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Energy Procedia 17 (2012) 444 – 449

Energy Procedia

2012 International Conference on Future Electrical Power and Energy Systems

The Effects of Thermal Regeneration Conditions and Inorganic Compounds on the Characteristics of Activated Carbon Used in Power Plant

Yingqing Guo[1,2 *], Erdeng Du[2]

1. College of Environmental Science and Engineering, Tongji University, 200092, China.
2. School of Environmental & Safety Engineering, Changzhou University, 213164, China

Abstract

Activated carbon filters are widely used to eliminate the contaminants in water, especially in power plant water treatment. Once exhausted, its adsorption capacity is normally recovered by thermal regeneration, and then activated carbon is reused. This paper summarizes the process of thermal GAC (Granular Activated Carbon) regeneration and the factors in this process. Inorganic salts adsorbed in GAC could play a negative role during catalyzed oxidation reactions when GAC is regenerated and lead to deterioration of its adsorbent properties.

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Keywords- Activated Carbon; Thermal Regeneration; Inorganic Salts

1. Introduction *(Heading 1)*

A number of municipal water utilities employ granular activated carbon (GAC) to remove organic impurities from potable water sources. These impurities include compounds imparting taste and odors, algal toxins, synthetic organic compounds, endocrine disruptors, pharmaceutically active compounds, and disinfection by-product precursors [1]. Now GAC are widely used in the treatment of cooling water in electric power plant.

After exhaustion, activated carbon must be regenerated or replaced by fresh carbon. The first opting is preferred due to the high cost of this adsorbent [2]. What's more, activated carbon regeneration is more conducive to protect the environment and conserve resources. Some regeneration methods have been

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proposed, such as supercritical fluid, wet oxidation or classical solvent regeneration, but on an industrial scale only thermal regeneration is used [2].

The process of thermal regeneration involves:

- Drying at around 105°C;
- Pyrolysis under inert atmosphere;
- Gasification of residual organics by oxidizing gas, such as stem or carbon dioxide [3].

The course of thermal regeneration is shown in Figure 1.

The pyrolytic stage occurs when the spent carbon is exposed to temperatures up to 800°C under inert conditions. This results in the elimination of any volatile compounds adsorbed in the carbon porosity, including residual moisture, and the thermal decomposition of other less-volatile compounds [3]. A residue of carbonized char will stored in activated carbon pores, and become part of the structure of activated carbon.

The oxidative stage involves the controlled gasification of the pyrolysed carbon at temperatures usually around 800°C in the presence of a mildly oxidizing atmosphere, usually steam or carbon dioxide or a mixture of both [3].

Water vapor, with a weak oxidation at high temperature, could react with and oxidize the residual carbonated compounds. Therefore, the carbonated carbon will be eliminated. And activated carbon will restore the original structure and adsorption properties. This results in the elimination of the charred residue and the exposure of the original carbon-pore structure.

Regenerated activated carbon can still be used to recycle repeatedly, and the wasted activated carbon can be used after retreating.

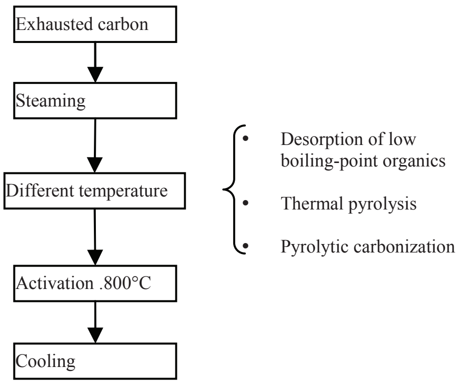

Figure 1. The principles of thermal regeneration of spent GAC (adapted form Lambert, 2002 [4])

2. Regeneration conditions and its effect on adsorption characteristics

2.1 Regeneration conditions

Characteristics of activated carbon are mainly determined by the parameters of thermal regeneration process. If the regeneration conditions meet the requirements, the activated carbon adsorption capacity cannot be fully restored, while if the regeneration conditions are too harsh, the adsorption properties and the original carbon structure of activated carbon are likely to be damaged. What’s more, the loss of activated carbon will also happen [3]. Makeup carbon used to replace that lost during regeneration, typically around 10-12% of the total GAC mass, can represent 20-40% of the total costs associated with GAC regeneration [4].

Adsorption capacity, mass loss, and regeneration granular strength of regenerated GAC are the main indicators of evaluating the thermal regeneration method. However, the three indicators have the antagonistic relations with each other. To achieve more adsorption capacity will inevitably lead to more mass loss of GAC, therefore, lead to increasing cost.

From the use of point of view, to restore the adsorption properties of activated carbon is desirable. However, in order to fully recover activated carbon adsorption, the regeneration conditions should be strengthened. This often leads to a decline in carbon intensity and size, increasing regeneration mass loss, additional increase in the number of new coal for makeup of carbon loss. The total mass of added activated carbon usually accounted for 20 to 40% of regeneration cost [4]. It is possible to achieve 100% recovery of the adsorption performance of spend activated carbon, though the loss of regenerated carbon is huge.

When considering a whole adsorption-regeneration system used in the water treatment process, the target should be to control the recovery rate of adsorption in a certain range to keep the whole system in the best balance.

Often in practice, however, the skeletal carbon of spent GAC is partly gasified or over-burned, in addition to the pyrolyzed organic adsorbate residues. This could lead to the extent to which GAC over-burning occurs depends on the following parameters:

- the GAC physical structure;
- the functional groups on the GAC surface;
- the concentration of H_2O vapor or CO_2;
- the temperature; and
- the inorganic compounds on the GAC surface [4].

2.2 The effects of physical structure

Adsorption properties of activated carbon depend on its porous structure. Therefore, pore-size distribution is the important factor determining the adsorption characteristics of activated carbons. According to IUPAC (International Union of Pure and Applied Chemistry) classification, activated carbon is divided into three types, i.e. micro-pores, meso-pores, and macro-pores.

Macro-pores are larger than 50nm size. The role of macro-pores is to supply the way for adsorbate molecules into the depth of activated carbon. Meso-pores are the pores of width between 2 and 50nm. Meso-pores play an important role during the adsorption process. Micro-pores are less than 2nm. And micro-pores account for a large part of the whole pores.

It is usually believed that, the activated carbon adsorption is better with more developed micro-pores and meso-pores. However, the molecular sieve division role hinders the adsorption of large molecular compounds on the pores of activated carbon. The research showed that, if the adsorbate molecular diameter is 1.5~2 times larger than carbon pores diameter, the activated carbon adsorption capacity of the organic compound will obviously decrease [3] .

San Miguel [3] investigates the regeneration adsorption of GAC on phenol and methylene blue. Phenol (molecular weight 94) with the molecular diameter of 0.5nm can be preferentially adsorbed in the small and medium pores of activated carbon. And methylene blue (MW 394) with larger diameter 0.8nm, mainly is adsorbed on the micro-pore and larger diameter pore of activated carbon.

Activated carbon producers and their customers have often agreed with the belief that, organic compounds adsorb in pores with widths 1.5 to 2 times larger than the largest diameter of adsorbate, which evidenced by the ubiquitous inclusion of the iodine number in PAC specifications. Tennant [5] proposed that the pore volume in the feeder pores (meso-pores) had the greatest effect on MIB removal. This was due to the importance of intra-particle diffusion in PACs under short contact times and high competition from NOM (natural organic materials).

2.3 The effects of surface chemistry

The adsorptive characteristics of GAC are not only determined by its pore structure, but also greatly determined by its surface chemistry, such as functional groups on the surface. Specific area and pore structure could affect activated carbon adsorption capacity, while the surface chemistry also affects the interaction face between activated carbon and polar or non-polar adsorbate. More than 90% of the GAC surface is formed by carbon basal planes. However there are heterogeneous surface functional groups that might significantly affect overall adsorption capacity.

Tennant investigated the role of surface acidity in the adsorption of 2-methlisoborneol (MIB) via powdered activated carbon [6]. His research proved that an increase in acidic functional groups on a carbon surface will cause an increase in water adsorption.

When acidic functional groups become density arranged on activated carbon, water clusters can form via hydrogen bonding between water molecules previously adsorbed. Therefore, the large water clusters formed at the edges for carbon pores due to the presence of a dense arrangement of acidic functional groups on the surface can explain how surface chemistry impacts s MIB adsorption [6].

It is generally believed that the effect of functional groups on the adsorption of activated carbon is caused by three mechanisms, i.e., π-π dispersion mechanism, hydrogen bond formation mechanism, the electronic mechanism of complex formation.

π-π dispersion mechanism is that, the oxygen-containing functional groups, as a kind of electron withdrawing group, can reduce the π-electron density of activated carbon skeleton, thus weaken the π-π interaction role between the adsorbent and the adsorbate, and finally lead to the decreasing adsorption of activated carbon.

Hydrogen bond formation mechanism is that, the oxygen-containing functional groups strength the binding energy between activated carbon surface and adsorbate. The adsorption forces are mainly from hydrogen bonds between functional groups and adsorbate.

3. The deleterious effects of inorganic compounds

3. 1 Accumulation of inorganic compounds

In addition to organic matter in activated carbon adsorption process, the metal ions also accumulated in the activated carbon. The number and type of accumulating metal ions could change with the raw water characteristics, water treatment process, and water treatment chemicals used. San Miguel [3] investigated 7 types of activated carbon used for 2~6 years, and found that, among these activated carbon, carbon ash accounted for 10% to 14%, which is significantly higher than new coal ash (4.8%). The used activated carbon used in Orchard Bridge water supply plant was regenerated. The analysis showed that the average ash content is 14.9% in the regenerated carbon, which was 91.5% larger than the original activated carbon [7]. The accumulation of inorganic ions was investigated in Europe and North America, as shown in Table I [3]. The survey illustrated that the problem of metal ions accumulation happened widely in water supply plant of Europe and North America.

Table I shows that calcium is usually the most commonly occurring metal species found on spent GAC. Aluminum (Al), iron (Fe), manganese (Mn) and magnesium (Mg) may also accumulate in significant quantities.

Table 1. Ash content and inorganic composition of field-spent GAC from several water treatment plants in Europe and the United States [3]

Activated Carbon Type	ash (wt%)	Inorganic content (wt%)						
		Ca	Al	Fe	Na	K	Mg	M_n
New carbon	4.8	0.089	0.618	0.467	0.026	0.069	0.02	0.002
HEIGH	12.6	4.045	0.480	0.543	0.029	0.061	0.062	0.006
BECK1	10.4	3.066	0.506	0.492	0.023	0.061	0.038	0.002
BECK2	12.3	4.207	0.546	0.482	0.017	0.051	0.046	0.002
THORPE	14.0	4.228	0.652	0.609	0.041	0.071	0.143	0.006
ETTON	10.0	2.290	0.636	0.819	0.058	0.067	0.112	0.031
SF1	10.7	2.846	0.630	0.567	0.032	0.064	0.045	0.026
SF2	13.9	4.559	0.609	0.769	0.030	0.068	0.050	0.084

3.2 Catalytic mechanism of metals during thermal regeneration

The metal ions can catalyze the activating reaction during the regeneration process. First, the presence of metal ions enhances the activity of carbon, reduces the required activation temperature, and reduces the activation time. Secondly, the metal ions adsorb water molecular through oxygen transmission mechanism, make the oxygen transfer to carbon, and promote the excessive activation of carbon around the ions. Therefore, macro-pores appear. And the yield of activated carbon decreases [8].

During the regeneration process of used activated carbon, the adsorbate is eliminated by the pyrolysis and the activation reaction with water vapor or CO_2.

CO_2 ordinarily reacts with active carbon sites on GAC surfaces via the Boudouard reaction, in which R-Cf and R’-Cf are active carbon sites on the GAC surface and R-C(O) is a surface carbon-oxygen complex [4] .

$$\text{R-Cf} + CO_2 \leftrightarrow \text{R-C(O)} + CO \tag{1}$$

$$\text{R-C(O)} \leftrightarrow \text{R'-Cf} + CO \tag{2}$$

3.3 The catalytic effects of metals on the property of regenerated GAC

The metal ions on the activation act as a catalyst to accelerate the activation process, resulting in excessive carbon activation. This increases the regeneration of mass loss. In addition, inorganic salts formed from metal ions in the regeneration furnace will melt and damage regeneration furnace.

A number of measures can be taken to avoid or remediate the effects of metal catalyzed-C gasification. Modification of the furnace conditions, however, is likely to be only partially successful and may compromise the effectiveness of regeneration. Acid-washing is the option offering the most potential [4].

Accumulating metal ions can be removed by acid-washing before regeneration, thus improve the yield of regenerated activated carbon and reduce the ash. During the acid-washing process, hydrochloric acid is usually used.

Acid-washing process usually includes two steps: activated carbon by acid-washing, and water rinsing. First, hydrochloric acid (5% hydrochloric acid, pH<2.5) is used to acid activated carbon for 3 to 30 minutes. The actual acid-washing time could change with the type of activated carbon and adsorbate. Finally, pure water is used to rinse activated carbon until pH is large than 5.0 [9].

4. Conclusions

Activated carbon is widely used in water treatment plant for the adsorption of pollutants in water. Now there are lots of real engineering cases concerning the application of activated carbon in the treatment of cooling water in electric power plant. However, activated carbon should be replaced with fresh carbon or be regenerated when activated carbon is exhausted. The method of regeneration of activated carbon is helpful to current environment.

The characteristics of the regenerated GAC are determined by the regeneration conditions, such as activation temperature, time, used activated carbon, and so on. Physical structure (pore-size distribution) is the primary factor determining the adsorption characteristics of activated carbon. GAC with a distribution of micro- and meso-pores is good for the adsorption of contaminants.

What's more, the surface chemistry (the functional groups on the surface of activated carbon) also play an important role of the contaminants adsorption in aqueous solution.

Inorganic salts adsorbed in GAC could play a negative role during catalyzed oxidation reactions when GAC is regenerated and lead to deterioration of its adsorbent properties.

The management of water treatment plant, especially in electric power plant, should take measures to optimize the process parameters to improve the characteristics of used activated carbon and decrease the cost of regenerated activated carbon.

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