Pyrolysis and Carbocoal Characteristics for Biophysical Drying Sewage Sludge

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ABSTRACT: With the sewage sludge yield increasing, the sludge treatment becomes a major problem in China. The pyrolysis technology is used to treat the sewage sludge, because of a lot of advantages, such as good economic returns, the less secondary pollution and the higher utilize value of pyrolysis products. And it is considered as one of the great potential thermo-chemical treatment technology. A series of experiments were carried out to study the biophysics of drying sludge and how to get the variation of production gas, oil and coke at the different pyrolysis temperatures. Also, how to obtain high-value pyrolysis products at optimum pyrolysis temperature. At the same time, by studying the biophysical drying sludge’s char formation mechanisms and physic-chemical properties at the different pyrolysis temperature conditions, the indirect reference data for pyrolysis of sludge were provided. It is providing theoretical guidance for the safe disposal of sludge, through sequential extraction method of European Communities Bureau of Reference (BCR) exploring different forms of semi-coke in the enrichment of heavy metals.

INTRODUCTION

SLUDGE is the major by-production from urban sewage treatment plants. Mud cake has a high moisture content (80 wt%), high organic content, inorganic mineral and more compact structure, and so on [1]. There will be significant environmental risks if we cannot effectively deal with these solid wastes. Sludge amounts were increasing more than 10% every year in China which creates a significant problem for Chinese sewage treatment industry and municipal administration. Sludge pyrolysis is considered to be one of potential thermochemical treatment technology, because of its good economic returns, less secondary pollution, high use value of pyrolysis products, and so on. Sludge pyrolysis remains at the experimental stage in China.

Shen [2] got the pyrolysis temperatures, which were between 300–600°C obtaining the distribution of gas and oil production. The results showed that the maximum oil production rate was 30% at 525°C. When the temperature was higher than 450°C the cracking of heavy oil created a secondary decomposition reaction to become light oil. When the temperature was higher than 525°C it formed more lightweight oil and gaseous hydrocarbons and gas production increased. Inguanze et al. [3] studied pyrolysis temperatures of 450°C, 650°C, and 850°C with heating rates of 5 K/min and 60 K/min. They found that heating rate was very important only for the lower pyrolysis final temperature such as 450°C. At higher pyrolysis temperatures (i.e., more than 650°C) the effects of heating rate would be neglected. At 450°C the improvement of heating rate made pyrolysis more efficient and more pyrolysis oil and pyrolysis gas would be produced.

Piskorz et al. [4] took use of fluidized bed reactor to do experiment of the sludge pyrolysis, at the conditions of the final pyrolysis temperature of 450°C, residence time of 0.3 s, 0.5 s, and 1 s. They found that the best time was 0.5 s, and the bio-oil yield was maximum (52 wt%) at this moment. Canadians Kim & Parker [5] studied the influence of different zeolite addition quantity on sludge pyrolysis. The final pyrolysis temperature was 500°C, the results showed when the zeolite addition amount was greater than 0.2 g/g dry sludge, the yield of coke decreased with catalytic amounts increasing, and the changes of tar yield were not obvious. Catalyst added into the reactor, is helpful for promoting the conversion from solid coke to gas, and producing more pyrolysis gas, but little effect on the tar.
About sludge pyrolysis mechanism, some researchers studied pyrolysis production (pyrolysis gas, tar, and coke). Dominguez et al. [6] studied the change of pyrolysis gas production in the range of 250–1000°C. They found pyrolysis gas production increased with the pyrolysis temperature increasing at the low temperature stage (< 700°C), and arrived at peak about 700–850°C, and then, reduced significantly along with the temperature rising (> 850°C). The final pyrolysis gases were mainly H₂, CO, CH₄ and the other gas composition of high calorific value. Lutz et al. [7] obtained the calorific value of tar which is 35–38 kJ/mol, dealing with sludge by the low temperature pyrolysis treatment. And the main compositions of tar were pentadecane and heptadecane, which belonged to heavy oil. Tay et al. [8] studied adsorption characteristics of phenol using sludge pyrolysis coke activated by ZnCl₂. They pointed out that absorbent BET surface area was 867.61 m²/g at 500°C for 2 hrs.

The current researches about the sludge pyrolysis mechanism are rare. In this paper, we adopt biophysical drying sludge to carry out a series of experiments in order to realize sludge harmless utilization and disposal. Our aims focuses on how to realize biophysics drying sludge to obtain high-value pyrolysis products at optimum pyrolysis temperature in the pyrolysis process, and how to decrease the environmental risk from heavy metal of the pyrolysis treatment of biophysics drying sludge.

MATERIALS AND METHODS

Experimental Materials

The pyrolytic raw material uses a biophysical drying sludge. Sludge, which is from Beijing Qinghe sewage treatment plant, is treated with in belt filter press processing. Sewage sludge was dried in 159L vertical tubular reactor (height of 1000 mm, inner diameter 450 mm) by short-term warming-intensified ventilation dehydrated biophysical drying effect. The physical and chemical properties of pyrolysis raw materials are send in Table 1 and Table 2.

| Table 1. Biophysical Drying Sludge Industrial Analysis. |
| Received Base Water (wt.%, d) | Volatiles (wt.%, d) | Ash Content (wt.%, d) | Fixed Carbon (wt.%, d) | Lower Calorific Value (kcal/kg, d) |
| Biological and physical drying sludge | 4.56 | 43.09 | 48.47 | 3.89 | 2282.54 |

Table 2. Thermal Drying Sludge and Biological Physics Drying Sludge Element Analysis.

| Elemental Analysis (wt.%, d) | C | H | N | S | O |
| Biological and physical drying sludge | 24.30 | 3.54 | 2.30 | 0.66 | 18.92 |

Experimental Apparatus and Instruments

The fast pyrolysis experiment device is shown in Figure 1. It mainly consists of the carrier gas systems, pyrolysis system, gas condensation system, the gas volume measurement and collection system. The carrier gas system includes cylinders and mass flowmeter, which fill the high purity nitrogen to provide an inert atmosphere. The pyrolysis system includes a horizontal tube resistance furnace, quartz tube and the console. The horizontal tube resistance furnace is controlled by the console, and its rated power is 4 kW and its maximum rated temperature is 1,000°C. Quartz tube is placed on the central axis in the furnace. When the temperature of the furnace achieves the established temperature, we immediately pushed the sample into the quartz tube by porcelain boat. The gas condensation system includes primary condenser (spherical condenser pipe), after-condenser (snakelike condenser pipe and cotton filter tube) and gas-washing bottle. Then the coke particles were removed by filtering and washing after the twice condensation for attaining purification pyrolysis gas. Gas volume metering and collection system includes electronic mass flowmeter and gas collection bag. The gas after purification was collected into this system to detect.

Experimental Methods

The 3.0 g biophysical drying sludge sample was put into the porcelain boat, and then the porcelain boat was put into the quartz tube. Bubbling into 30 ml/min high purity nitrogen, and purging 40 min to let air out in the experimental device for keeping inert atmosphere in the furnace. Adjusting the horizontal tube furnace, and letting the temperature increase to the preset temperature, we adjusted the high purity nitrogen flowing
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down to 3 ml/min, and quickly put porcelain boat into the middle reaction area of tube furnace to pyrolysis. Then we continued to turn down nitrogen flowing to 0 ml/min. The reaction gaseous product volume was metered by electronic flowmeter. Next, we stopped heating after 20 min, and adjusted the high purity nitrogen flow to 30 ml/min, and kept on purging 40 min, and collecting purge gas at the same time. After cooling the reaction system, we took the porcelain boat and weighted it to obtain carbocoal quality by means of difference heavy method.

Pyrolysis gas is mainly composed of hydrogen, oxygen, methane, carbon dioxide, in addition to a certain amount of ethane, ethylene, propane, propylene and acetylene, etc. Gas quality is calculated according to the volume of gas and all kinds of gas composition contents. The yield of liquid tar is calculated by weighing the condensation system before and after the reaction, while the solid carbocoal is calculated according to the weight difference before and after the porcelain boat reaction.

ASAP2010 specific surface area and pore size analyzer from American Micrometrics Company was used to measure the coke pore structure parameters. The pore size measurement ranges from 1.7–300 nm, and the relative pressure $P/P_0$ ranges from 0.01–0.995. We used scanning electron microscope (SEM) to analyze the pyrolysis coke surface, so as to understand the volatile changes in the precipitation process and the pyrolysis coke pore structure.

RESULTS AND DISCUSSION

Influence of Temperature on Yield of Pyrolysis Products

The main pyrolysis products of biophysical drying sludge are divided into three parts: solid carbocoal, tar and pyrolysis gas. When pyrolysis temperature changed, the output of three kinds of products changed. At relatively high pyrolysis temperature, macromolecular substances of the tar and solid carbocoal would decompose into small molecule gaseous products, so that the yields of semi-coke and tar decline and the gas products increase. For this reason, lower pyrolysis temperature is more appropriate for generating solid carbocoal [9]. The yields of gas, oil and coke of biophysical drying sludge with the change of temperature is seen in Figure 2.

Seen in Figure 2 along with the pyrolysis reaction temperature increasing, the yields of pyrolysis semi-coke of biophysical drying sludge decrease from 65.38–57.95 wt% at 850°C. When the temperature arrives at 900°C, the yields of semi-coke increase slightly. The yields of tar decrease significantly with the temperature increasing from 450–600°C. When the temperature is higher than 600°C, the yields of tar decline slightly. The yields of pyrolysis gas follow the same rule to tar yields, and the highest value of pyrolysis is 35.11% at 850°C. The above experimental phenomena described that organics and secondary pyrolysis for generating tar of biophysical drying sludge can be completely proceeded above 600°C. When the pyrolysis temperature is 450–600°C, the pyrolysis of sludge is not complete. Even if the reactions stop, there are still some organics for further decomposition in the solid carbocoal and tar. Thus, where there is the higher temperature there is the more gas production and less tar yield. When the reaction temperature surpasses 600°C, the increasing trends of gas production change slightly. It means when the pyrolysis temperature is
above 600°C, almost all the cleavable organic matter in semi-coke and tar involve in pyrolysis reaction, and the higher temperature will not improve the condition of the pyrolysis. However, at this time, the gas production increases and the yields of semi-coke and tar decline. The endothermic reaction between water, carbon dioxide in gas production and organics in tar and semi-coke strengthen with increasing temperature.

**Evolutionary Changes of Surface Area, Pore Volume, and Pore Size of Semi-coke at Different Pyrolysis Temperatures**

Semi-coke is a major media material to pyrolysis reaction and transformation process. In this experiment, the pyrolysis coke at temperatures 500°C, 600°C, 700°C, 800°C, and 900°C were detected and analyzed.

The Brunauer, Emmett, Teller’s (BET) model was used to calculate the surface area of char in this experiment. ASAP 2010 was used to analyze the original sludge and the coke obtained at the pyrolysis temperature 500°C, 600°C, 700°C, 800°C, and 900°C, and IUPAU classification method was selected to analyze the hole. Table 3 includes information of BET specific surface area, the total pore volume and average pore size parameters of semi-coke. Taking the semi-coke particles and Biophysics drying sludge for comparison, it can be found that in general, the pyrolysis can effectively increase the pore volume and reduce the pore size. With the temperature increasing, the total pore volume of semi-coke increases. But when the temperature is changing from 500–900°C, the pore size remains almost stable, and this is related to the prior analysis of the mesopore’s formation. In addition, it can be seen from Table 3 that the surface area of the char is small (3.105 m²/g under 500°C) at low temperatures. However the temperature rises to 800°C, the surface area grows up to a maximum of 30.503 m²/g. This may due to the release of gas. And when the temperature rises to 900°C, the surface area decreases to some extent. The specific surface area of semi-coke decreasing at 900°C, may be related to the phenomena of semi-coke compaction and melting.

**Microstructure Analysis of Semi-coke**

Figure 3 shows the SEM morphology photograph of pyrolysis coke particles from 300–900°C, and by the SEM images, we can be more intuitively understanding of the char pore structure characteristics. Figure 5 is a high magnification photo (×1000) of coke, it can be seen from these pictures that the pore size becomes larger, and the pore structure becomes complicated (identical to the BET model results anastomosis in previous section) with the pyrolysis temperature increasing. The coke surface changes from the beginning relatively flat layered structure to scattered particulate. Its surface becomes more rough and irregular, and the number of pits and round holes significantly increase. Especially at the temperature of 800–900°C, the molten or sintering phenomenon of semi-coke occurs. The channel and pits left during pyrolysis are much larger than that around the holes. There is a large amount of volatile gathering at some pyrolysis stage, and ultimately discharged in the form of bubbles [12]. Therefore, volatile take very irregular paths in the precipitation process to form irregular hole channels.

**Elemental Qualitative Analysis of SEM Images for Semi-coke Surface**

As the pyrolysis temperature gradually increased from 300–900°C, certain elements of coke have some regular changes. From Table 4, C element content decreases with the temperature increasing, while the O element content has an increasing trend. And Mg, Al, Fe, Ca contents all increase with the temperature increasing. This may be the result of relative increasing of the precipitation and volatile ash.

**C, H, O, N, and S Elemental Variation at Different Temperatures**

Figure 4 reflect the variation of five elements of C, H, O, N, S by CE-440 quantitative analysis at different temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original Sample</td>
<td>0.70</td>
<td>0.0034</td>
<td>16.03</td>
</tr>
<tr>
<td>500°C char</td>
<td>3.105</td>
<td>0.023</td>
<td>3.784</td>
</tr>
<tr>
<td>600°C char</td>
<td>19.187</td>
<td>0.034</td>
<td>3.828</td>
</tr>
<tr>
<td>700°C char</td>
<td>24.104</td>
<td>0.036</td>
<td>3.827</td>
</tr>
<tr>
<td>800°C char</td>
<td>30.503</td>
<td>0.049</td>
<td>3.829</td>
</tr>
<tr>
<td>900°C char</td>
<td>30.068</td>
<td>0.057</td>
<td>3.819</td>
</tr>
</tbody>
</table>
carbon coke and the organic matter in the sludge pyrolysis completely at the pyrolysis reaction temperature of 850°C. Therefore, the ideal conditions for hydrogen production are the pyrolysis temperature above 800°C.

Nitrogen in inorganic substances in sludge mainly exists in the form of nitrate, but in the organic matter, it mainly presents in proteins and amino acids. In the pyrolysis process, the nitrogen is converted to ammonia, hydrogen cyanide, nitrogen oxides, nitrogen, and organic nitrogen. With the pyrolysis temperature increasing, nitrogen contents of the semi-coke decrease. It indicates that the protein, amino acids and other organic matter are fully decomposed at high temperatures.

Oxygen contents reduce with the pyrolysis temperature increasing. Because the pyrolysis reactions of tar, aggravated carbocoal are more thorough at higher pyrolysis temperature.

Sulfur contents first increase and then decrease with the pyrolysis temperature increasing. This is because the pyrolysis reaction of sulfur-containing organic compounds becomes gradually strengthened with the pyrolysis temperature increasing, resulting in the decreasing of sulfur at lower pyrolysis temperature. When the pyrolysis temperature increases to a certain extent, the pyrolysis reaction can completely reacted and all the sulfur can be removed from the semi-coke. However, the gaseous products of coke and semi-coke can continuously react, so that the semi-coke yield will decrease with increasing temperature, resulting in slightly higher sulfur content.

Figure 3. SEM scanning images at different temperatures.
Change Rules of Semi-coke Characteristic Functional Groups with Different Pyrolysis Temperature

Sludge pyrolysis follows the general rules of organic matters, that is, when the heating temperature rises to a certain level, the corresponding chemical bond will break, and the volatile gas precipitates. The kind of semi-coke group types of solid carbocoal at different temperatures is analyzed by FTIR spectra (Fourier Transform Infrared Spectrometer), in order to explore the reasons for pyrolysis effect change at different temperature, and the results are seen in Figure 5.

Vibration peaks at about wave number of 3,200~3,600 cm$^{-1}$ are the stretching vibration peaks of hydroxyl OH bond (alcohols, phenols), and amine hydrogen-nitrogen bond in semi-coke. Their height reflects the dehydrogenation effect during char pyrolysis. It can be seen that, the peak height decreases with the temperature increasing. It means that dehydrogenation process of the biophysical dry sludge pyrolysis is strengthened with increasing temperature. It is obvious that high pyrolysis temperature is benefit to produce hydrogen.

Twin peaks at wavenumber of 2,800~3,000 cm$^{-1}$ are respectively the carbon-hydrogen bonds (alkanes) symmetric and asymmetric stretching vibration of methyl in semi-coke. The bimodal disappear when the pyrolysis reaction temperature is above 500°C, and the vibration intensity changed little when the pyrolysis reaction temperature is lower than 500°C. This phenomenon indicates that pyrolysis reaction of the organics is not violent below 500°C, even the methyl at the end of the carbon skeleton cannot be completely removed. This is further evidence of the fact that pyrolysis gas increases when the pyrolysis temperature increases.

### Table 4. Surface Element Content of Semi-coke Under Three Different Pyrolysis Temperatures.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>300°C</th>
<th>400°C</th>
<th>500°C</th>
<th>650°C</th>
<th>800°C</th>
<th>900°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Weight %</td>
<td>Weight %</td>
<td>Weight %</td>
<td>Weight %</td>
<td>Weight %</td>
<td>Weight %</td>
</tr>
<tr>
<td>C</td>
<td>55.1</td>
<td>48.42</td>
<td>34.05</td>
<td>36.03</td>
<td>26.01</td>
<td>30.97</td>
</tr>
<tr>
<td>O</td>
<td>25.47</td>
<td>29.87</td>
<td>35.76</td>
<td>31.47</td>
<td>36.51</td>
<td>31.39</td>
</tr>
<tr>
<td>Na</td>
<td>0.35</td>
<td>0</td>
<td>0</td>
<td>0.26</td>
<td>1.1</td>
<td>0.47</td>
</tr>
<tr>
<td>Mg</td>
<td>0.66</td>
<td>1.01</td>
<td>1.15</td>
<td>0.58</td>
<td>1.93</td>
<td>2.23</td>
</tr>
<tr>
<td>Al</td>
<td>1.75</td>
<td>2.25</td>
<td>3.44</td>
<td>2.69</td>
<td>5.22</td>
<td>5.25</td>
</tr>
<tr>
<td>Si</td>
<td>5.21</td>
<td>5.15</td>
<td>9.19</td>
<td>16.07</td>
<td>1.05</td>
<td>8.97</td>
</tr>
<tr>
<td>P</td>
<td>1.96</td>
<td>3.26</td>
<td>3.79</td>
<td>1.55</td>
<td>0.95</td>
<td>3.86</td>
</tr>
<tr>
<td>S</td>
<td>1.5</td>
<td>0.57</td>
<td>0.51</td>
<td>0.59</td>
<td>0.49</td>
<td>1.63</td>
</tr>
<tr>
<td>K</td>
<td>1.04</td>
<td>0.93</td>
<td>1.26</td>
<td>1.3</td>
<td>0.91</td>
<td>1.31</td>
</tr>
<tr>
<td>Ca</td>
<td>5.16</td>
<td>6.04</td>
<td>5.66</td>
<td>6.34</td>
<td>22.36</td>
<td>22.53</td>
</tr>
<tr>
<td>Fe</td>
<td>1.79</td>
<td>2.5</td>
<td>5.19</td>
<td>3.12</td>
<td>3.47</td>
<td>5.4</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 4. Different variations of elements in the semi-coke at different temperature.

Figure 5. FTIR spectra pyrolysis char at different temperatures.
reactions are enhanced with the pyrolysis temperature increasing below 600°C.

The vibrational peaks at wavenumber of 1,400–1,450 cm⁻¹ are the scissor vibration of carbon-hydrogen bonds on the secondary carbon, and the vibration is gradually decreased with the temperature increasing, and disappears when the pyrolysis temperature goes up to 700°C. It suggests that the pyrolysis of organic matter is more complete with the temperature increasing, and almost complete decomposition at 600–700°C; even the hydrogen in the middle of the carbon skeleton on the secondary carbon has been largely removed. This is further evidence that when the pyrolysis temperature is higher than 600°C, organic matter in solid carbocoal will pyrolysis entirely.

**Regularity of Heavy Metal Enrichment**

We take 0.5 g raw sludge and pyrolysis coke at 300°C, 400°C, 450°C, 500°C, 600°C, 650°C, 700°C, 750°C, 800°C, 900°C respectively, and select sequential extraction BCR process [13], which consists of the following three steps and one additional step [14] and the second step of the process is corrected. G. Rauret improved the BCR four steps, and used 0.5 mol/L of NH₃OH • HCl to substitute 0.1 mol/L of NH₃OH • HCl in the second step, and the acidity was adjusted to pH = 1.5. This method is called the modified BCR method [15].

Table 5 shows the original contents of heavy metals in sludge, and sludge samples contain relatively more Zn and Pb, and less Cu and Cr. Heavy metals in the sludge exist in four main forms [16]: exchangeable, reduction state, oxidation state and residuals, which are precisely corresponding to four samples of each step in BCR extraction system. According to BCR sequential extraction scheme, some representatives of the exchangeable section are metal in ionic form and combination of carbonate, such form of metal has strong ability of migration, and when the acidity of surrounding environment changes, the exchangeable sections quickly release into the environment and can be used by creatures. Some representatives of reduced state are iron and manganese oxides combined amorphous part metal of hydroxides. Some representatives of the oxidation are combined organic matter and sulfide metal; these two forms may be indirectly used by plants. The representatives of residue are combine with silicate crystals, crystalline iron and part of the manganese oxides metals [14,16], which are difficult to be released under natural conditions, and are difficult to be used by organisms [16,17]. By exploring the amounts of Cr, Cu, Pb and Zn in semi-coke, we discussed the variation of different forms of heavy metals. With the above modified BCR sequential extraction process, the resulting data are uniformed and seen in Figure 6.

Seen in Figure 6(a), Zn in original sludge is mainly in oxidation states. Different forms of Zn in Pyrolysis coke change regularly with temperature changes. From 300–900°C, exchangeable states show a gradual decline, and reduction states show a trend from increasing to decreasing, which peek to a maximum at 600°C. The oxidation states decrease with increasing temperature, while the residuals gradually increase. It describes that there is the higher pyrolysis temperature, the better for Zn to be fixed.

From Figure 6(b), Pb in original sludge is mainly in oxidation states. The forms of Pb vary greatly in pyrolysis coke in different temperature. From 300–600°C, the residual states of Pb increase and oxidation state decrease, while the oxidation states increase and the residual states reduce from 600–900°C. For Pb fixed, the best pyrolysis temperature is 600°C. That could prevent Pb migrating into the environment and causing environmental harm.

In Figure 6(c), Cu in original sludge is mainly in oxidation states [18]. This may be related to the fact that Cu mainly exists on sulfides in nature. The main forms of Cu Pyrolysis carbocoal also change at different temperatures. From 300–500°C, the main forms of Cu are oxidation state, and the oxidation states of Cu increase with temperature increasing. From 500–900°C, the oxidation states of Cu become less, and the residues of Cu increase, and the exchangeable states of Cu increase. At temperature of 850°C, the main forms of Cu become residuals, and the various forms of Cu in coke are almost stabilized. This relates to that the organic matter and Cu can form a stable complex.

As shown in Figure 6(d), Cr in original sludge is mainly in oxidation state, and the forms of Cr changes greatly in the pyrolysis process. When the pyrolysis temperature changes from 300–900°C, the residual states of Cr have a trend from increasing to decreasing. At 750°C, the residuals of Cr in coke reach to the maximum. It indicates that the best pyrolysis temperature is

**Table 3. Content of Heavy Metals in Sewage Sludge (mg/g).**

<table>
<thead>
<tr>
<th>Element</th>
<th>Cr</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (mg/g)</td>
<td>0.060</td>
<td>0.091</td>
<td>0.726</td>
<td>0.768</td>
</tr>
</tbody>
</table>
750°C in order to avoid Cr contamination. So the higher the temperature is, the more effective for destructing the chemical bonds of Cr.

CONCLUSION

With the pyrolysis temperature increasing, the semi-coke yields decreased, and reached 57.95% at 850°C. When the pyrolysis temperature was 900°C, the semi-coke yields increased slightly. The yields of tar also tended to decreasing, while the pyrolysis gas increased with increasing temperature, and reached to the maximum value of 35.11% at 850°C. When pyrolysis temperature was 600°C almost all of the organics in sludge were involved in the pyrolysis reaction. Then, if kept on increasing the temperature and the energy consumption, the pyrolysis of organic matters were not increased. The original contents of heavy metals in sludge samples contained relatively more Zn and Pb, and less Cu and Cr. Heavy metals in the sludge existed in four main forms: exchangeable, reduction state, oxidation state and residuals. When pyrolysis temperature changed from 300–900°C, exchangeable states showed a gradual decline, and reduction states showed a trend from increasing to decreasing, which peek to a maximum at 600°C. The oxidation states of Zn decreased with increasing temperature, while the residuals gradually increased. When pyrolysis temperature changed from 300–600°C, the residual states of Pb increased and oxidation state decreased. Then, the oxidation states of Pb increased and the residual states reduced from 600–900°C. For Pb fixed, the best pyrolysis temperature is 600°C. The main forms of Cu are oxidation state, and the oxidation states of Cu increase with temperature increasing from 300–500°C. The oxidation states of Cu become less, and the residues of Cu increased, and the exchangeable states of Cu increased from 500–900°C. At 850°C, the residual states of Cr had a trend from increasing to decreasing. At 750°C, the residuals of Cr in coke reached to the maximum value.

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ABBREVIATIONS

BCR – Communities Bureau of Reference  
IUPAC – International Union of Pure and Applied Chemistry  
ASAP – Automatic Physical Adsorption Instrument  
SEM – Scanning Electron Microscope  
BET – Brunauer, Emmett, Teller’s  
FTIR spectra – Fourier Transform Infrared Spectrometer

REFERENCES