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Hung -Lung Chiang<sup>a</sup>; Jiun -Horng Tsai<sup>b</sup>; Chien -Liang Tsai<sup>b</sup>; Yi -Chun Hsu<sup>b</sup>

<sup>a</sup> DEPARTMENT OF ENVIRONMENTAL ENGINEERING, FOoyIN INSTITUTE OF TECHNOLOGY, KAOSHUNG, TAIWAN, REPUBLIC OF CHINA <sup>b</sup> GRADUATE INSTITUTE OF ENVIRONMENTAL ENGINEERING, NATIONAL CHENG KUNG UNIVERSITY, TAINAN, TAIWAN, REPUBLIC OF CHINA

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## Adsorption Characteristics of Alkaline Activated Carbon Exemplified by Water Vapor, H<sub>2</sub>S, and CH<sub>3</sub>SH Gas

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HUNG-LUNG CHIANG\*

DEPARTMENT OF ENVIRONMENTAL ENGINEERING  
FOOYIN INSTITUTE OF TECHNOLOGY  
KAOSHISUNG, TAIWAN, REPUBLIC OF CHINA

JIUN-HORNG TSAI, CHIEN-LIANG TSAI, and YI-CHUN HSU

GRADUATE INSTITUTE OF ENVIRONMENTAL ENGINEERING  
NATIONAL CHENG KUNG UNIVERSITY  
TAINAN 70101, TAIWAN, REPUBLIC OF CHINA

### ABSTRACT

Activated carbon adsorption is an widely used process in environmental engineering. Alkaline impregnated activated carbon has been used to enhance the adsorption capacity for odorous compounds from gas streams. This study investigated the physicochemical and adsorption characteristics of one virgin and four alkaline-impregnated activated carbon samples. The four alkaline additives were NaOH, Na<sub>2</sub>CO<sub>3</sub>, KOH, and K<sub>2</sub>CO<sub>3</sub> and the impregnated activated carbons were referred to as NaOH-IAC, Na<sub>2</sub>CO<sub>3</sub>-IAC, KOH-IAC, and K<sub>2</sub>CO<sub>3</sub>-IAC. The specific surface area, micropore area, and micropore volumes were reduced in the impregnated activated carbon systems. The adsorption capacity of H<sub>2</sub>S and CH<sub>3</sub>SH increased. This indicated that the physical properties were not the predominant influence on adsorption behavior. The impregnated activated carbons were ranked NaOH > Na<sub>2</sub>CO<sub>3</sub> > KOH > K<sub>2</sub>CO<sub>3</sub> for H<sub>2</sub>S adsorption. The NaOH-IAC demonstrated 3.2 and 2.2 times the adsorption capacity for H<sub>2</sub>S and CH<sub>3</sub>SH, respectively, compared to the virgin AC sample. Increasing the vacuum and immersion duration increased the alkaline quantity of NaOH impregnated on activated carbon. The NaOH-IAC<sub>50</sub> (50 mg NaOH/g carbon) sample performed the best. It had 6.9 times the adsorption capacity of the virgin AC. The humidity that coexisted in the H<sub>2</sub>S and CH<sub>3</sub>SH gas

\* To whom correspondence should be addressed.

streams enhanced the  $\text{H}_2\text{S}$  and  $\text{CH}_3\text{SH}$  adsorption capacity of NaOH-IAC. At 50% relative humidity and 50 ppm  $\text{H}_2\text{S}$ , the NaOH-IAC sample exhibited the maximum adsorption capacity for  $\text{H}_2\text{S}$ . This carbon attained 30.3 times more capacity than the virgin AC.

**Key Words.** Hydrogen sulfide; Methyl mercaptan; Alkaline activated carbon; Humidity; Adsorption capacity; Principle component analysis

## INTRODUCTION

The natural sources of sulfur that are emitted to the atmosphere are primarily reduced sulfur compounds such as dimethyl sulfide ( $\text{C}_2\text{H}_6\text{S}$ ), dimethyl disulfide ( $\text{C}_2\text{H}_6\text{S}_2$ ), hydrogen sulfide ( $\text{H}_2\text{S}$ ), and methyl mercaptan ( $\text{CH}_3\text{SH}$ ) rather than sulfur dioxide ( $\text{SO}_2$ ) (1). Turk et al. (2) and Koe and Tan (3) reported the physical adsorption of such sulfur compounds on activated carbon.  $\text{H}_2\text{S}$  was usually removed from sour gas by absorption in an alkaline solution (4). Activated carbon has been used to remove  $\text{H}_2\text{S}$  and other odorous compounds from gas streams (5, 6). Alkaline-activated carbon, made by impregnating virgin AC with sodium hydroxide (NaOH), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) or sulfonated solutions, has successfully removed  $\text{H}_2\text{S}$ ,  $\text{CH}_3\text{SH}$ , and trimethylamine [ $(\text{CH}_3)_3\text{N}$ ] from gas mixtures with concentrations of 10 to 800 ppm (5). Impregnated activated carbon has also been used to remove ammonia ( $\text{NH}_3$ ) and  $\text{H}_2\text{S}$  from a gas mixture (6). Furthermore,  $\text{H}_2\text{S}$  was efficiently removed from a sour gas with an alkaline-activated carbon (5–7).

When humidity is high, capillary condensation of water vapor takes place and the adsorption of solvents is hindered (8). Freeman et al. (14) indicated the adsorption of hydrogen cyanide (HCN) discouraged additional adsorption of water vapor. The adsorption of water vapor on activated carbon depends strongly on the concentrations of surface oxide groups and on the specific adsorption of water molecules in the micropore (9). Barton et al. (10) showed that the adsorption site initiating adsorption of water molecules on activated carbons are the CO-desorbing surface groups. Stoeckli et al. (11) suggested that the carbonyl-type groups are the primary adsorption centers for water molecules on various types of charcoal. Pore filling was possibly promoted by the presence of hydrophilic surface oxides (12).

The objectives of this study were: 1) to investigate which impregnated alkaline-activated carbon(s) increased adsorption capacity (including hydroxide and carbonate salts); 2) to determine the physicochemical characteristics of the impregnated activated carbons; 3) to determine the adsorption characteristics of a  $\text{H}_2\text{S}$  and  $\text{CH}_3\text{SH}$  mixture as gas systems; and 4) to determine the influence of water vapor on adsorption capacities.



## EXPERIMENTAL

### Preparation of Impregnated Activated Carbons

An activated carbon (RB<sub>2</sub>; size: 2 mm, Norit Company, Netherlands) made from peat was used in this study. All solutions were prepared with analytical chemicals (Merck). A Mettler pH meter (Model 420A) was used for pH measurement. A strong acid (1 N HCl) and a base (1 N NaOH) were used for alkaline addition analysis. Unless otherwise noted, a strong acid [perchloric acid (0.1 M HClO<sub>4</sub>)] and a strong base (0.2 M NaOH) were used for pH adjustments.

Fifty grams of the activated carbon were put into a stainless steel tube (15 mm in diameter, 35 cm in length). Nitrogen was added at 140°C for 6 hours to dewater and activate the activated carbon. Following the pretreatment process, each carbon was immersed in a 1 N NaOH, potassium hydroxide (KOH), Na<sub>2</sub>CO<sub>3</sub>, or potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) solution for 4 hours. The slurry was then stirred for 30 minutes. After the carbon was vacuum processed for 30 minutes, it was filtered and dried in an oven at 130°C for 60 hours. The impregnated activated carbons were labeled NaOH-IAC, KOH-IAC, Na<sub>2</sub>CO<sub>3</sub>-IAC, and K<sub>2</sub>CO<sub>3</sub>-IAC, respectively. The nonimpregnated sample was identified as virgin AC.

### Alkaline Addition Measurement

The alkaline content of NaOH, KOH, K<sub>2</sub>CO<sub>3</sub>, and Na<sub>2</sub>CO<sub>3</sub> on each impregnated activated carbon was determined by titration. The carbon was placed in a vacuum oven (10<sup>-2</sup>–10<sup>-3</sup> mmHg, 105°C) for 24 hours. Distilled water and a 1 N hydrochloric acid (HCl) solution were added to the impregnated carbon, and the slurry was shaken at 25°C for 24 hours. The supernatant was then titrated with a 1 N NaOH solution.

### Physicochemical Characteristics Analysis

The physical characteristics of activated carbon, including specific surface area, micropore area, total pore volume, micropore volume, pore size distribution, and pore diameter, were measured by liquid N<sub>2</sub> adsorption at 77 K with an ASAP 2000 Micropore Analyzer.

An Element Analyzer (HERAEUS CHN-O Rapid Element Analyzer, USA) analyzed surface compositions of carbon, nitrogen, hydrogen, and oxygen. Acetanilide was used as the standard. Sulfur and chlorine were analyzed with a Tacussel Coulomax 78. Sulfanilic acid and 1-chloro-2,4-dinitrobenzene were prepared as standards. Five samples were analyzed in duplicate.

Activated carbon samples were ground to a fine powder in an agate grinder. The mixture of KBr and the activated carbon powder was mixed in a weight



ratio of 300 to 1, then 150 mg of the mixture was weighed to prepare KBr pellets. The KBr pellets were stored in a desiccator until IR analysis. The IR spectrum was monitored over a frequency of 500 to 4000  $\text{cm}^{-1}$  (Bohem, Model DA 3.002 FTIR).

### Adsorption Process

The adsorption column was 8 cm long and 16 mm in diameter. The bottom of the column was packed with 3 cm of glass beads. The glass beads were used to assure adsorbates were mixed well. Activated carbon was packed in the adsorption column on top of the glass beads. Cylinder gas  $\text{H}_2\text{S}$  was blended with  $\text{N}_2$  gas. A Sierra Mass Flowmeter (Series 9000) controlled the flow rate between 2.0 and 10 L/min. The concentrations of  $\text{H}_2\text{S}$  and  $\text{CH}_3\text{SH}$  ranged from 20 to 8000 ppm and 50 to 100 ppm, respectively, as analyzed by a Varian 3400 Gas Chromatograph/Flame Photometric Detector. The relative humidity of influent water vapor was between 0 to 80%. The capacity of the carbon to adsorb water vapor was weighed with a balance.

### Principal Component Analysis

Influence factors in the  $\text{H}_2\text{S}$ ,  $\text{CH}_3\text{SH}$ , and water vapor mixed gas adsorption system were examined by principle component analysis and performed by the Statistical Analysis System (SAS).

## RESULTS AND DISCUSSIONS

### Physicochemical Characteristics

#### *Pore Characteristics*

Table 1 shows the specific surface area, micropore area, micropore volume, and pore diameter of various activated carbons. The specific surface areas ranged from 683 to 931  $\text{m}^2/\text{g}$ . The virgin AC had the largest surface area. The reduction ratio of the BET surface area was 18.6, 6.02, 11.4, and 26.6% for NaOH-IAC,  $\text{Na}_2\text{CO}_3$ -IAC, KOH-IAC, and  $\text{K}_2\text{CO}_3$ -IAC, respectively, compared to the virgin AC. Micropore area for the NaOH-IAC,  $\text{Na}_2\text{CO}_3$ -IAC, KOH-IAC and  $\text{K}_2\text{CO}_3$ -IAC impregnated activated carbons decreased from 646 to 529, 577, 518, and 397  $\text{m}^2/\text{g}$ , respectively. This is a decrease of 18.1, 13.8, 19.8 and 38.5%, respectively, with respect to the virgin AC. The micropore volume for the impregnated activated carbon was also reduced, from 0.19 to 0.26  $\text{cm}^3/\text{g}$ . When compared to the virgin AC 0.30  $\text{cm}^3/\text{g}$ , the ratio decreased between 13.3 and 36.7%. The average pore diameters for the various activated carbon showed only a slightly variation between 15.57 and 15.73 Å. Experimental results clearly indicated that the NaOH,  $\text{Na}_2\text{CO}_3$ , KOH, and  $\text{K}_2\text{CO}_3$  impregnated activated carbons decreased in specific surface area, micropore area, and micropore volume.



TABLE 1  
Pore Characteristics of Alkaline Impregnated Activated Carbons and Their Adsorption Capacity for H<sub>2</sub>S and CH<sub>3</sub>SH Adsorption

Adsorbents	AC	NaOH-IAC	Na <sub>2</sub> CO <sub>3</sub> -IAC	KOH-IAC	K <sub>2</sub> CO <sub>3</sub> -IAC
Alkaline additive (mg/g)	—	23	25	20	39
BET surface area (m <sup>2</sup> /g)	931	758	875	825	683
Micropore area (m <sup>2</sup> /g)	646	529	557	518	397
Total pore volume (cm <sup>3</sup> /g)	0.49	0.40	0.46	0.42	0.37
Micropore volume (cm <sup>3</sup> /g)	0.30	0.25	0.26	0.25	0.19
Average pore diameter (Å)	15.61	15.57	15.66	15.62	15.73
Adsorption capacity of H <sub>2</sub> S (mg/g)	6.14	19.44	16.27	12.30	11.91
Adsorption capacity of CH <sub>3</sub> SH (mg/g)	24.13	52.64	38.74	45.48	32.28

Although, the specific surface area, micropore area, and micropore volume of the impregnated activated carbons decreased, H<sub>2</sub>S and CH<sub>3</sub>SH adsorption increased. These phenomena demonstrate that physical properties were not the dominant adsorption capacity factors. The additive alkali was the significant factor. However, the four additives performed differently during H<sub>2</sub>S and CH<sub>3</sub>SH adsorption, and that can be attributed to the molecular size of the additives.

### Elemental Compositions

Table 2 shows the results of elements on the activated carbon surface. The elemental compositions of C, H, and S on the activated carbon surface

TABLE 2  
Element Composition of Alkaline Activated Carbons

Adsorbents	C (%)	H (%)	S (%)	N (%)	Cl (%)
AC	73.99	2.83	0.52	<0.01	<0.01
NaOH-IAC	71.17	2.28	0.28	<0.01	<0.01
Na <sub>2</sub> CO <sub>3</sub> -IAC	74.55	1.76	<0.01	<0.01	<0.01
KOH-IAC	68.57	2.18	<0.01	<0.01	<0.01
K <sub>2</sub> CO <sub>3</sub> -IAC	70.86	2.14	<0.01	<0.01	<0.01



changed after alkaline treatment. Carbon contents were 73.99, 71.17, 74.55, 68.57, and 70.86% for AC, NaOH-IAC, Na<sub>2</sub>CO<sub>3</sub>-IAC, KOH-IAC, and K<sub>2</sub>CO<sub>3</sub>-IAC, respectively. The hydrogen content decreased from 2.83% for AC to 2.28, 1.76, 2.18, and 2.14% for NaOH-IAC, Na<sub>2</sub>CO<sub>3</sub>-IAC, KOH-IAC, and K<sub>2</sub>CO<sub>3</sub>-IAC, respectively. The sulfur content decreased from 0.52% (virgin AC) to 0.28% (NaOH-IAC), and was not detectable in the Na<sub>2</sub>CO<sub>3</sub>-IAC, KOH-IAC and K<sub>2</sub>CO<sub>3</sub>-IAC samples. An Element Analyzer did not detect nitrogen or chlorine on the activated carbon samples.

Impregnated activated carbon elements (C, H, and S) decreased after alkaline treatment. The alkaline may have extracted the elements from the activated carbon. However, there was no evidence that the change of elemental composition changed the H<sub>2</sub>S and CH<sub>3</sub>SH adsorption capacity.

### Surface Functional Groups

Results of the activated carbon surface IR analysis are summarized in Table 3. The virgin AC aromatic ring, CH, and aromatic CH band positions were at 548–570, 699, and 759–776 cm<sup>-1</sup>, respectively. The spectra of the alkaline-impregnated activated carbon showed no significant absorption peaks between 540 to 700 cm<sup>-1</sup>. The absorption positions of the C—O band were 1125–1170 and 1208–1216 cm<sup>-1</sup>. The absorption bands at 1383–1386 and 1456–1466 cm<sup>-1</sup> can be attributed to phenol. The aromatic C=C stretching

TABLE 3  
Surface Functional Groups of the Activated Carbons by IR Analysis

Functional groups	Absorption peaks (cm <sup>-1</sup> )				
	AC	NaOH-IAC	KOH-IAC	Na <sub>2</sub> CO <sub>3</sub> -IAC	K <sub>2</sub> CO <sub>3</sub> -IAC
Aromatic ring	548	—	—	570	—
C—H	699	—	—	—	—
C—H <sup>a</sup>	776	759	—	—	—
C—O stretch and vibration	—	1170	—	1170	1125
C—O or phenoxy absorption	1208	1216	1212	—	—
Phenol	1384	1384	1383	1386	1386
	—	1466	—	1456	—
C=O stretch, carboxyl	1571	1565	1568	1567	1570
C=O <sup>b</sup>	—	1738	—	—	—
Aliphatic CH <sub>2</sub> and CH <sub>3</sub>	2922	2923	2920	2923	2922
—OH	3441	3434	3470	3345	3508

<sup>a</sup> With ring vibration.

<sup>b</sup> Unsaturated  $\delta$ -lactone.





vibration peaks were observed at  $1571\text{ cm}^{-1}$  of the AC as well as at  $1565\text{ cm}^{-1}$  for NaOH-IAC,  $1568\text{ cm}^{-1}$  for KOH-IAC,  $1567\text{ cm}^{-1}$  for  $\text{Na}_2\text{CO}_3$ -IAC, and  $1570\text{ cm}^{-1}$  for  $\text{K}_2\text{CO}_3$ -IAC. There was a weaker band in the carboxylic acid  $\text{C}=\text{O}$  region at  $1738\text{ cm}^{-1}$  for NaOH-IAC. A strong and broad OH region band at  $3345\text{--}3508\text{ cm}^{-1}$  was shown for all activated carbon samples. The spectra of  $\text{CH}_3$  and  $\text{CH}_2$  stretch were at  $2920\text{--}2923\text{ cm}^{-1}$ . However, the weak band at  $1738\text{ cm}^{-1}$  in the sodium salt of activated carbon may have been due to a normal carbonyl group. The activated carbon spectra revealed a chemical shift that was due to the reaction of alkaline with activated carbon.

### Alkaline Impregnation

Table 1 also shows the alkaline impregnation ratios on activated carbons. The alkaline additives impregnated on virgin AC ranged from 0.18 to 0.58 mmol/g and were ranked  $\text{NaOH} > \text{Na}_2\text{CO}_3 > \text{KOH} > \text{K}_2\text{CO}_3$ . The moles of NaOH impregnated on the virgin AC were 1.6–3.2 times greater than the other impregnation solutions. The molecular size of NaOH is smaller than  $\text{Na}_2\text{CO}_3$ , KOH, or  $\text{K}_2\text{CO}_3$ , which implies that it is easier to transport into the activated carbon pores, thus making it the best impregnating additive on carbon.

### ***H<sub>2</sub>S and CH<sub>3</sub>SH Adsorption Capacity of Alkaline Activated Carbons***

When the  $\text{H}_2\text{S}$  loading in the influent stream was 1.08 mg/min (250 ppmv, 3.1 L/min at  $25^\circ\text{C}$ ), the  $\text{H}_2\text{S}$  adsorption capacity on the impregnated adsorbents was 19.44 mg/g (NaOH-IAC), 16.27 mg/g ( $\text{Na}_2\text{CO}_3$ -IAC), 12.30 mg/g (KOH-IAC), 11.91 mg/g ( $\text{K}_2\text{CO}_3$ -IAC), and 6.14 mg/g (AC). The results are summarized in Table 1. The  $\text{H}_2\text{S}$  adsorption capacity for NaOH-IAC was 3.2 times that of the virgin AC. When the influent concentration of  $\text{CH}_3\text{SH}$  was 1.96 mg/min (100 ppmv, 10 L/min at  $25^\circ\text{C}$ ) the  $\text{CH}_3\text{SH}$  adsorption capacities on AC, NaOH-IAC,  $\text{Na}_2\text{CO}_3$ -IAC, KOH-IAC, and  $\text{K}_2\text{CO}_3$ -IAC were 24.14, 52.64, 38.74, 45.48, and 32.28 mg/g, respectively. NaOH-IAC had the maximum adsorption capacity (up to 2.2 times the virgin AC). It was selected as the test system for the series experiments.

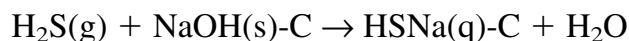
$\text{H}_2\text{S}$  and  $\text{CH}_3\text{SH}$  adsorption capacities were enhanced with NaOH-IAC; more NaOH was impregnated on the activated carbons than the other alkalines. Molecularly, NaOH is smaller than KOH, which is smaller than  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ . NaOH was impregnated on the activated carbons in a 0.575 mmol/g ratio while KOH,  $\text{K}_2\text{CO}_3$ , and  $\text{Na}_2\text{CO}_3$  were absorbed in 0.357, 0.282, and 0.236 mmol/g ratios, respectively (Table 1). The smaller molecules were transported into the small pores of the activated carbon more easily and, therefore, produced higher adsorptive capacities. Conceptually, the enhanced adsorption capacity reaction system can be explained by two mechanisms: the





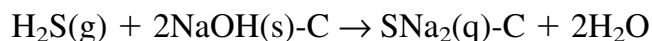
H<sub>2</sub>S mixture gas with or without water vapor. CH<sub>3</sub>SH can be substituted in the following NaOH-IAC examples.

**(1) Without Water Vapor Reaction.** H<sub>2</sub>S was transported to the surface of the alkaline activated carbon and then reacted (adsorbed) with the NaOH. The H<sub>2</sub>S adsorbed on solid surface and generated two products and a water film on the surface of alkaline activated carbon.



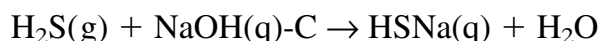
and

(1)



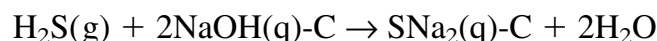
where H<sub>2</sub>S(g) is H<sub>2</sub>S gas without water vapor. NaOH(s)-C is NaOH impregnated on the activated carbon. HSNa(q)-C, and SNa<sub>2</sub>(q)-C are the compounds formed on the activated carbon and covered by a water film.

Following Eq. (1), the impregnated activated carbon would be covered by the generated H<sub>2</sub>O. H<sub>2</sub>S would then react with the water film (absorption and acid-base reaction) as follow:



and

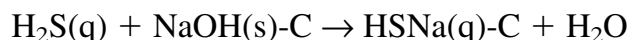
(2)



where NaOH(q)-C is the NaOH impregnated on the activated carbon covered by the water film.

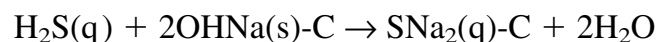
**(2) With Water Vapor Reaction.** The adsorption of H<sub>2</sub>S on the impregnated activated carbon could proceed in two directions depending on whether the mixture of H<sub>2</sub>S gas water vapor had reacted or not before activated carbon impregnation.

First, if the H<sub>2</sub>S was previously absorbed by (dissolved into) water vapor, the reactions follows Eq. (3):



and

(3)



where H<sub>2</sub>S(q) is H<sub>2</sub>S gas dissolved in water vapor.

Second, if the H<sub>2</sub>S had not been previously dissolved in the water vapor mixture, the reaction would follow Eq. (2). Because alkaline (NaOH) easily absorbs water vapor, a water film will form on the surface of alkaline-activated carbon (Table 5). Since the H<sub>2</sub>S and water vapor mixture showed much greater H<sub>2</sub>S adsorption ability (Table 6), the H<sub>2</sub>S was transported into and reacted with the water film (absorption and acid-base reaction). Equation (2) would be the dominant reaction mechanism.



TABLE 4  
NaOH Impregnated on Activated Carbon under Various Preparation Conditions

Stir time (min)	Vacuum time (min)	Stationary time (min)	Impregnated dosage (mg/g)	Adsorption of H <sub>2</sub> S (mg/g)
30	20	190	23	19.4
30	30	200	50	43.5
30	40	210	65	33.3
30	40	230	70	29.3

### ***NaOH Impregnated on Activated Carbon***

The amount of NaOH impregnated on activated carbon depends on the impregnation procedure. The NaOH concentrations impregnated on carbon under diverse conditions of vacuum and immersion duration are shown in Table 4. Increasing the vacuum and immersion duration increased the alkaline concentration of the NaOH-impregnated activated carbons.

The H<sub>2</sub>S adsorption capacity of impregnated NaOH-IAC is shown in Table 4. With a H<sub>2</sub>S flow rate of 1.08 mg/min (250 ppmv, 3.1 L/min at 25°C), the adsorption capacity of NaOH-IAC<sub>50</sub> (50 mg NaOH impregnated on 1 g virgin AC) was 43.5 mg/g while NaOH-IAC<sub>65</sub>, NaOH-IAC<sub>70</sub>, and NaOH-IAC<sub>23</sub> capacities were 33.3, 29.3, and 19.4 mg/g, respectively. Increasing NaOH impregnation on virgin AC did not ensure increased adsorption capacity.

Experimental results indicate that NaOH-IAC<sub>50</sub> had the maximum adsorption H<sub>2</sub>S capacity among the four preparative conditions, thus making it the optimal concentration. NaOH concentrations greater than 50 mg/g may have plugged the activated carbon micropores and reduced the effective area for adsorption. Furthermore, the NaOH may have crystallized during the drying procedure, which would result in less effective adsorption. Smaller NaOH additions, however, were less effective on adsorption capacity than the NaOH-IAC<sub>50</sub>.

## **Adsorption Characteristics of Humidified Gas**

### ***Adsorption of Water Vapor***

The water vapor adsorption capacities for AC and NaOH-IAC are shown in Table 5. The relative humidity (RH) of influent gas increased from 20 to 80%. The adsorption capacity of water vapor improved from 6 to 321 mg/g for virgin AC and from 258 to 334 mg/g for NaOH-IAC. The cross-section area of water is 12.5 Å<sup>2</sup> (13); the percentage of AC surface coverage was from 2.70

TABLE 5  
Adsorption Capacity of Water Vapor for AC and NaOH-IAC

Adsorbent <sup>a</sup>		Relative humidity (%)				
		80	65	50	30	20
AC	Adsorption capacity of H <sub>2</sub> O <sup>1</sup> (mg/g)	321	318	14	8	6
	Adsorption capacity of H <sub>2</sub> O (mmol/g)	17.8	17.7	0.8	0.4	0.3
	Surface area of adsorbate <sup>b</sup> (m <sup>2</sup> )	1340.8	1330.3	59.4	33.4	25.1
	Percentage of surface coverage (%)	144	143	6.4	3.6	2.7
NaOH-IAC	Adsorption capacity of H <sub>2</sub> O (mg/g)	334	329	296	290	258
	Adsorption capacity of H <sub>2</sub> O (mmol/g)	18.6	18.3	16.4	16.1	14.3
	Surface area of adsorbate (m <sup>2</sup> )	1398.3	1377.4	1237.4	1213.5	1078.0
	Percentage of surface coverage (%)	186	182	163	160	142

<sup>a</sup> The BET surface areas of AC and NaOH-IAC are 931 and 758 m<sup>2</sup>/g, respectively.

<sup>b</sup> The cross-sectional area of H<sub>2</sub>O is 12.5 Å<sup>2</sup> (13).

to 144% for relative humidity between 20 and 80%. The percentage of NaOH-IAC surface coverage was from 142 to 184% for relative humidity between 20 and 80%. The adsorption capacity of water vapor for AC and NaOH-IAC is obviously different at a relative humidity less than 60% and is similar at a relative humidity greater than 60%.

Two distinct adsorption sites for virgin AC are postulated to account for the small amount of adsorption followed by the rapid rise. Initially, surface oxides in the micropores act as adsorption centers and permit adsorption by the formation of hydrogen bonds between the water molecules and surface oxides. The adsorbed water molecules act as secondary adsorption sites that can retain other water molecules by means of hydrogen bonds. As the number of secondary adsorption sites increases, the rapid adsorption increases between 40 and 60% RH. This is due to the increasing probability of adsorption followed by the eventual coalescence of these complexes (14, 15). The NaOH-impregnated activated carbon could increase the activated carbon surface oxides or the NaOH could absorb water vapor more easily. NaOH-IAC could therefore adsorb more water vapor at a lower relative humidity.



### Adsorption Capacity of H<sub>2</sub>S in Humidified Gas

Table 6 shows the adsorption capacity of water vapor and H<sub>2</sub>S mixed gas on NaOH-IAC. With an influent flow of 100 ppm H<sub>2</sub>S and relative humidities of 50 and 80%, the H<sub>2</sub>S adsorption capacities were 151 and 79 mg/g. The water vapor adsorption capacities were 204 and 248 mg/g, respectively. When the H<sub>2</sub>S concentration in the influent concentration was 50 ppm and the relative humidities were 50 and 80%, the H<sub>2</sub>S adsorption capacities were 186 and 142 mg/g, and the water vapor adsorption capacities were 166 and 205 mg/g, respectively. Obviously, water vapor was beneficial in the mixed gas. The vapor easily adsorbed on the NaOH-IAC and formed a film on the surface of NaOH-IAC. Then the H<sub>2</sub>S reacted with the basic surface of NaOH-IAC.

Experimental results indicated that the adsorption capacities of H<sub>2</sub>S and water vapor on NaOH-IAC were much greater than on virgin AC. When water vapor was added to the H<sub>2</sub>S gas stream, the H<sub>2</sub>S adsorption capacity of NaOH-IAC was 2.6–6.9 times the value at the dry H<sub>2</sub>S gas stream condition. This enhancement has been shown in other results (9–11). Water vapor and H<sub>2</sub>S mixed gas may transfer to the IAC by adsorption and adsorption, but adsorption is the predominant mechanism between H<sub>2</sub>S and NaOH-IAC.

We used a cross-sectional area of adsorption to measure the coverage of activated carbon. Results indicated that two molecular layers covered the activated carbon at a relative humidity higher than 50%. Without water vapor, the

TABLE 6  
Adsorption Capacity of Water Vapor and H<sub>2</sub>S Mixture Gas on NaOH-IAC

	Relative humidity (%)						
	0		50		80		
Concentration (ppm)	30	50	100	50	100	50	100
Adsorption capacity of	25	27	31	186	151	142	79
H <sub>2</sub> S <sup>a</sup> (mg/g or mmol/g)	(0.74) <sup>b</sup>	(0.80)	(0.92)	(5.47)	(4.45)	(4.17)	(2.31)
Adsorption capacity of	—	—	—	166	204	205	248
H <sub>2</sub> O <sup>a</sup> (mg/g or mmole/g)				(9.23)	(11.34)	(11.38)	(13.80)
Surface area of H <sub>2</sub> S (m <sup>2</sup> /g)	112	120	138	822	669	627	347
Surface area of H <sub>2</sub> O (m <sup>2</sup> /g)	—	—	—	694	853	857	1037
Percentage of surface coverage (%) <sup>c</sup>	14.8	15.9	18.3	200	201	183	196

<sup>a</sup> Molecular cross-sectional areas of H<sub>2</sub>S and H<sub>2</sub>O are 25 and 12.5 Å<sup>2</sup> (13).

<sup>b</sup> Adsorption capacity of H<sub>2</sub>S and H<sub>2</sub>O (mmol/g).

<sup>c</sup> Total surface area = (surface area of H<sub>2</sub>S) + (surface area of H<sub>2</sub>O). The surface area of NaOH-IAC is 758 m<sup>2</sup>/g.



TABLE 7  
Adsorption Capacity of Water Vapor, H<sub>2</sub>S, and CH<sub>3</sub>SH Mixture Gas on NaOH-IAC

Concentration ratio	Relative humidity (%)								
	0			50			80		
	1/1	2/1	1/2	1/1	2/1	1/2	1/1	2/1	1/2
Adsorption capacity of H <sub>2</sub> S (mg/g or mmol/g)	29 (0.86) <sup>a</sup>	49 (1.44)	10 (0.40)	27 (0.79)	64 (1.87)	60 (1.76)	38 (1.13)	33 (0.97)	60 (1.77)
Adsorption capacity of CH <sub>3</sub> SH (mg/g or mmol/g)	48 (1.00)	30 (0.62)	58 (1.22)	11 (0.24)	81 (1.68)	22 (0.45)	25 (0.52)	21 (0.44)	49 (1.03)
Adsorption capacity of H <sub>2</sub> O (mg/g or mmol/g)	—	—	—	292 (16.22)	219 (12.18)	275 (15.27)	301 (16.74)	323 (17.95)	285 (15.86)
Surface area of H <sub>2</sub> S (m <sup>2</sup> /g)	129	212	46	119	282	265	169	147	266
Surface area of CH <sub>3</sub> SH (m <sup>2</sup> /g)	211	129	255	50	353	95	110	92	216
Surface area of H <sub>2</sub> O (m <sup>2</sup> /g)	—	—	—	1220	917	1149	1260	1351	1193
Percentage of surface coverage (%) <sup>c</sup>	45	46	40	183	205	199	203	221	210

<sup>a</sup> Adsorption capacity of H<sub>2</sub>S, CH<sub>3</sub>SH, and H<sub>2</sub>O (mmol/g).

<sup>b</sup> Molecular cross-sectional areas of H<sub>2</sub>S, CH<sub>3</sub>SH, and H<sub>2</sub>O are 25, 34.8, and 12.5 Å<sup>2</sup> (13).

<sup>c</sup> Total surface area = (surface area of H<sub>2</sub>S) + (surface area of H<sub>2</sub>O). The surface area of NaOH-IAC is 758 m<sup>2</sup>/g.

H<sub>2</sub>S adsorption capacity was less than 18.3%, while with water vapor the capacity was greater than 183% (Table 6). That showed that water vapor was easily adsorbed on the surface of NaOH-treated activated carbon.

### Adsorption Capacity of H<sub>2</sub>S and CH<sub>3</sub>SH in Humidified Gas

Table 7 shows the adsorption results of a H<sub>2</sub>S, CH<sub>3</sub>SH, and water vapor mixed gas system. The surface coverage was between 40 and 45% in the H<sub>2</sub>S and CH<sub>3</sub>SH mixed gas system without water vapor. When the influent concentration ratios of H<sub>2</sub>S and CH<sub>3</sub>SH were 1/1, 2/1, and 1/2 (100/100 ppm, 100/50 ppm, and 50/100 ppm), the corresponding adsorption capacities of H<sub>2</sub>S and CH<sub>3</sub>SH were from 0.30 to 1.44 mmol/g and 0.62 to 1.22 mmol/g, respectively.

In the water vapor mixed gas system the adsorption capacity of H<sub>2</sub>S increased to between 0.79 and 1.87 mmol/g while the CH<sub>3</sub>SH adsorption capacity increased to between 0.24 to 1.68 mmol/g. The adsorption capacity of water vapor was between 12.18 to 17.95 mmol/g for the H<sub>2</sub>S and CH<sub>3</sub>SH. The percentage of surface coverage was a nearly constant 203 ± 12.5%. The re-

sults again indicate that water vapor is advantageous for adsorption in the  $H_2S$ ,  $CH_3SH$ , and water vapor mixture gas system.

### Factors Affecting the Adsorption of Odor Gas

Tables 8 and 9 shows the principal component analysis results for operation factors and surface coverage on odorous gas adsorption. The results for the  $H_2S$  and water vapor adsorption mix show that Group I factors are important. These included relative humidity (RH), adsorption capacity of  $H_2S$  (AC- $H_2S$ ), adsorption capacity of  $H_2O$  (AC- $H_2O$ ), surface coverage (SC), and the mole of total adsorption capacity (MTAC). Group II factors are important in  $H_2S$  (C- $H_2S$ ) concentration. The percentages of total variance as explained by Groups I and II were 78.6 and 16.2, respectively. The results of Group II analysis indicated that AC- $H_2S$  could influence the  $H_2S$  and water vapor mixture gas adsorption system.

Results of the principle component analysis show that four factors could affect the adsorption system of the  $H_2S$ ,  $CH_3SH$ , and water vapor mixture gas. The major parameters of Factor I were RH, AC- $H_2O$ , SC, and MAC, and the minor parameter was AC- $H_2S$ . The major parameter of Factor II analysis was AC- $CH_3SH$ , and the minor parameters were CR and AC- $H_2S$ . The major parameter of Factor III was CR. The minor parameter of Factor IV was AC- $H_2S$ . Based on Factor I, the results imply that RH, AC- $H_2O$ , SC and MAC could affect the  $H_2S$ ,  $CH_3SH$ , and water vapor adsorption system.

According to the results of the principle component analysis, the relative humidity, AC- $H_2O$ , SC, and MAC are important in both  $H_2S$  and water vapor, and the  $H_2S$ ,  $CH_3SH$ , and water vapor mixture gas adsorptions are important on alkaline-activated carbon samples.

TABLE 8  
Results of Principal Components Analysis among Operation Factors, Surface Coverage, and Adsorption Capacities: Water Vapor and  $H_2S$  Adsorption

Items	Factor I	Factor II
Relative humidity, RH (%)	0.951	0.029
Concentration, C (ppm)	0.330	-0.933
Adsorption capacity of $H_2S$ , AC- $H_2S$ (mg/g)	0.862	0.307
Adsorption capacity of $H_2O$ , AC- $H_2O$ (mg/g)	0.985	-0.059
Surface coverage, SC (%)	0.995	0.045
Mole of adsorption capacity, MAC (mmol/g)	0.999	0.030
Variance explained	4.713	0.972
Percentage of total variance explained	78.55	16.19
Major parameters	RH, AC- $H_2S$ , AC- $H_2O$ , SC, MAC	C

TABLE 9  
Results of Principal Components Analysis among Operation Factors, Surface Coverage, and Adsorption Capacities: Water Vapor, H<sub>2</sub>S, and CH<sub>3</sub>SH Adsorption<sup>a</sup>

Items	Factor I	Factor II	Factor III	Factor IV
Relative humidity, RH (%)	0.966	-0.041	0.020	0.162
Concentration, CR	0.025	0.574	-0.812	0.100
Adsorption capacity of H <sub>2</sub> S, AC-H <sub>2</sub> S (mg/g)	0.536	0.646	0.195	-0.507
Adsorption capacity of CH <sub>3</sub> SH, AC-CH <sub>3</sub> SH (mg/g)	-0.313	0.740	0.457	0.381
Adsorption capacity of H <sub>2</sub> O, AC-H <sub>2</sub> O (mg/g)	0.987	-0.125	-0.015	0.078
Surface coverage, SC (%)	0.989	0.074	0.030	0.090
Mole of adsorption capacity, MAC (mmol/g)	0.995	-0.039	0.025	0.067
Variance explained	4.261	1.319	0.908	0.457
Percentage of total variance explained	60.87	18.84	12.98	6.53
Major parameters	RH, AC-H <sub>2</sub> O, SC, MAC	AC-CH <sub>3</sub> SH	CR	—
Minor parameters	AC-H <sub>2</sub> S	CR, AC-H <sub>2</sub> S	—	AC-H <sub>2</sub> S

<sup>a</sup> Major factor is the factor loading higher than 0.7. Minor factor is the factor loading between 0.5 and 0.7.

## CONCLUSIONS

Although specific surface area and pore volumes decreased by nearly 20% on NaOH-IAC, the adsorption capacity of H<sub>2</sub>S was enhanced 3.2 times, which indicates that physical characteristics were not the predominant influence in the H<sub>2</sub>S adsorption capacity of NaOH-IAC. In addition, the element composition and function groups on the surface of NaOH-IAC were obviously different from those on AC. The NaOH-IAC adsorption capacity for H<sub>2</sub>S and water vapor is greater than that of virgin AC. When water vapor was present in the gas stream, the NaOH-IAC adsorption capacity for H<sub>2</sub>S increased. The results indicate NaOH-impregnated activated carbon (NaOH-IAC) adsorbs H<sub>2</sub>S and water vapor better than virgin AC.

## NOMENCLATURE

AC      activated carbon  
IAC     impregnated activated carbon





NaOH-, KOH-, Na <sub>2</sub> CO <sub>3</sub> <sup>-</sup> , or K <sub>2</sub> CO <sub>3</sub> -IAC	NaOH-, KOH-, Na <sub>2</sub> CO <sub>3</sub> <sup>-</sup> , or K <sub>2</sub> CO <sub>3</sub> -impregnated activated carbon
NaOH-IAC <sub>50</sub>	50 mg NaOH impregnated on 1 g virgin AC
RH	relative humidity (%)
C	concentration (ppm)
CR	concentration ratio
AC-H <sub>2</sub> S	adsorption capacity of H <sub>2</sub> S (mg/g)
AC-CH <sub>3</sub> SH	adsorption capacity of CH <sub>3</sub> SH (mg/g)
AC-H <sub>2</sub> O	adsorption capacity of H <sub>2</sub> O (mg/g)
SC	surface coverage (%)
MAC	mole of adsorption capacity (mmol/g)
I, II, III, IV	factors

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