 mesh) and coconut activated charcoal (8-12 mesh). The two types of carbon were obtained from EM Science. The surface area of the two carbons are 750,000 and 1,200,000 sqm/kg respectively.

Finally, two different types of sludge were obtained. The first one will be referred to as agglomerated sludge. The second will be referred to as nonagglomerated sludge. The first was collected from the clarifier after the coagulant or flocculent
was added. The second was obtained from the thickener prior to the addition of the coagulant or the flocculent (see Figure 1).

MEASUREMENT PERFORMED ON SLUDGE SAMPLES

Moisture Content

Several samples of each sludge were dried for 14 hours at 105°C. A Fisher Isotemp oven 200 Series, obtained from Fisher Scientific, Springfield, NJ was used for the drying. The difference between the dry weight and the wet weight was considered to be the weight of the sludge liquid. Accordingly, the percent solid in each sample was determined. The agglomerated sludge contained 18-20% solids, while the nonagglomerated sludge contained 2-4% solids.

Carbon Content

The carbon content of both types of sludge was difficult to determine. However, using thermogravimetric techniques the value of the carbon content could be accurately estimated. A clean virgin carbon sample was obtained and run in a nitrogen atmosphere. Table 1 gives the run conditions. A sample of the dried sludge was run under the same conditions and the difference in weight loss was assumed to be due to other materials that exist in the sludge, i.e., materials other than carbon. It should be mentioned here that the carbon content obtained using this technique was in total agreement with the values obtained from the plant manager. The carbon content for the agglomerated sludge was found to be 20% with respect to dry weight and 40 to 60% based on dry weight for the nonagglomerated sludge. The wide range was due to the sample date of collection. On any given day the waste produced at the facility may vary in concentration but not in content.

Two runs were performed by adding granular-activated carbon (GAC) to the sludge. The two runs were performed to clarify the possibility of depressing the fine carbon and other fine materials and floating the coarse contents of the sludge with the GAC. Also, the possibility of using GAC instead of PAC is attractive since screening separation is possible.

In several other runs, it was eminently to add powder-activated carbon to the sludge to prevent the generation of any faint odors and to magnify the visual observations of the carbon separation. The intent of this work was to study the separation of carbon from sludge and not to differentiate between both added carbon and biological cell-mass carbon.

Screen Analysis

Each type of sludge was screened using wet-sieving techniques. The screen analysis showed that both sludges contained more than 70% of their weight in particles finer than 200 mesh (0.074 mm diameter). These results show that the total separation of carbon may be difficult, if not impossible, because there is little difference in the size or density between the carbon particles and the other fine particles. Figure 3 shows the screen analysis results for both sludges.
### Table 2: Sludge Runs Measurements

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S1</td>
<td>Agglom.,</td>
<td>20257</td>
<td>0.069</td>
<td>0.493</td>
<td>None</td>
<td>3</td>
<td>10562</td>
<td>0.071</td>
<td>0.375</td>
<td>Tan</td>
<td>9695</td>
<td>0.067</td>
<td>0.625</td>
<td>Dk Brn</td>
</tr>
<tr>
<td>4</td>
<td>S4</td>
<td>Agglom.,</td>
<td>27779</td>
<td>0.102</td>
<td>0.631</td>
<td>398</td>
<td>3</td>
<td>9190</td>
<td>0.112</td>
<td>0.229</td>
<td>Tan</td>
<td>18589</td>
<td>0.097</td>
<td>0.721</td>
<td>Black</td>
</tr>
<tr>
<td>5</td>
<td>S5</td>
<td>Agglom.,</td>
<td>23100</td>
<td>0.131</td>
<td>0.716</td>
<td>None</td>
<td>3</td>
<td>9800</td>
<td>0.1</td>
<td>0.68</td>
<td>Tan</td>
<td>13300</td>
<td>0.154</td>
<td>0.766</td>
<td>Gray</td>
</tr>
<tr>
<td>6</td>
<td>S7</td>
<td>Agglom.,</td>
<td>3975</td>
<td>0.208</td>
<td>0.204</td>
<td>None</td>
<td>15</td>
<td>1984</td>
<td>0.13</td>
<td>0.189</td>
<td>Dark Tan</td>
<td>2462</td>
<td>0.231</td>
<td>0.2</td>
<td>Gray</td>
</tr>
<tr>
<td>7</td>
<td>S9</td>
<td>Agglom.,</td>
<td>7141</td>
<td>0.17</td>
<td>0.369</td>
<td>60</td>
<td>3</td>
<td>1635</td>
<td>0.151</td>
<td>0.198</td>
<td>Dark Tan</td>
<td>5506</td>
<td>0.175</td>
<td>0.39</td>
<td>Dk Brn</td>
</tr>
<tr>
<td>8</td>
<td>S10</td>
<td>Unagglom.,</td>
<td>16630</td>
<td>0.029</td>
<td>0.742</td>
<td>None</td>
<td>3</td>
<td>13170</td>
<td>0.034</td>
<td>0.74</td>
<td>Dark Blk</td>
<td>3460</td>
<td>0.008</td>
<td>0.784</td>
<td>Lt Tan</td>
</tr>
<tr>
<td>9</td>
<td>S11</td>
<td>Unagglom.,</td>
<td>13931</td>
<td>0.028</td>
<td>0.490</td>
<td>None</td>
<td>3</td>
<td>5532</td>
<td>0.019</td>
<td>0.619</td>
<td>Dark Blk</td>
<td>8323</td>
<td>0.034</td>
<td>0.447</td>
<td>Gray</td>
</tr>
<tr>
<td>10</td>
<td>S12</td>
<td>Unagglom.,</td>
<td>80182</td>
<td>0.046</td>
<td>0.660</td>
<td>202</td>
<td>8</td>
<td>2179.2</td>
<td>0.045</td>
<td>0.3</td>
<td>Tan</td>
<td>5839</td>
<td>0.046</td>
<td>0.8</td>
<td>Black</td>
</tr>
<tr>
<td>11</td>
<td>S13</td>
<td>Unagglom.,</td>
<td>8213</td>
<td>0.036</td>
<td>0.600</td>
<td>604</td>
<td>1</td>
<td>1681</td>
<td>0.036</td>
<td>13.33</td>
<td>Tan</td>
<td>6532</td>
<td>0.036</td>
<td>0.72</td>
<td>Lt Brn</td>
</tr>
<tr>
<td>12</td>
<td>S14</td>
<td>Unagglom.,</td>
<td>8667</td>
<td>0.099</td>
<td>0.703</td>
<td>454</td>
<td>3</td>
<td>2655</td>
<td>0.082</td>
<td>0.44</td>
<td>Dark Tan</td>
<td>5549</td>
<td>0.12</td>
<td>0.3</td>
<td>Lt Black</td>
</tr>
<tr>
<td>13</td>
<td>S15</td>
<td>Unagglom.,</td>
<td>6712</td>
<td>0.093</td>
<td>0.660</td>
<td>250</td>
<td>3</td>
<td>&lt;6</td>
<td>4293</td>
<td>0.1</td>
<td>Red</td>
<td>2419</td>
<td>0.089</td>
<td>0.93</td>
<td>Brick Red</td>
</tr>
</tbody>
</table>

### Table 3: Summary of Separation Results

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Code No.</th>
<th>SLUDGE FEED</th>
<th>Composition</th>
<th>Biologic Carbon (BC/SS)</th>
<th>Hydroclone Time (min)</th>
<th>Sorptive Carbon (SC/SS)</th>
<th>Attrition Time (min)</th>
<th>WASHING COLLECTOR</th>
<th>FLOTATION COLLECTOR</th>
<th>FROTHER (name)</th>
<th>CARBON ENRICHMT [%C (tally)/%C (feed)]</th>
<th>CARBON YIELD [%TC (tally)/%TC (feed)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S1</td>
<td>Agglom.,</td>
<td>0.074</td>
<td>0.388</td>
<td>0</td>
<td>0.207</td>
<td>30</td>
<td>Pine Oil</td>
<td>1.268</td>
<td>0.589</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>S4</td>
<td>Agglom.,</td>
<td>0.175</td>
<td>0.420</td>
<td>0</td>
<td>0.57</td>
<td>20</td>
<td>Ca(OH)2</td>
<td>1.143</td>
<td>0.847</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>S5</td>
<td>Agglom.,</td>
<td>0.231</td>
<td>0.630</td>
<td>0</td>
<td>0.301</td>
<td>35</td>
<td>4M,2 Pentanone</td>
<td>1.070</td>
<td>0.702</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>S6</td>
<td>Agglom.,</td>
<td>0.208</td>
<td>0.204</td>
<td>0</td>
<td>0</td>
<td>25</td>
<td>4M,2 Pentanone</td>
<td>0.980</td>
<td>0.702</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>S7</td>
<td>Agglom.,</td>
<td>0.197</td>
<td>0.270</td>
<td>0</td>
<td>0.157</td>
<td>30</td>
<td>H2O2 + Starch</td>
<td>1.057</td>
<td>0.880</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>S8</td>
<td>Unagglom.,</td>
<td>0.015</td>
<td>0.500</td>
<td>0</td>
<td>0.935</td>
<td>15</td>
<td>Pine Oil</td>
<td>1.057</td>
<td>0.880</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>S9</td>
<td>Unagglom.,</td>
<td>0.028</td>
<td>0.490</td>
<td>0</td>
<td>0</td>
<td>12</td>
<td>Pine Oil</td>
<td>0.912</td>
<td>0.880</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>S10</td>
<td>Unagglom.,</td>
<td>0.047</td>
<td>0.660</td>
<td>0</td>
<td>0</td>
<td>10</td>
<td>Rubbercem.</td>
<td>1.212</td>
<td>0.890</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>S11</td>
<td>Unagglom.,</td>
<td>0.042</td>
<td>0.600</td>
<td>0</td>
<td>0</td>
<td>15</td>
<td>Starch</td>
<td>1.200</td>
<td>0.950</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>S12</td>
<td>Unagglom.,</td>
<td>0.049</td>
<td>0.703</td>
<td>0</td>
<td>0</td>
<td>12</td>
<td>Na silicate</td>
<td>0.427</td>
<td>0.702</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>S13</td>
<td>Unagglom.,</td>
<td>0.036</td>
<td>0.600</td>
<td>0</td>
<td>0</td>
<td>15</td>
<td>Pot. perman.</td>
<td>1.409</td>
<td>0.486</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Soxhlet Extraction

The dried samples of each sludge were extracted using soxhlet equipment and methylene chloride. Although no numerical values were obtained from the analysis, it was virtually obvious from the extract, that the majority of the samples consisted of plastics.

EXPERIMENTAL RUNS

A total of 14 runs (12 flotation and 2 hydroclone) were performed in this study. Tables 2 and 3, attached, give the type of equipment and additive used in each run.

In each flotation run a sample was collected from the feed, froth and tails. In case of the hydroclone runs, a sample was collected from the overflow and underflow. Each sample was dried at 105°C and the percent solid in each sample was calculated. Each sample was run in the TGA equipment in the same manner described above, to determine the percent carbon in the matrix. When an additive was added to the sludge as a depressant, a pure sample of the additive was run in the TGA module in nitrogen atmosphere. Three temperatures were chosen to carry the following calculation.

Total weight loss = Carbon weight loss
+ Other material weight loss + Depressant weight loss

DISCUSSION

The separation results presented in Tables 2 and 3 are shown graphically in Figure 4 for those runs involving flotation. The carbon enrichment on the ordinate can be viewed as a separation factor, while the abscissa reflects how much of the feed carbon ends up in the tails. These results show that the permanganate provided the best separation, but at a low carbon yield of only 50%. The starch additive was good at depressing all the carbon to the tails, but too much of the plastic and cell mass came down with the carbon to make its use practical.

It is apparent that two major issues need to be addressed separately in order to recover more completely the biological and decontaminating carbon added to the wastewater. The first is to effect a separation of the other materials (probably plastic particles) from the rest of the sludge. These particles do not float with the cell mass, but instead appear to be depressed with the carbon. Either these particles should be filtered prior to processing the cell mass, or they should be separated from the flotation tails before the carbon is returned for reactivation. The large burden of nonactivated carbon combustibles in the tails would overload any carbon reactivation system.

From the results in Figure 4, one process option that might be followed is first to float the cell mass and carbon away from the plastic particles, and then to separate the carbon from the cell mass. The sodium silicate appears to be an excellent collector for the carbon and cell mass, floating it away from the plastic particles. Once this separation is accomplished, a second attrition washing would be performed using a potassium permanganate to break up the cell mass with a second flotation to follow using the starch as a carbon depressant.

To break the cell mass, hot water (80°C) was mixed with the agglomerated sludge in the attrition scrubber (Run 5). In Run 7, hydrogen peroxide was added to the agglomerated sludge in the attrition scrubber to achieve the same purpose. In both runs, the bacteria might have been destroyed, but the cell mass was only partially broken. This partial breakdown of the cell mass is reflected in the carbon percentage of yield of Runs 5 and 7 (see Table 3). The percentage of yield was 7.2% and 88% for Runs 5 and 7, respectively, compared to 58.9% for Run 1, in which no steps were taken to break the cell mass. It was felt that a longer mixing time of the sludge with both or any of the above additives with a reasonable residence attrition time will increase the cell mass breakdown and consequently the percentage of carbon yield.

Table 4 Comparison Between Agglomerated and Unagglomerated Sludges

<table>
<thead>
<tr>
<th>Percentage Solid</th>
<th>Unagglomerated</th>
<th>Agglomerated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Odor</td>
<td>Weak</td>
<td>Very Strong</td>
</tr>
<tr>
<td>Cell Mass</td>
<td>Did not exist</td>
<td>Exists and always floated</td>
</tr>
<tr>
<td>Carbon Separation</td>
<td>Moderately difficult</td>
<td>Extremely difficult</td>
</tr>
<tr>
<td>Color</td>
<td>Black</td>
<td>Gray</td>
</tr>
<tr>
<td>Sample Location</td>
<td>Thickener</td>
<td>Clarifier with coagulant or flocculant</td>
</tr>
</tbody>
</table>

Rubber
Cement

Na Silicate

Starch

FIGURE 4. Yield of carbon to tails (C in tails/C in feed).
AGGLOMERATED VS. NONAGGLOMERATED SLUDGE

A comparison between the two sludges is given in Table 4. The two sludges behaved differently in the flotation cell. The cell mass of the agglomerated sludge always floated even when depressant was used. Accordingly, it was easier to depress the carbon and contain it to the tails and let the cell mass float. This idea was successful in most runs.

MASS BALANCE AND PERCENTAGE OF CARBON

Table 2 summarizes the mass balance obtained for each run. Mass balance error never exceeded 7%. This is considered satisfactory, keeping in mind the large dilutions in the process and the scale of the experiments. The mass balance was forced to close through the increase or decrease on the added clean water in the flotation cell.

AGGLOMERATED SLUDGE RESULTS

The results of the agglomerated sludge are summarized as carbon percentage split in Figure 5, and as percentage of carbon in both the froth and the tail in Figure 6. The carbon split itself between the tails and the froth at the values are shown in Figure 5. The percentage of carbon showed in the tails ranged from 59% with no additive (Run 1) to 89% when calcium hydroxide was added (Run 4). Although these results appear to be satisfactory, it has no value without finding the actual carbon concentration in every produced flotation stream (see Figure 6). If successful separation is to be achieved, the percentage of carbon in the tails or even in the froth should be high enough to grant economical carbon regeneration. The existence of impurities with the carbon will translate into more energy input for the regeneration and consequently higher cost. On the other hand, the existence of the depressant with the regenerated carbon will allow saving the addition of the fresh depressant. This balance should be studied in each run.
calcium hydroxide (Run 4) had the highest success since the percentage of carbon in the tails was 72% and only 28% impurities, which were mostly starch.

NONAGGLOMERATED SLUDGE RESULTS

The same analysis was applied to the nonagglomerated sludge. Figure 7 shows the carbon percentage split in the tails and the froth and Figure 8 shows the percentage of carbon in each flotation stream. It is clear from Figure 7 that the percentage of carbon recovered with the tails increased when a depressant was used. Starch, potassium permanganate and rubber cement did depress the carbon extremely well. Again these results remain inconclusive without examining the percentage of carbon in each flotation stream (see Figure 8). The percentage of carbon in each stream of the nonadditive runs were almost equal, i.e., the separation was poor. The rubber cement (Run 10) and potassium permanganate (Run 14) runs showed tails-with carbon concentration of 80% and 93% respectively. These results are considered a great success.

If the depressant is to be recycled in the process, both the starch and sodium silicate runs are considered a success in separation. It should be mentioned here that because of the low solid percentage of it in the feed (2-5%) the additives or depressant to the sludge affected the calculation of the percentage of carbon in each stream. The numbers were extremely sensitive to the amount of additive in the sludge.

HYDROCYCLONE RUNS

The carbon separation results obtained using the hydrocyclone are summarized in Figures 9 and 10. The carbon split in
almost equal amounts between the overflow and the underflow regardless of the spigot/vortex combination. In addition, the percentage of carbon in the overflow stream was close to 50%. This means that both the impurities and the carbon were recovered in almost equal amounts in both the overflow and the underflow. In conclusion, the hydrocyclone failed to produce any separation regardless of the spigot/vortex combination. It should be mentioned here that the hydrocyclone runs were difficult because of the existence of large plastic particles which caused plugging of the spigot.

CONCLUSIONS

The following are the conclusions resulting from this research:

- In general it was clear that the carbon in the nonagglomerated sludge was much easier to separate and to handle than that in the agglomerated sludge. The biomass was hard to break in the latter case. Even the existence of the polymer in the agglomerated sludge might have altered the performance of the flotation cell.
- The hydrocyclone failed to obtain any sludge separation. The flotation equipment was a more powerful tool in the separation process.
- Sodium silicate and starch appear to be excellent collectors and depressants for carbon.
- The concentration of the solids in the nonagglomerated sludge (1.5-5%) was considered very low. Any additive to the sludge will affect the final performance of the separation. The additives should be recycled back to the feed to make the process more attractive economically.
- The pH, hydrogen peroxide, and the attrition scrubber residence time increased the cell mass breakdown and consequently improved the carbon separation with flotation.
- If a good separation of carbon from the cell mass can be achieved, there is a good opportunity to decontaminate the discarded sludge and perhaps reactivate the carbon.

RECOMMENDATIONS

The following recommendations are made:

- Two-stage flotation is recommended to achieve a better carbon separation. In the first stage, plastic materials should be recovered using a cell mass/carbon collector such as sodium silicate. In the second stage, a carbon depressant, such as rubber cement or potassium permanganate, should be used to depress the carbon and float the cell mass.
- More work is needed in the biocell breakdown in order to obtain better carbon separation.
- The amount of the solids in the nonagglomerated sludge needs to be increased through decanting the water or filtration, thus eliminating the sensitivity of the results to the percentage of additive or depressant.

ACKNOWLEDGMENT

The authors appreciate the tireless efforts of Lynn Ann Smullen, who assisted with the experimentation and conducted most of the analytical work, and of Barbara Whitten, who also provided assistance in entering the data into spreadsheets and drawing most of the figures, as well as putting the text into its final form. Tom Wrobleski provided the sludge samples and described the operation of the plant wastewater system.

LITERATURE CITED

2. <i>Chemical Engineering Progress Symposium Series</i>, No. 15, Collected Research Papers, AIChE, 1954.