THE IMPROVEMENT OF MERCURY REMOVAL IN NATURAL GAS BY ACTIVATED CARBON IMPREGNATED WITH ZINC CHLORIDE

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First Registered on January 30th 2012; Received after Corection on March 14th 2012
Publication Approval on : April 30th 2012

ABSTRACT

Natural gas being produced from gas fields around Indonesia areas, along with a large number of other harmful substances (CO_2,H_2S, RSH,COS etc) often contains mercury. Even in small amounts, mercury and its compounds have an extremely harmful effect on human health. Mercury content in the natural gas should be removed to avoid equipment damage in the gas processing plant or the pipeline transmission system from mercury amalgamation and embrittlement of aluminium. Mercury can be removed by using adsorption processes such as activated carbon that is impregnated with chlor, iodine or sulfur. This research is dealing with the process of mercury removal from gas based on principle of adsorption and of chemisorption of mercury by means of activated carbon impregnated with $ZnCl_2$. Time of impregnation is a significant variable that can effect adsorption capacity. The experiment results showed that $ZnCl_2$ impregnation time of 12 hours significantly enhanced the adsorptive capacity for mercury vapour.

Keywords: *mercury removal, activated carbon, impregnated zinc chloride*

I. INTRODUCTION

Mercury is a trace element in the natural gas with relatively low contents. Mercury is vaporized from the natural gas and exists as elemental mercury (Hg^0). Mercury is emitted to the atmosphere as a hazard air pollutant if without effective gas purification systems. Generally, mercury can be removed from the natural gas through activated carbons. In the natural gas processing industry, activated carbon is frequently employed for the removal of mercury to protect aluminum heat exchangers as well as providing a safe working environment at the plant. Mercury content in the natural gas should be removed to avoid damaging equipment in the gas processing plant or the pipeline transmission system from mercury amalgamation and embrittlement of aluminium. Mercury is then removed by using adsorption processes such as activated carbon that is impregnated with zinc chloride ($ZnCl_2$).

Elemental mercury (Hg^o) is oxidised to form mercuric oxide (HgO), mercuric chloride ($HgCl_2$) and mercurous chloride (Hg_2Cl_2). Only a small amount of vapor-phase mercury is removed by particulate control devices, e.g. electrostatic precipitators or bag house and the rest are emitted to the atmosphere as a hazard air pollutant if without effective gas purification systems. Mercury may accumulate and concentrate within living organism by food chain, causing various diseases and disorders to animals and humans. Generally, oxidized mercury can be removed from the natural gas or flue gas through wet scrubbing or dry sorbent injection.

Adsorption by activated carbons, particularly those impregnated with sulfur (S), chloride (Cl) or Iodine (I), is a technology that offers great potential for the removal of Hg^o from the natural gas. The main scope of this paper is to investigate the removal of Hg^o from the natural gas by granular activated carbons treated with zinc chloride ($ZnCl_2$) impregnation. The effects of $ZnCl_2$ time impregnation at an adsorption temperature and $ZnCl_2$ solution concentration on the mercury removal performance were studied.

The treatment with $ZnCl_2$ impregnation on activated carbon have been effectively reducing the mercury content in natural gas. Hypothesis of this research is increasing time of $ZnCl_2$ impregnation will improve the mercury adsorption by activated carbons.

II. EXPERIMENTAL

A. Sample Preparation

The test material in this research used was carbon black or activated charcoal and the chemical used were Zinc Chloride ($ZnCl_2$) 5%, Chloride Acid (HCl) 0,5 N dan 5%, Iodium (I_2) 0,1 N, Sodium thiosulphat ($Na_2S_2O_7$) 0,1 N, Kalium dichromat ($K_2Cr_2O_7$) 0,1 N, Indicator, Whatman paper No.40 and distillation water.

Commercial granular activated carbons was sieved to have 70 mesh size, prepared from coconut shells charcoal by activation at 700°C in a tubular stainles steel reactor. The obtained Activated carbons were then by impregnated with 5% (w/v) $ZnCl_2$ solution for 6, 12 and 24 hours. Impregnated activated carbons were dried in an oven at 90°C, cooled down to the room temperature and then stored in a desiccators for future use.

B. Sample Characterization

The characteristics of adsorbent sample were determined by Iodine number, BET (Brunauer-Emmett-Teller) and Scanning Electron Microscope (SEM). The Iodine Number is determined by iodometric method. BET analysis is a measurement of surface area and pore distribution by adsorption and desorption of N_2 gas. SEM-EDX is a scanning Electron Microscopy to determine the micro structure of a material including texture, morphology, composition and christallography particle surface. The morphology is monitored by SEM analysis were shape, size and particle formation. EDX (*Energy Dispersive X-ray*), is a material characterization method using x-ray emission. The Result data of EDX analysis will show the constituent of Cl-impregnated activated carbons (see Table 1). The EDX analysis used ZAF method quantitative analysis.

C. Adsorption of Mercury Removal from Natural Gas

The working principal of this mercury removal equipment is to follow the natural gas containing mercury vapor at known concentration through an adsorbent. An amount of mercury will be adsorbed and the remaining mercury in the natural gas will be adsorbed by $KMnO_4$ solution. After that the solution is analyzed by Lumex mercury analyzer. The volume of the flowing gas is measured by a wet test meter equipment.

A schematic diagram of the experimental setup used in mercury adsorption tests is shown in Figure 1.

Table 1
Adsorbent composition analyzed by ZAF method

Element	Mass %
C K	81.99
O K	5.87
Al K	1.32
Si K	0.23
Cl K	4.94
Zn K	5.65
Total	100.00

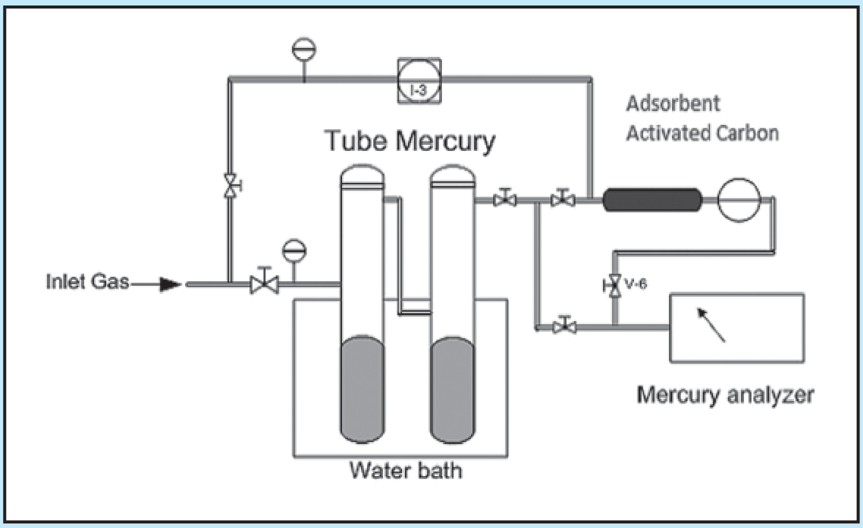

Figure 1
An experimental setup of mercury adsorption test

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Measurement of standard mercury and mercury sample in Outlet Adsorber

- The natural gas is flown through mercury cylinder placed in a water bath at a temperature of 37^{o}C.
- The gas from the outlet of the mercury cylinder is put into a mercury solution ($KMnO_4 + H_2SO_4$) .
- The mercury concentration is in the solution analyzed by *Mercury Analyzer* (Lumex 91), measured in µg/m^3.

III. RESULTS AND DISCUSSION

A. Experimental Result

SEM and EDX Characterization

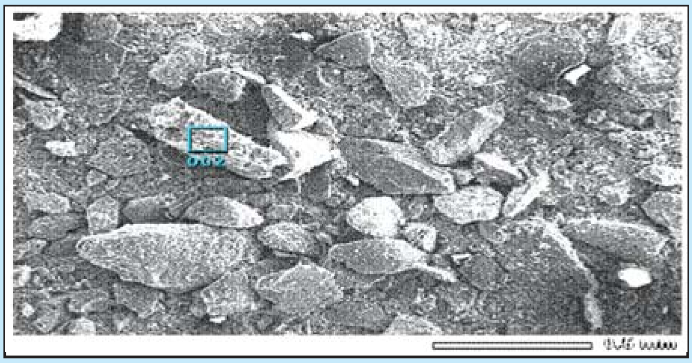

Figure 2
SEM foto of the sample at T = 700^{o}C, 12 h impregnation after activation

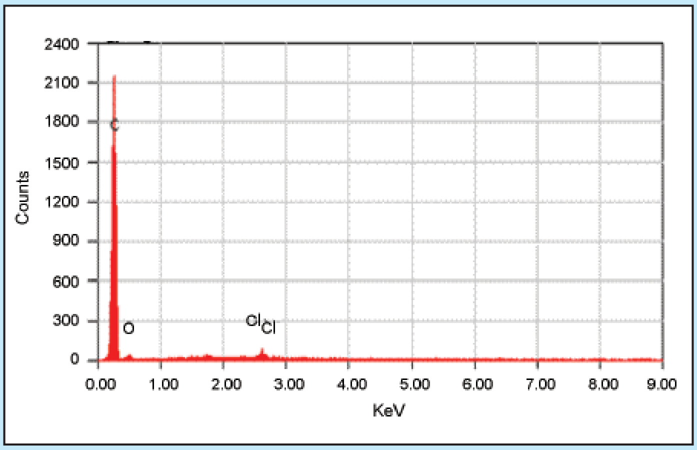

Figure 3
EDX result of the sample at T = 700^{o}C, 12 h impregnation after activation

BET Characterization

Table 2
BET (Brunauer-Emmett-Teller) result

Temperature (^{o}C)	Pore diametre (nm)	Surface Area (m^2/g)
700	219,26	463,17

B. Discussion

Adsorption results of Hg^0 onto the untreated as well as impregnated $ZnCl_2$ activated carbons for 6, 8, 12 and 24-h testing time are shown in Figure 4 and 5. It can be seen that Hg concentration at the outlet of adsorber having no adsorbent is 27.633 µg/m^3 (Table 3). For the untreated activated carbon, the amount of Hg^o adsorbed decreased progressively, indicating a typical physisorption mechanism due to van der Waals forces between the adsorbate and the adsorbent. For the activated carbon with impregnated of $ZnCl_2$ solution, the amount of Hg^o adsorbed increased progressively, because $ZnCl_2$ properties can behavior as chemical activator, increasing the adsorption capacity of the activated carbon and $ZnCl_2$ solution can create new pores and can form C-Cl bonding whenever Cl group can attach the mercury (Hg) by chemical bonding to be HgCl or $HgCl_2$

Optimum adsorption occurs for adsorbent of 12 hours impregnation time and in vertical position adsorber. Amount of mercury adsorbed in the adsorbent was 96 %. Impregnation with $ZnCl_2$, particularly with the solution concentration of 5%, increased the Hg^0 adsorption amount significantly. This optimum adsorption probably due to the occurrence of chemisorption by forming chemical bonds between the adsorbate and the chlorides present on the adsorbent. It is worth to note that the impregnation of $ZnCl_2$ longer than 12 hours decreased the mercury adsorption of the activated carbon samples. This probably due to the blockage of internal pores by incorporated $ZnCl_2$ molecules.

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Adsorption Result and Mercury Analysis

Table 3
Hg concentration measurement without adsorbent, and adsorbent without $ZnCl_2$

Experiment number	Type of Sample	Measurement Hg in KMnO4 solution ($\mu g/m^3$)
1	Without adsorbent	27.633
2	Adsorbent without $ZnCl_2$ Horizontal Adsorber	2.653
3	Adsorbent without $ZnCl_2$ Vertical Adsorber Position	2.564

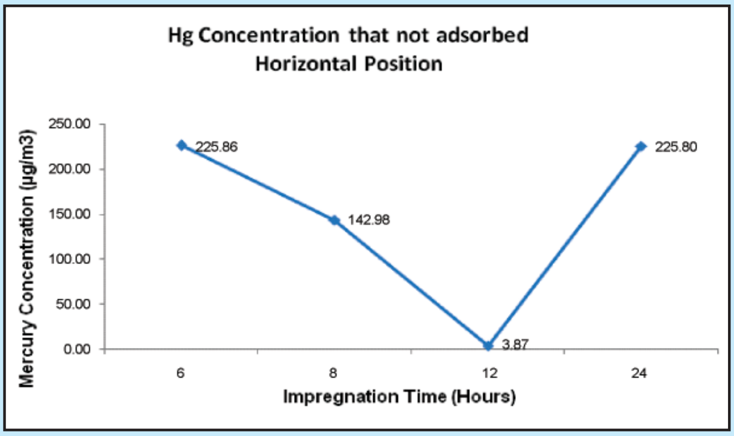

Figure 4
Mercury concentration at adsorber outlet horizontal position

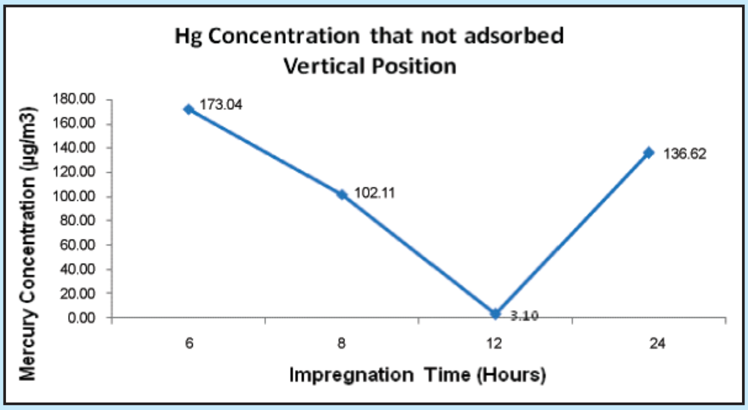

Figure 5
Mercury concentration at adsorber outlet vertical position

While generally, for pure physisorption process, the adsorptive capacity of the activated carbon increases with increasing the specific surface area, in this research is suggested the occurrence of chemisorption of elemental mercury onto the Cl-impregnated samples. Hg^0 adsorbed onto the Cl-impregnated samples attributed to a combined physisorption and chemisorption. A typical physisorption mechanism due to van de Waals forces between the adsorbate and the adsorbent. The mechanism of chemisorptions of elemental mercury onto the Cl-impregnated activated carbons was proposed as follows. During impregnation, $ZnCl_2$ was reduced by the carbon content in activated carbons and some Cl-contained complexes were formed:

$$ZnCl_2 + C_nH_xO_y \rightarrow Zn + [\ Cl_2\text{-}C_nH_xO_y\ ]$$

These Cl-contained functional groups accounted for the chemisorption of Hgo through the following reactions below :

$$Hg^0 + [Cl]^- \rightarrow [HgCl]^+ + 2e \quad \text{and}$$

$$Hg^0 + 2[Cl]^- \rightarrow [HgCl_2] + 2e$$

In the presence of extra Cl species, the mercury atom even is tended to adopt four-coordination numbers as:

$$[HgCl_2] + 2[Cl]^- \rightarrow [HgCl_4]^{2-}$$

The characterization test by SEM-EDX instrument has detected Cl-contained functional group on the activated carbon adsorbent.

IV. CONCLUSIONS

1. $ZnCl_2$ as chemical activator is very important for increasing the adsorption capacity activated carbon because it can create new pores and can form C-Cl bonding the Cl group can then catch the mercury by chemical bonding to be HgCl or $HgCl_2$
2. Hg^0 adsorbed onto the Cl-impregnated adsorbent attributed to a combined physisorption and chemisorption
3. Mercury adsorption by activated carbons that impregnated $ZnCl_2$ for 12 hours shows the best result.

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4. As chemisorption of mercury by Cl-contained functional groups, created by $ZnCl_2$ impregnation, were probably due to the formation of various complexes.
5. The experiment test showed that indicating the impregnated adsorbent was able to adsorp mercury (Hg) as much as 27.629,94 µg/m^3.
6. The mechanism of chemisorptions of elemental mercury onto the Cl-impregnated activated carbons.

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