

# Chlorine behavior during co-hydrothermal treatment of high alkali coal and PVC

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**Abstract.** The hydrothermal treatment (HT) is an effective method to remove chlorine from chlorinated wastes under mild conditions. However, the alkali was required to improve the dechlorination efficiency. Meanwhile, the alkalis contents removed was necessary to realize the clean and highly efficient utilization of coal. This work was trying to investigate the feasibility of simultaneously removal alkalis and chlorine by co-hydrothermal treatment of PVC and high-alkali coal. The effect of operating conditions including the HT temperature, the holding time and particle sizes of coal on the dechlorination efficiency (DE) of PVC during the HT process was experimentally studied in this work. The results show that the DE increased with the rise of: 1) particle sizes (0.054~0.22mm), 2) holding time (30~90 min) and 3) temperature (240~300 °C). In detail, under 300 °C and 60min of holding time, the 85.18% of DE with first PS was lower than the 93.93% of DE with second PS and 100% of DE with third PS. The organic chlorine mainly transferred into chloridion in aqueous solution in HT process. All the results indicate that it is a prospective way to simultaneously removal alkalis and chlorine by co-hydrothermal treatment of chlorinated wastes and high-alkali coal.

## 1. Introduction

PVC [poly (vinyl chloride)] has been widely used in many fields including agriculture, households, automobiles, packing, toys, construction and electronic applications. A report from Ceresana (2014) stated that the global demand for PVC is supposed to increase by around 3.2% per year until 2021 [1]. The Asia-Pacific region holds the largest sales market for PVC with a market share of about 56%.

PVC is a good material in many aspects because of its low cost and high performance. However, the wide application of PVC also caused environmental pollution, called “white pollution”. With the development of the economy and society, the chlorine content of solid waste wastes keeps increasing and the decomposition of PVC has received more and more concern. As for the management of waste plastics, three types of methods including landfill, incineration and recycling are usually applied [2, 3]. Nevertheless, the landfilling of plastic wastes containing PVC has become an unsustainable option

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which poses a considerable problem to future generations because of the difficulty to decomposition, the destruction of soil structure, the adverse effect on vegetation and the exceeded occupation of lands. The incineration also faces the emission of toxic products (TCDD, tetrachlorodibenzo-p-dioxin), resulting in detrimental effect on human's health. Consequently, it is of great importance to develop an innovative method to remove the chlorine in PVC to avoid the emission of toxic products, high temperature corrosion, the pollution of soil and water etc. [4]. Many authors have studied the dechlorination of PVC (virgin and waste) [5-9] and stated that the hydrothermal treatment (HT) is an effective way to remove chlorine under mild conditions.

Hydrothermal dechlorination of PVC refers to decompose PVC in aqueous solutions with high temperature and pressure. Akimoto *et al.* (2004) found that 98% of chlorine could be eluted when municipal waste plastics were pretreated with 0.2 M NaOH [10]. Lu *et al.* (2002) suggested alkali is an effective additives on the dechlorination of PVC during HT process [11]. Inoue *et al.* (2005) have investigated the dechlorination performance of KOH and NaOH during the co-grinding with PVC and found that grinding of the mixture lead to the size reduction of PVC, with causing its mechanochemical reaction with the additive to form partially dechlorinated PVC and chloride (KCl or NaCl)[12]. Yoshioka *et al.* (2000) reported the major products were oxalic acid, a mixture of benzenecarboxylic acids, and CO<sub>2</sub> when oxidized PVC in NaOH solutions at elevated temperatures [13]. Takeshita *et al.*, (2004) stated the chlorine in PVC dissolved in water as hydrochloric acid. No harmful chlorinated organic compounds were observed in the liquid and gas fractions after treatment at 300 °C [14]. Between 250 and 350 °C, polyene low-molecular weight aromatic and aliphatic compounds were observed in the solid, liquid and gas fractions respectively. According to the previous introduction, the HT is effective to remove chlorine from virgin/waste PVC, whereas the alkalis are required to improve the dechlorination efficiency.

The utilization of alkalis in HT dechlorination of PVC would also cause some environmental problem, e.g., the treatment of the wastewater. The coals reserved in Zhundong, Xinjiang, China are featured with the very high quality and very low levels of impurities and could meet the coal consumption of China for the next 100 years according to the current coal consumption[15]. Whereas, the high alkalis content of Zhundong coal would erode the boiler tubes and boiler furnace when burning. Content of Na and Ca are 0.2~1 wt% and 0.6~2.5 wt%, respectively. Yang *et al.* (2016) found that Na is mainly water soluble ( $Na_w/Na_{total}=50\sim85\%$ ) and Ca is mainly acid soluble ( $Ca_{ac}/Ca_{total}=60\sim90\%$ ) [16]. Li *et al.* (2015) found that the release rates of Na and K were higher than those of Ca and Mg in all types of gas environments [17]. Naruse *et al.* (2005) found that high alkali metal compounds existed in the fine particulates with size of less than 1 μm and these sticky particles become easy to adhere on heat exchanger tube surfaces [18]. Alkali metal compounds could cause the slagging, fouling and erosion/corrosion. Therefore, it is crucial to remove the alkalis (main Na) before using Zhundong coal. Accordingly, co-hydrothermal treatment means the processing of mixture (PVC and high-alkali coal) in water slurries at elevated temperature and pressure to facilitate the chemical (chlorine, alkalis) conversion of the organic structures in PVC into chlorine and eliminate the alkalis from Zhundong coal simultaneously. The aim of this work was to investigate the chlorine behavior during the co-hydrothermal treatment of PVC and Zhundong coal to check the feasibility of this technology.

## 2. Materials and methods

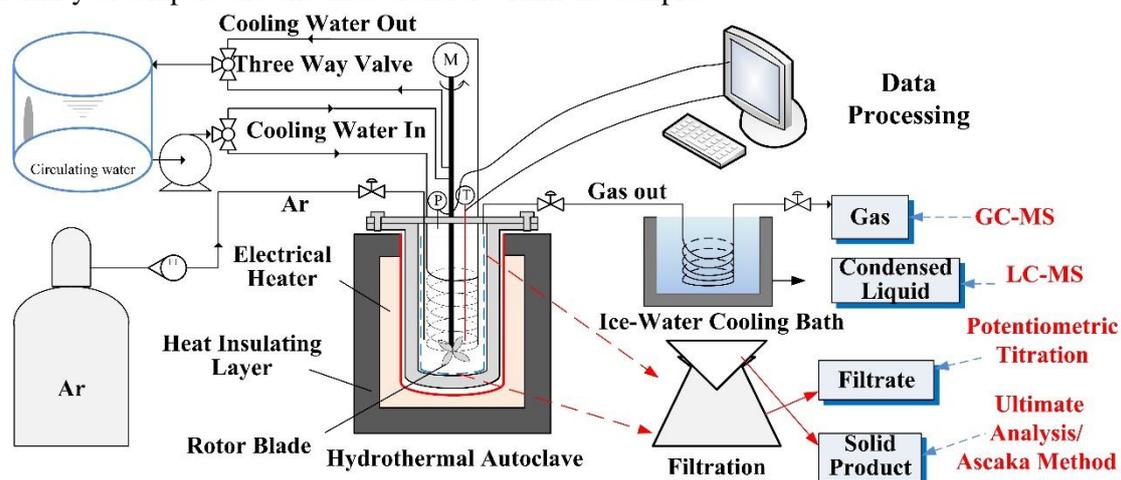
### 2.1. Materials

The polyvinyl chloride powder purchased from Shanghai Yangli Electromechanical Technology Co., Ltd with an average molecular weight ~90 000 Da and a chlorine content of 61.5% was utilized as raw material. The high-alkali coal was collected from Zhundong, China. The ultimate analysis of the materials was listed in Table 1. Before utilization, the coal was first dried in an electronic oven at a temperature of 65 °C and ground into three kinds of particle sizes, 0.054~0.075mm, 0.075~0.1mm and

0.1~0.22mm. All the chemicals were analytical reagent and purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

### 2.2. Co-hydrothermal treatment of PVC and coal

The HT dechlorination experiments were performed in an autoclave. The experimental procedures and the schematic diagram of the autoclave are illustrated in Figure 1. Before the HT process, 2 g of PVC and 18 g of coal were well mixed and immersed into 150 ml deionized water in a 500 ml quartz tube. The glass tube was then placed in the reactor which was subsequently sealed by 8 bolts. After that, the argon with a purity of 99.999% supplied from an argon cylinder was transported into the reactor to replace the air in the reactor. Then the autoclave was heated to the pre-determined temperature (240, 260 and 300 °C) by an electric heater, preserving for pre-determined time (30, 60 and 90 min). After that, the reactor was removed to atmosphere environment to cool down. When the pressure was reduced to atmosphere and the temperature was below 100 °C, the gaseous product was collected by a gas-sampling bag. And the reactor was then opened and the slurry samples were taken out from the glass tube. The slurry was divided into two parts as separated liquid and solid products by filtration. During the whole HT process, the stirrer was kept stirring at a rotary speed of 100 rpm to ensure uniformity of temperature and mass transfer within the samples.



**Figure 1.** The illustration of experimental procedures and schematic diagram of HT dechlorination

### 2.3. Determining Cl removal efficiency

The HT dechlorination efficiency (DE) can be expressed by the amount of chlorine removed, which was equal to that in the separated liquid and the gaseous product. As rare chlorine was observed in the gaseous products, the chlorine contained in the separated liquid was assumed to be the total amount of chlorine removed from PVC during the HT dechlorination process. The amount of Cl in the liquid sample was determined by potentiometric titration. In this method, the double saltbridge saturated calomel electrodes was used as the reference electrode, and the silver electrode was used as the indicator electrode. The end of titration was judged by the extreme point of potential changes, and the corresponding consumption of  $\text{AgNO}_3$  standard solution was noted as  $V_1$ . Then the DE can be calculated by the following equation.

$$\text{HT dechlorination efficiency (DE, \%)} = \frac{\text{Cl content in liquid}}{\text{Cl content in PVC} + \text{Cl content in coal}} \times 100\% \quad (1)$$

The chlorine content of solid particles was measured by using Eschka mixture method referring to GB/T 3558-2014 (eqv ISO 587:1997), which was introduced here briefly.

1 g sample of residue and 3g of Eschka mixture are well mixed with each other in a crucible, covered with an additional 2g of Eschka mixture to ensure that no chlorine is lost during combustion. After that, the mixtures are ignited gradually in a muffle furnace at  $680 \pm 20$  °C for 3 hours. After

cooling, the incinerated mixture is transferred to a beaker with hot water, acidified with 20 ml of 1:1 nitric acid to dissolve the mixture, and filtered. The chloride is then determined by potentiometric titration. Accordingly, the chlorine in the solid product could be derived from equation (2).

$$X = \frac{0.035453 \times c(V_1 - V_2)}{m} \times 100 \quad (2)$$

$V_1$ : consumption of  $\text{AgNO}_3$  standard solution (ml)

$V_2$ : consumption of  $\text{AgNO}_3$  standard solution for blank test (ml)

$c$ : concentration of  $\text{AgNO}_3$  standard solution, 1 mol/L

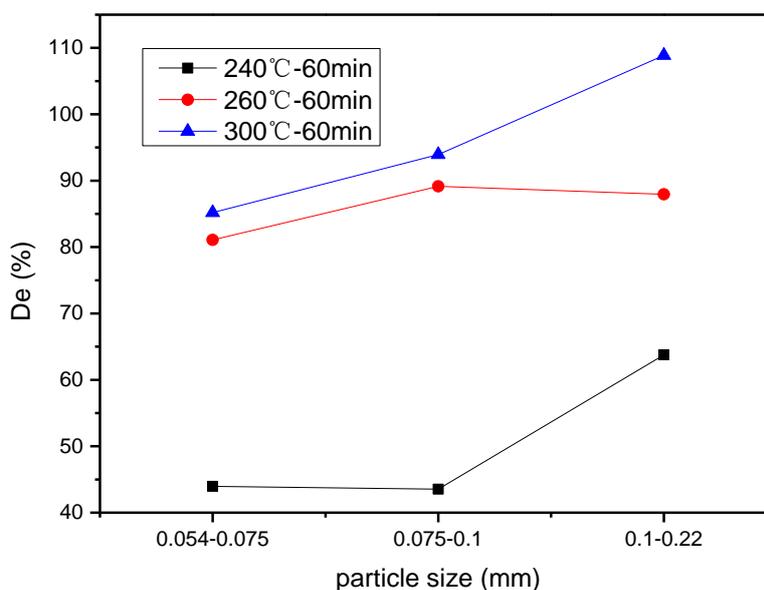
$m$ : quality of samples (g)

### 3. Results and discussion

#### 3.1. HT dechlorination of PVC with High-alkali coal

##### 3.1.1. Effect of coal particle sizes on the DE.

Figure 2 shows the effect of three coal particle size-0.054~0.075, 0.075~0.1 and 0.1~0.22mm on DE of PVC. As indicated, at a HT holding time of 60 mins, the DE of samples treated at a HT temperature of 260 and 300 °C both experience an upward trend, while it remains stable at around 44% for the sample treated at a HT temperature of 240 °C for the samples with a diameter of 0.054~0.075 and 0.075~0.1 mm. However, the DE of HT 240 and 300 °C noticeably keep going up between PS 0.075~0.1 and 0.1~0.22mm, while HT 260 °C, with 89.15% of DE, falls slightly back to 87.94%. It can be concluded that the DE increase with the rise of particle size, which could be due to the effect of coating by ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ) colloid. For example, the PS 0.054~0.075 of PCV/HAC composites was more incline to act as the colloidal nucleus than any other group of PS, resulting in the locking of chlorine by shell of ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ) colloid. Furthermore, Patel et al. (1992) had studied the thermal degradation of virgin and HCl-treated PVC in powder form, as well as of PVC films of different thicknesses as a function of time and temperature<sup>[19]</sup>. They had found that the rate of dehydrochlorination of even the thinnest film significantly exceeds that of the powder samples. In addition, the rate of HCl evolution grow with film thickness, which could be explained by noting that in thicker films the HCl generated takes longer to diffuse out of the sample. Hence, the autocatalysis was more effective in the thicker films, when considering the autocatalytic effect of evolved hydrochloric acid (HCl).



**Figure 2.** PS dependence of DE**3.1.2. Effect of HT temperature on the DE.**

The effect of temperature on HT dechlorination of PVC with high-alkali coal is illustrated in Figure 3. As has been anticipated, the DE of three kind of particle size-0.054~0.075, 0.075~0.1 and 0.1~0.22mm, all increase with HT temperature (from 240, 260 to 300 °C). Moreover, from almost the same value 44%, the DE of particle size-0.054~0.075 and 0.075~0.1mm both soar to 81% and 89%, respectively. Because of the relatively high value of 64% under 240 °C, DE of PS 0.1~0.22mm doesn't go up so much compared with the other two PS, yet up to 89%. Besides, DE of PS 0.1~0.22mm keeps going considerably up to 100%, while DE of the other two PS grow slightly. Poerschmann et al. (2015) have studied the hydrothermal carbonization of poly (vinyl chloride) [20]. They found that dehydrochlorination increased with increasing reaction temperature and quantitative hydrodechlorination was observed beyond temperatures of ~235 °C. Through the analysis of all DTA/TGA results, Castro et al. (2012) supposed that the release of chlorine starts at  $252 \pm 2$  °C [21]. Considering the competitive reaction model of dechlorination proposed by Wu et al. (1994), the sequences of reaction was [22]: (1) PVC converted into intermediate species and HCl; (2) the intermediates converted into polyene and some volatiles.

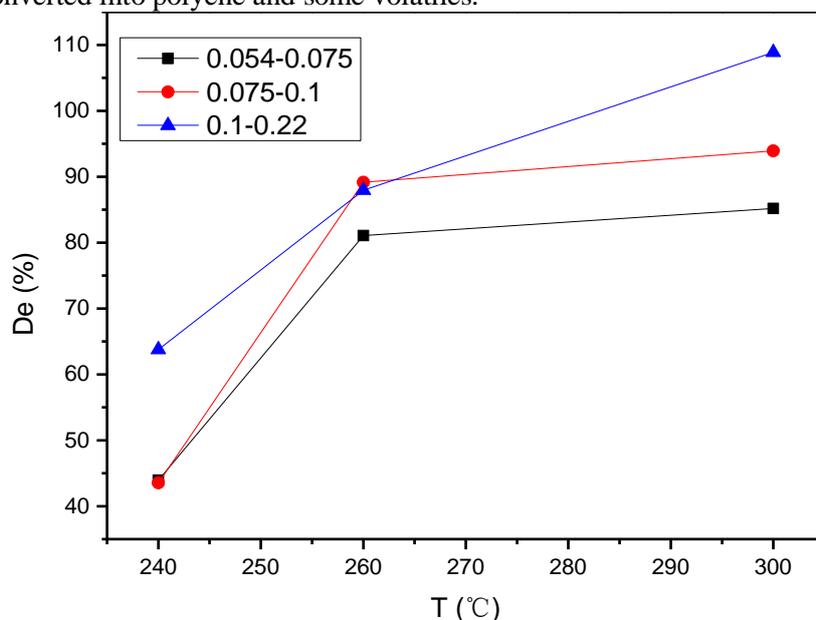
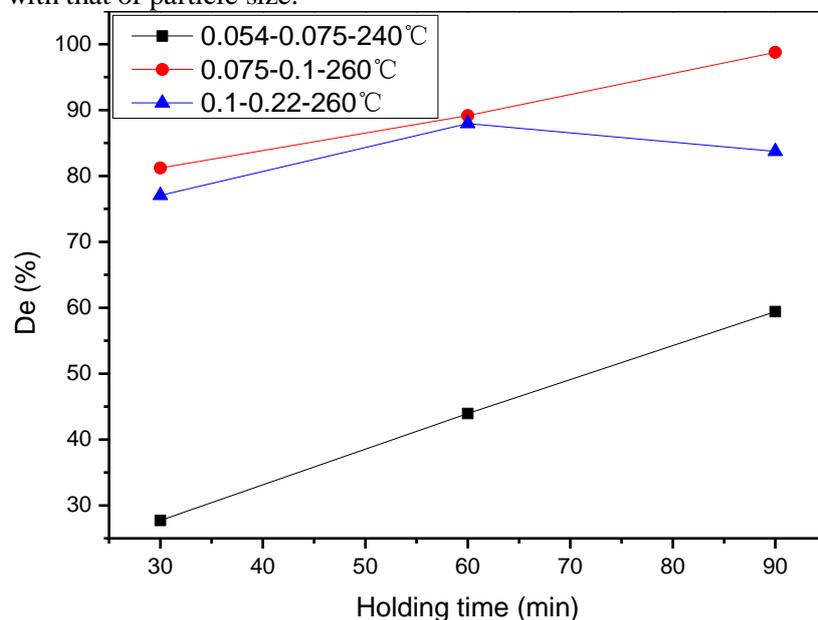
**Figure 3.** Temperature dependence of DE**3.1.3. Effect of HT holding time on DE.**

Figure 4 displays the effect of HT holding time on DE. 30 minutes of holding time here means the sample was firstly heated to pre-determined temperature (240, 260 and 300 °C) and then removed from the heater to cool down after holding the temperature for 30 minutes. As indicated in Figure 3, the DE of the three PS all keep rising with the extension of holding time. However, between the holding time of 60 and 90 minutes, the DE of PS 0.1~0.22 experience a marginal downward trend, from 88% (60 mins) to 84% (90 mins), while the other two rise consistently, from 44% and 89% with 60minutes to 59% and 99% with 90 minutes respectively. It came to conclusion that the DE went up with the increase of holding time, which could be explained by the autocatalytic effect of evolved hydrochloric acid (HCl). It was accordant with the effect of coal particle size on HT. For example, the autocatalysis of PVC/HAC composites over 90 min took more thoroughly than that over 60 min and 30min. In addition, the downward trend experienced by the 0.1~0.22 of PS could be due to that the larger size of composites locked the chlorine in the polymer backbone because of its steady structures

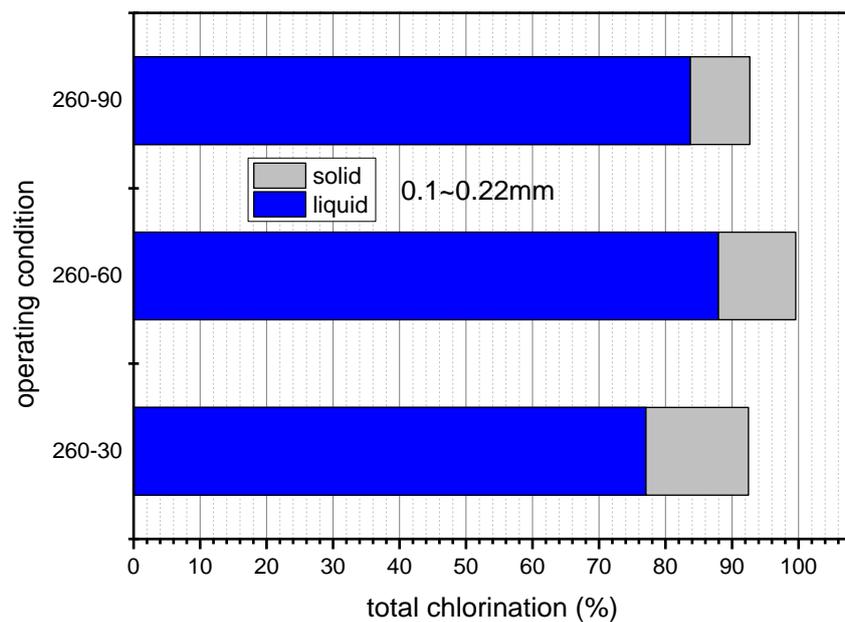
such as aromatic rings. Another reason could be that the effect of holding time could be negligible when compared with that of particle size.



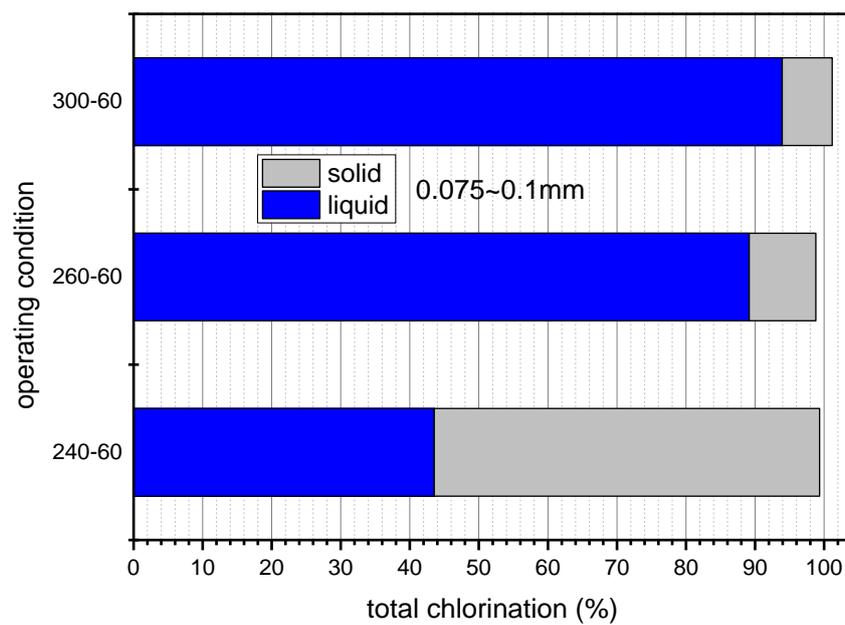
**Figure 4.** Holding time dependence of DE

### 3.2. Chlorine balance during HT dechlorination of PVC

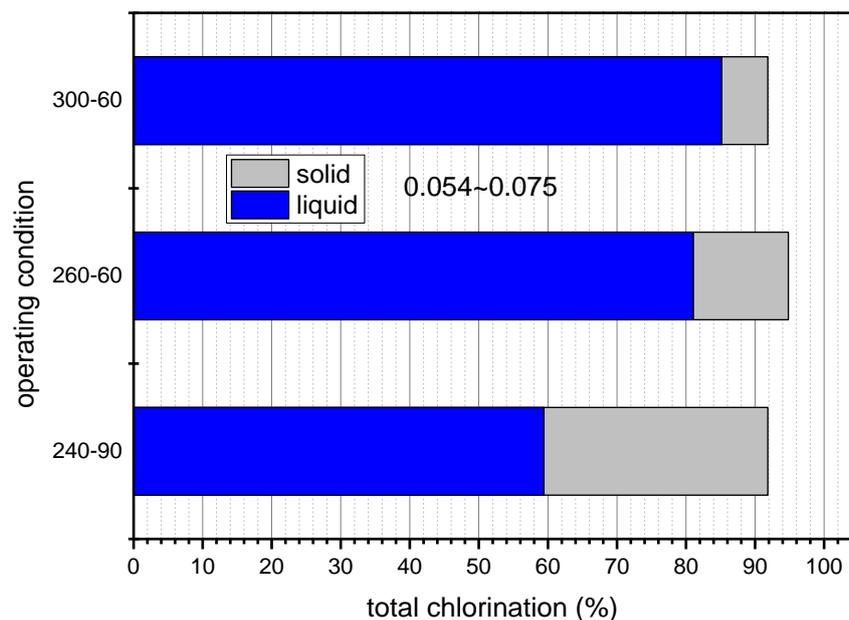
To validate whether the organic chlorine has been totally transferred into chloridion over the co-hydrothermal treatment of PVC and high-alkali coal, it is crucial to evaluate the chlorine mass balance by measuring the chlorine both in solid and liquid. The data shown in Figure 5, Figure 6 and Figure 7 represented the chlorine mass balance of particle size-0.1~0.22, 0.075~0.1 and 0.054~0.075mm during co-hydrothermal treatment. In the figures, the chlorine in liquid and solid represented the DE and chlorine in residues respectively. As illustrated, the gross of chlorine in liquid and solid was approximately 100% in all operating conditions, suggesting that the chlorine in PVC was mainly removed in the form of  $\text{Cl}^-$  during the HT dechlorination process. Castro *et al.* (2012) studied the kinetics of thermal de-chlorination of PVC under pyrolytic conditions [21] and found that the chloride could be fixed in the form of an aqueous solution of HCl or calcium chloride. Takeshita *et al.* (2004) found that the chlorine of PVC dissolved in water as hydrochloric acid, and there were no detrimental chlorinated compounds in the liquid and gas fractions after HT at 300 °C [14]. During dehydrochlorination, chlorine can be released from PVC, via elimination of HCl or nucleophilic substitution with water molecules as nucleophiles, respectively [20] and the HT of PVC is effected on the releasing of organic chlorine. Additionally, the chlorine loss of PS 0.054~0.075 was slightly higher than the two others, suggesting that there was a little chlorine in the gaseous product apart from the losing component in operating process and measuring error. Tsuji *et al.* (1998) had reported the observation of the hydrogen chloride(HCl) in fractionated gas [23], but Takeshita *et al.* (2004) thought that the hydrogen chloride dissolved in the water soon after its elimination from the PVC, due to its high solubility in water<sup>[14]</sup>. Anyway, the chlorine loss of PS 0.054~0.075 was also accordant with the effect of coal particle size on HT, that is, in smaller PS, gas products was more easily to escape from HT systems, which could be explained by noting that in smaller PS the HCl generated takes shorter to diffuse out of the PVC/HAC composites sample.



**Figure 5.** The change of chlorine in solid and liquid CPVC products with PS 0.1~0.22mm



**Figure 6.** The change of chlorine in solid and liquid CPVC products with PS 0.075~0.1mm



**Figure 7.** The change of chlorine in solid and liquid CPVC products with PS 0.054~0.075mm

#### 4. Conclusions

HT dechlorination of PVC and coal has been proved to be an effective method of dechlorination of PVC according to previous analyses. The results are summarized as follows:

- High-alkali coal can accelerate the dechlorination process of PVC during HT. The DE increased with the rise of: 1) particle size (0.054~0.22mm), 2) holding time (30~90 min) and 3) temperature(240~300 °C). the DE was 100% when 300 °C and 60min of holding time, while the DE was 98.77% when 260 °C and 90min of holding time. When 300 °C and 60min of holding time, the 85.18% of DE with first PS was lower than the 93.93% of DE with second PS and 100% of DE with third PS.
- The organic chlorine mainly transferred into chloridion in aqueous solution in HT process. Little chlorine existed in gaseous products and it increased with the decrease of particle size.

#### Acknowledgement

The authors gratefully acknowledge the financial support of the Natural Science Foundation of Jiangsu Province NO.BK20150174 and the Fundamental Research Funds for the Central Universities under grant NO. 2015QNA15 and No. 2015XKMS057.

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