

Gas Adsorption Properties of the Ternary ZnO/CuO/CuCl₂ Impregnated Activated Carbon System for Multigas Respirator Applications Assessed through Combinatorial Methods and Dynamic Adsorption Studies

Jennifer V. Romero,[†] Jock W. H. Smith,[†] Braden M. Sullivan,[†] Matthew G. Mallay,[†] Lisa M. Croll,[‡] Judy A. Reynolds,[‡] Carrie Address,[‡] Monika Simon,[‡] and Jeff R. Dahn^{*,†}

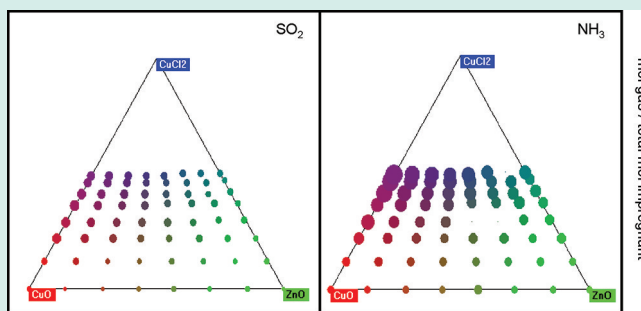
[†]Department of Physics, Dalhousie University, Halifax, Nova Scotia, Canada B3H 3J5

[‡]3M Canada Company, Brockville, Ontario, Canada K6V 5V8

Supporting Information

ABSTRACT: A ternary library of 64 ZnO/CuO/CuCl₂ impregnated activated carbon samples was synthesized and screened automatically using a combinatorial (combi) method. The ability of the samples to adsorb toxic gases was screened gravimetrically. The stoichiometric ratio of reaction (SRR) between the moles of toxicant and the total moles of impregnant was obtained from the calculated mass increase of the samples after chemisorption, with a high SRR indicating high efficiency of toxicant removal. The combi samples that exhibited good dry SO₂ and NH₃ adsorption were prepared in bulk using the incipient wetness method and were evaluated for multigas respirator function by dynamic adsorption studies of SO₂, NH₃, HCN, and C₆H₁₂ gases in either dry or humid conditions at ambient temperature. The bulk samples showed equivalent gas adsorption capacities when exposed to the different challenge gases indicating the value of the combi method for initial screening. Cu₂Cl(OH)₃ was identified to be a potential multigas adsorbent.

KEYWORDS: high-throughput methods, combinatorial carbon materials, multigas adsorbents, multigas respirator carbons, toxic gas adsorbent materials, gas adsorption capacity, ternary ZnO/CuO/CuCl₂ impregnated activated carbon, SO₂, NH₃, HCN, C₆H₁₂, dynamic adsorption



1. INTRODUCTION

Filter-based respirator protection systems include the use of impregnated carbon materials that are capable of removing a wide variety of toxicants.¹ Unimpregnated activated carbons are usually unable to remove low molecular weight, highly polar gases, such as SO₂, NH₃, and HCN. Copper-based impregnated activated carbons have been studied for multigas adsorbent applications.^{1–4} The addition of one or more additional metallic impregnants to the copper formulations may be beneficial in improving the performance of these copper-based multigas adsorbents. Earlier formulations of multigas adsorbents included chromium containing impregnants which were used to control the generation of cyanogen (NCCN) when Cu²⁺ impregnant is exposed to HCN gas.^{2,5,6} Chromium exposure however, has long been reported to be a human health risk.⁷ The need to find new multigas adsorbents arises from new regulations governing the use of filtration devices and the elimination of chromium in the formulation of multigas filtration masks. Examples of multigas IACs that have replaced the toxic chromium with hexavalent tungsten or molybdenum have been reported in the literature.^{1,6} These types of IACs

offer some improvements over chromium containing materials, however some health related issues remain.⁸

The gas adsorption process is dependent on several factors including the physical and chemical surface characteristics of the base carbon and the reactivity, as well as the composition of impregnants used in the formulation of the adsorbent material. It is also necessary to determine that the addition of reactive species onto the base carbon does not compromise its ability to physically adsorb toxicants nor produce undesirable byproduct. The development of new multicomponent impregnated activated carbon materials can prove to be a difficult and expensive process if done using the traditional “trial and error” method of making samples and then testing the adsorption properties of the materials if all of these factors are to be considered. Since there are so many different combinations of materials conceivable, a faster and more efficient method of preparation and testing must be employed to accelerate the discovery of new multigas adsorbent materials.

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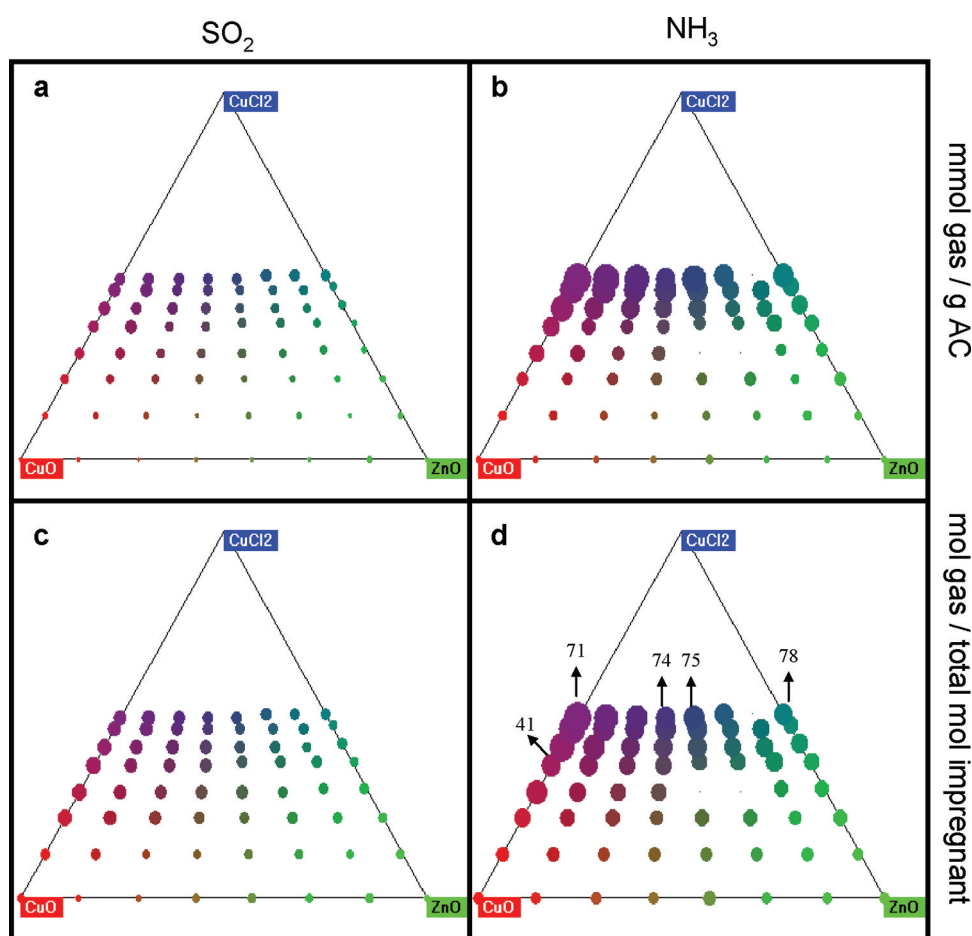


Figure 1. Visualization plots of the gas adsorption capacity shown in panels A (SO_2) and B (NH_3) and the stoichiometric ratio of reaction (SRR) shown in panels C (SO_2) and D (NH_3) with respect to varying impregnant composition in mole fractions. The data points indicated by numbered arrows (41, 71, 74, 75, and 78) indicate samples with compositions that were used to prepare bulk samples for dynamic adsorption tests. The scales used were 0–1.3 for SRR's and 0 to 3.3 mmol of gas/g AC for adsorption capacity.

The combinatorial materials science method is suitable for studies involved in developing multigas adsorbents.⁹ The combinatorial approach has been used to generate libraries of materials for catalysis, high temperature superconductivity, ferroelectricity and other applications.^{10–14} Employing this method can improve the efficiency of preparing and screening samples, reduce the amount of material needed for testing, minimize waste production and increase the rate of discovery of new multigas adsorbent materials.

A library consisting of: 64 different compositions of ZnO/CuO/CuCl₂ mixed impregnants dispersed onto activated carbon; was generated. The selection of the impregnant starting materials was based on low cost, ease of decomposition or dehydration, and on the SO_2 or NH_3 gas adsorption ability of the individual components when impregnated into carbon. CuO on activated carbon has been studied and used for SO_2 removal in multigas formulations while ZnO was found to be effective in SO_2 removal from flue gases.^{2–4,15} Mixtures of ZnO and CuO impregnated into HNO_3 -treated activated carbon showed effective SO_2 and NH_3 gas adsorption.⁹ CuCl₂-impregnated activated carbon was found to chemisorb NH_3 gas.¹⁶ Combining the metal oxides and copper chloride may result in improved SO_2 and NH_3 gas adsorption which is desirable for multigas adsorbent materials. Mixed-metal or mixed-valent (Cu^{1+} or Cu^{2+}) phases may form during the decomposition of this ternary that may improve the gas

adsorption ability of the IACs. No reports on the study of the gas adsorption properties of ternary ZnO/CuO/CuCl₂ impregnated carbon materials were found in the literature.

2. EXPERIMENTAL PROCEDURES

The samples were prepared and screened using a combinatorial method for studying impregnated activated carbon materials.⁹ Impregnating solutions were dispensed onto grains of activated carbon (AC) using a solutions handling robot. The decomposition of the impregnants to the desired active phases was achieved using several heating steps, which also ensured that the samples were dried well. Gravimetric analysis before and after exposure to SO_2 or NH_3 was used to monitor gas adsorption of the ternary samples. The actual mass of gas adsorbed by chemisorption is taken to be the difference between the recorded mass increase of the sample and the average mass increase recorded for all the unimpregnated carbon after gas exposure. The stoichiometric ratio of reaction (SRR) was calculated from the actual mass of gas adsorbed after exposure, with a high SRR indicating that the material has good gas removal capacity for the toxic gas. The visualization of the SRR in relation to the ternary composition was performed using in-house developed software.¹⁷

To facilitate further testing, bulk material samples were prepared for samples having compositions that showed high SRR values for both NH_3 and SO_2 gases in the combinatorial

Table 1. List of the Different Ternary Compositions and Control Samples Screened via the Combi Method and the Corresponding Calculation of the Stoichiometric Ratios of Reaction and Gas Adsorption Capacities^a

vial no.	ZnO	CuO	CuCl ₂	SO ₂ SRR	NH ₃ SRR	mmol SO ₂ /g AC	mmol NH ₃ /g AC	vial no.	ZnO	CuO	CuCl ₂	SO ₂ SRR	NH ₃ SRR	mmol SO ₂ /g AC	mmol NH ₃ /g AC
1	0	1	0	0.33	0.49	0.37	0.56	51	0	0.59	0.41	0.65	1.19	1.42	2.77
2	0.14	0.86	0	0.27	0.44	0.37	0.61	52	0.08	0.51	0.41	0.58	1.03	1.28	2.27
3	0.29	0.71	0	0.19	0.47	0.28	0.66	53	0.17	0.42	0.41	0.57	0.86	1.19	2.17
4	0.43	0.57	0	0.34	0.44	0.46	0.64	54	0.25	0.34	0.41	0.53	0.89	1.11	2
5	0.57	0.43	0	0.38	0.6	0.47	0.88	55	0.33	0.25	0.41	0.5	0.85	1.03	2.12
6	0.71	0.29	0	0.3	0.46	0.42	0.68	56	0.42	0.17	0.41	0.5	0.78	1.01	1.68
7	0.86	0.14	0	0.37	0.42	0.49	0.65	57	0.5	0.09	0.41	0.4	0.83	0.87	1.85
8	1	0	0	0.28	0.46	0.44	0.75	58	0.58	0	0.42	0.41	0.79	0.87	1.98
11	0	0.88	0.12	0.42	0.59	0.63	0.93	61	0	0.54	0.46	0.58	1.24	1.36	2.94
12	0.12	0.75	0.12	0.41	0.61	0.52	0.96	62	0.08	0.46	0.46	0.57	1.04	1.41	2.94
13	0.25	0.63	0.12	0.34	0.55	0.51	0.82	63	0.15	0.38	0.46	0.53	0.94	1.16	2.66
14	0.37	0.5	0.12	0.32	0.52	0.47	0.73	64	0.23	0.31	0.46	0.47	0.95	1.1	2.55
15	0.5	0.38	0.12	0.39	0.55	0.55	0.82	65	0.31	0.23	0.46	0.43	0.94	1	2.42
16	0.62	0.25	0.12	0.4	0.53	0.53	0.89	66	0.39	0.15	0.46	0.42	0.78	1	1.91
17	0.75	0.13	0.12	0.34	0.53	0.39	0.95	67	0.46	0.07	0.46	0.45	0.8	0.99	2.01
18	0.87	0	0.12	0.36	0.47	0.54	0.81	68	0.54	0	0.47	0.38	0.72	0.89	1.97
21	0	0.78	0.22	0.67	0.75	0.93	1.36	71	0	0.51	0.49	0.6	1.29	1.28	3.25
22	0.11	0.67	0.22	0.58	0.72	0.81	1.21	72	0.07	0.44	0.49	0.59	1.15	1.28	3.21
23	0.22	0.56	0.22	0.56	0.66	0.81	1.17	73	0.14	0.36	0.49	0.55	1.05	1.24	3.03
24	0.33	0.45	0.22	0.47	0.62	0.76	1.17	74	0.21	0.29	0.49	0.48	0.92	1.13	2.35
25	0.44	0.34	0.22	0.46	0.67	0.71	1.26	75	0.28	0.22	0.49	0.48	0.95	1.15	2.83
26	0.56	0.22	0.22	0.47	0.67	0.7	1.33	76	0.36	0.15	0.5	0.47	0.85	1.25	2.4
27	0.67	0.11	0.22	0.42	0.59	0.69	0.95	77	0.43	0.08	0.5	0.43	0	1.17	0
28	0.78	0	0.22	0.4	0.67	0.66	1.37	78	0.5	0	0.5	0.43	0.87	1.05	2.52
31	0	0.71	0.29	0.65	1	1.09	1.72	C1	0	0	0			0.52	0.20
32	0.1	0.61	0.29	0.62	0.78	1.07	1.59	C2	0	0	0			0.51	0.19
33	0.2	0.51	0.29	0.55	0.72	0.94	1.41	C3	0	0	0			0.57	0.28
34	0.3	0.41	0.29	0.52	0.7	0.93	1.55	C4	0	0	0			0.57	0.17
35	0.4	0.31	0.29	0.54	0	0.91	0	C5	0	0	0			0.62	0.11
36	0.5	0.21	0.29	0.42	0	0.8	0	C6	0	0	0			0.59	0.11
37	0.6	0.11	0.3	0.45	0.63	0.89	1.29	C7	0	0	0			0.61	0.04
38	0.7	0.01	0.3	0.42	0.65	0.73	1.33	C8	0	0	0			0.58	0.02
41	0	0.64	0.36	0.68	0.94	1.17	2.05	C9	0	0	0			0.57	0.03
42	0.09	0.55	0.36	0.62	0.86	1.31	1.7	C10	0	0	0			0.65	0.01
43	0.18	0.45	0.36	0.54	0.74	0.93	1.47	C11	0	0	0			0.57	0.12
44	0.27	0.36	0.36	0.54	0.74	1.03	1.54	C12	0	0	0			0.56	0.07
45	0.36	0.27	0.37	0.51	0.69	0.93	1.43	C13	0	0	0			0.51	0.06
46	0.46	0.18	0.37	0.51	0.68	0.94	1.35	C14	0	0	0			0.52	0.09
47	0.55	0.09	0.37	0.5	0.82	0.87	1.8	C15	0	0	0			0.54	0.04
48	0.64	0	0.37	0.38	0.7	0.73	1.63	C16	0	0	0			0.54	0.01

^aPlease note that the average gas capacities of the controls have been subtracted from those of the impregnated samples.

studies. The gas adsorption capacities of the bulk materials were evaluated by dynamic adsorption studies of SO₂, NH₃, HCN, and C₆H₁₂ gases under dry or humid conditions at ambient temperature.

3. RESULTS AND DISCUSSION

3.1. High-Throughput Screening of an 8 × 8 Array of ZnO, CuO, and CuCl₂-Impregnated Activated Carbons.

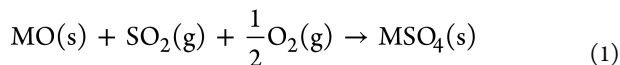
The preparation of multigas adsorbents requires careful selection of type and amounts of the precursor solution used. Its effectiveness relies on exactly the right amount and combination of ingredients since the addition of an excess of one component can compromise the adsorption of the other components. It is also common to find that the inclusion of the reactive species reduces or completely inhibits the physical adsorption capacity of the carbon base material. The

combinatorial preparation and screening method rapidly determines if such problems arise when different combinations of precursors are used.

A library containing a ternary ZnO, CuO, and CuCl₂-impregnated activated carbons was prepared and screened using the combinatorial method. The compositions of the library were selected so that all samples contained ZnO or CuO, which have been shown to adsorb SO₂.⁹ CuCl₂ was added sequentially across the library to study its impact. CuCl₂ has been shown to perform well as an NH₃ adsorber.¹⁶ Ideally, the SO₂ adsorption properties of the metal oxides will be maintained with the addition of CuCl₂ while the NH₃ adsorption is improved.

After exposure to the toxic gas, the increase in the mass of each of the samples indicated the effective chemisorption of these gases onto the impregnated carbon. This mass increase

(the recorded mass increase of the sample – average mass increase of unimpregnated control samples) after exposure was translated into gas adsorption capacity denoted as mmol of gas adsorbed per gram of AC. The stoichiometric ratio of reaction (SRR) was also calculated from the mass increase of the sample and is the ratio between the number of moles of the toxicant absorbed and the total number of moles of impregnant added. For SO₂ chemisorption, the SRR should be 1 if the reaction between SO₂ and the metal oxide impregnant (MO) follows the net reaction given in eq 1 below²



The SRR for NH₃ chemisorption should be 2 if the reaction between NH₃ and metal chlorides takes place according to eq 2^{16,18}

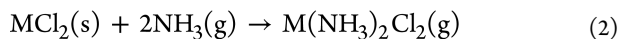


Figure 1 shows the gas adsorption capacity (Figure 1A and 1B) and SRR (Figure 1C and 1D) of the impregnated samples. The size of the data point indicates the magnitude of the property measured while the color of the data point gives an indication of composition. Table 1 gives the composition in mole fractions of the samples prepared as well as the measured SO₂ and NH₃ gas adsorption capacities and SRRs.

Data points shown at the base of each of the ternary plots represent samples that were impregnated with copper or zinc oxides as in (CuO)_{1-x}(ZnO)_x. The sizes of each of the data points along the base of each plot are about the same showing the approximate equivalence of ZnO and CuO impregnants on AC for SO₂ or NH₃ adsorption.

Figure 1A shows that there is a gradual increase in SO₂ gas adsorption capacity when increasing amounts of CuCl₂ were added in the impregnant. Figure 1B shows that the SRR gradually increases with increasing CuCl₂ up until a CuCl₂ mole ratio of 0.3. From this point, SRR remains constant despite the addition of more CuCl₂ to the impregnant. SRR values ranging from 0.4 to 0.6 were obtained for a CuCl₂ to metal oxide mole ratio of 0.3 and higher.

Figure 2 shows the SO₂ and NH₃ SRR's versus CuCl₂ content of samples that were impregnated with similar proportions of CuO to ZnO (0.7 mmol CuO/g AC and 0.5 mmol ZnO/g AC). A best fit line was drawn for each set of data points showing the increase of the SRR with the CuCl₂ content of the samples. The slopes of the best fit lines were 0.4 ± 0.2 for the SO₂ plot and 1 ± 0.2 for the NH₃ plot, therefore the SRR increases slower with CuCl₂ content for SO₂ than it does for NH₃.

The increase in SO₂ gas adsorption with CuCl₂ content is an unexpected behavior for CuCl₂-containing IACs since they are not known for their SO₂ removal properties. A typical application for these materials is for Hg remediation.¹⁹ In a separate report, however, CuCl₂ impregnated onto activated carbon fibers was shown to effectively remove SO₂ from flue gases.²⁰ The addition of CuCl₂ helped improve the adsorption of SO₂ by changing the impregnant phase present in the material and the further characterization experiments reported below help explain why.

Figures 1 and 2 show that both the NH₃ capacity and SRR increased as the CuCl₂ concentration increased. This result is not surprising since metal chloride IAC's are known for their NH₃ removal properties.^{16,18} In addition, the presence of the metal oxide impregnants did not appear to compromise the

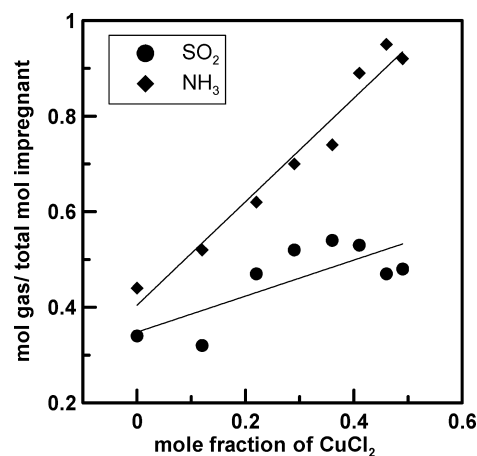


Figure 2. Calculated SO₂ and NH₃ stoichiometric ratio of reaction (SRR) of samples impregnated with similar proportions of CuO to ZnO (0.7 mmol CuO/g AC and 0.5 mmol ZnO/g AC) plotted against the molar ratio of CuCl₂ added. A best fit line was drawn for each set of data points.

ability of the CuCl₂ IAC's to remove NH₃ from the gas stream. The SO₂ adsorption capacity of the material was likewise maintained while NH₃ adsorption capacity was enhanced. Thus, the metal oxides and the metal chlorides together have compatible gas adsorption properties and are likely to perform well for multigas removal.

Control samples that contained unimpregnated Kuraray GC were simultaneously exposed to the toxic gas together with the arrays of IAC's. Two control samples were strategically placed together with other samples within each row to ensure reproducibility and reliability of data. Virgin Kuraray GC showed a considerable amount of SO₂ adsorption and almost no capacity for NH₃ adsorption.² The control samples exposed using the combi method showed similar results. The impregnated samples exhibited higher adsorption capacities for both SO₂ and NH₃ relative to the unimpregnated samples (Table 1) indicating that the addition of these metallic impregnants contributes to the enhanced SO₂ and NH₃ adsorption of these materials.

3.2. XRD Studies of the Ternary ZnO/CuO/CuCl₂-Impregnated Activated Carbon Samples. Representative samples were chosen from the unexposed array of the combi prepared ternary ZnO/CuO/CuCl₂ IACs for XRD studies. Table 2 gives the composition of the samples and the identified phases from powder diffraction patterns. Figure 3 shows that the XRD patterns of samples 1, 4 and 8, which contained no CuCl₂, are consistent with the presence of only CuO and ZnO. Samples 41, 44, and 48 contained about 0.37 mol ratio of CuCl₂ or 0.7 mmol CuCl₂/g AC as indicated in Table 2. Figure 3 shows that the Cu₂Cl(OH)₃ phase began to be observed in sample 41, which contained no ZnO. Figure 3 shows that only the metal oxide phases were observed for samples 44 and 48. Figure 3 shows the Cu₂Cl(OH)₃ phase was present in samples impregnated with the most CuCl₂; samples 71 and 74, which also were impregnated with Cu(NO₃)₂. Very little, if any, CuO was observed in these samples. Sample 78, which only contained CuCl₂ and Zn(NO₃)₂ impregnating solutions at the start, still shows some evidence for Cu₂Cl(OH)₃. The formation of Cu₂Cl(OH)₃ is initially thought to arise from a reaction that may occur between CuCl₂ and CuO in the presence of moisture.²¹ However, the presence of this

Table 2. Summary of Powder X-ray Diffraction Results Obtained from Representative Combi Prepared Samples

vial no.	composition (mmol/g GC)				total	phases identified in samples using powder XRD
	CuO	ZnO	CuCl ₂			
1	1.2	0	0		1.2	CuO with disordered C
4	0.7	0.5	0		1.2	CuO with disordered C
8	0	1.2	0		1.2	ZnO with disordered C
41	1.2	0	0.7		1.9	CuO, Cu ₂ Cl(OH) ₃ with disordered C
44	0.7	0.5	0.7		1.9	CuO with disordered C
48	0	1.2	0.7		1.9	ZnO with disordered C
71	1.2	0	1.2		2.4	Cu ₂ Cl(OH) ₃ with disordered C
74	0.7	0.5	1.2		2.4	CuO, Cu ₂ Cl(OH) ₃ with disordered C
78	0	1.2	1.2		2.4	ZnO, Cu ₂ Cl(OH) ₃ with disordered C

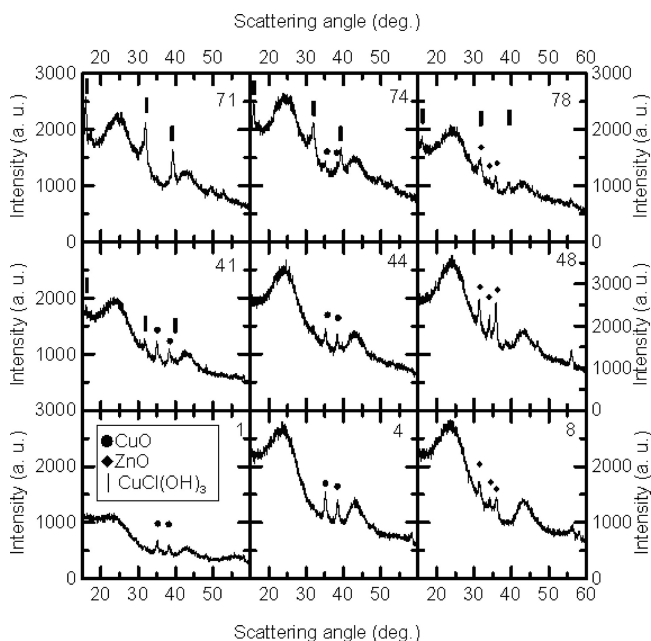


Figure 3. Powder diffraction patterns obtained for samples labeled 1, 4, 8, 41, 44, 48, 71, 74, and 78. ZnO and CuO phases were observed. An additional Cu₂Cl(OH)₃ phase was observed for many samples with high CuCl₂ content.

Cu₂Cl(OH)₃ in samples that did not contain CuO as in vial 78 suggests that a different formation mechanism may be involved. This Cu₂Cl(OH)₃ phase may be responsible for the unusual SO₂ adsorption behavior of the impregnated material. Materials containing large crystals of Cu₂Cl(OH)₃ show high adsorption for both SO₂ and NH₃ which suggests that this impregnant does not have to be fully dispersed to function as an effective gas adsorbent. This phase may react with SO₂ in the presence of moisture to form CuSO₄·xH₂O and possibly CuCl₂·xH₂O.²²

Table 3. Gas Adsorption Test Results of Bulk Materials

sample no.	composition (mmol/g GC)			breakthrough time (min)					
	Zn(NO ₃) ₂	Cu(NO ₃) ₂	CuCl ₂	dry SO ₂	dry NH ₃	dry HCN	dry NCCN	dry C ₆ H ₁₂	wet C ₆ H ₁₂
1	0	1.2	0.7	42.7 ± 3.8	131.3 ± 4.7	45.8 ± 1.8	12.5 ± 2.1	135.5 ± 6.4	2.5 ± 0.7
2	0	1.2	1.2	39.8 ± 5.1	203.6 ± 26.5	43.5 ± 4.9	11 ± 0	124 ± 4.2	1 ± 0
3	0.5	0.7	1.2	35.3 ± 4.5	199 ± 19.3	36.2 ± 2.6	12 ± 3.5	125.5 ± 0.7	2 ± 0
4	0.7	0.5	1.2	37.9 ± 4.4	188.3 ± 17.9	41.7 ± 0.1	13.7 ± 2.5	131 ± 7.1	1.5 ± 0.7
5	1.2	0	1.2	42.4 ± 2.5	209 ± 13.7	43.7 ± 1.3	11 ± 4.2	111 ± 0	2.7 ± 1.5
GC	0	0	0	21 ± 1.9	4 ± 0.4	5 ± 0	0	163.5 ± 7.8	20 ± 4.2
URC	0	2.0 (total Cu)		47 ± 3.0	56 ± 1.3	76 ± 0	65 ± 1.0	108.5 ± 3.5	11 ± 1.4

However, this is speculation and understanding will require further studies.

Similar diffraction patterns were obtained (data not shown) for bulk samples prepared with corresponding compositions. Therefore, the bulk samples decomposed in exactly the same manner as the combi-prepared samples.

3.3. Gas Adsorption Studies of Bulk-Prepared ZnO/CuO/CuCl₂-Impregnated Samples. Bulk samples were prepared using traditional methods to assess the filtering of a wide selection of toxic gases. SO₂ and NH₃ testing used bulk flow-testing situations at Dalhousie University. HCN and dry or humid C₆H₁₂ testing was performed at 3M Canada.

Five samples were chosen for bulk dynamic adsorption testing. Samples with compositions corresponding to the samples in vials 41, 71, 74, 75, and 78 (See the arrows in Figure 1) were chosen based on the large magnitude of the SRR calculated for both gases and are labeled as samples 1 to 5 respectively in Table 3. Figure 4 shows the breakthrough times for the indicated gases to pass through the various IAC samples. Figure 4 and Table 3 also include results for virgin GC and for Calgon URC tested under identical conditions for comparative purposes.

Figure 4 and Table 3 show that the addition of CuCl₂ improves NH₃ filtering capacity as expected based on the combi results. Sample 1 contained 0.7 mmol CuCl₂/g AC. The CuCl₂ content in sample 2 was doubled compared to sample 1 and resulted in a higher NH₃ adsorption capacity. Samples that were impregnated with the same amount of CuCl₂ (samples 2 to 5) showed relatively similar NH₃ gas adsorption capacities. Dry HCN adsorption stayed relatively constant at a range of between 36 to 45 min despite the addition of twice as much CuCl₂. NCCN detection was also performed since this gas is very toxic and must also be removed. The NCCN gas is a byproduct of the reaction between the copper impregnant in the form of CuO and the cyanide ion and is described by eq 3²³

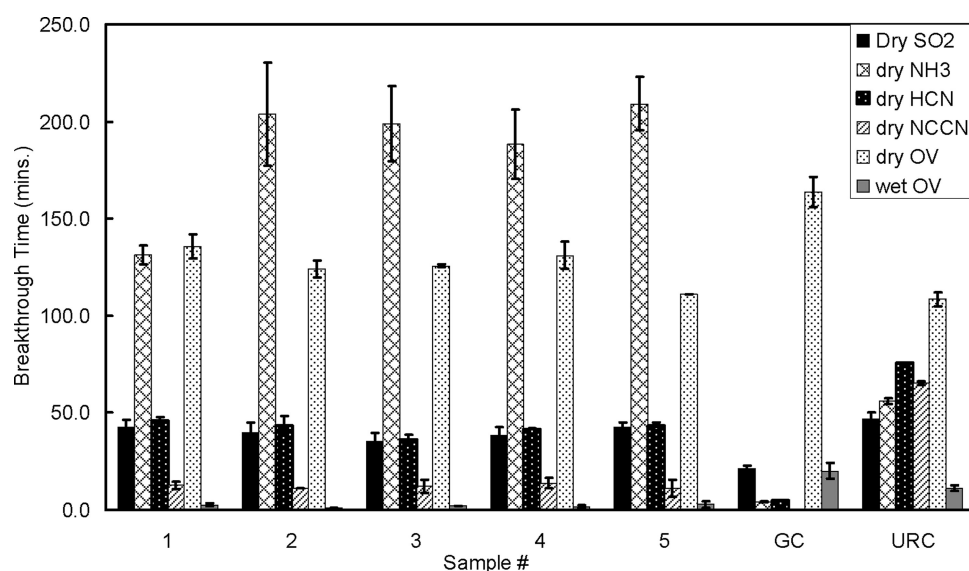
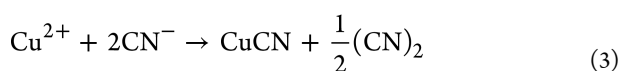


Figure 4. Results of the dry SO₂, NH₃, HCN/NCCN, C₆H₁₂, and humid C₆H₁₂ adsorption tests performed on bulk prepared samples with compositions indicated in Table 3. The gas adsorption capacity of the materials is reported to be the time that challenge gas was detected from the effluent gas stream.



The NCCN adsorption was also observed to be independent of the amount of CuCl₂ added onto the carbon. From the dynamic adsorption studies, the ZnO/CuO/CuCl₂ IACs offer very little protection against dry NCCN. Therefore, to form a truly functional multigas carbon a Mo-containing impregnant species would need to be added^{1,6,23} to capture the generated NCCN. This has been done in our previous work on similar materials.² In addition, none of these materials offer good protection against humid C₆H₁₂ and therefore must also be addressed.

Historically, universal respirator carbons (URC) have been the material of choice for the removal of a broad range of toxic gases. One such URC is prepared using about 2.0 mmol Cu/g AC and utilizes ammonia and ammonium salts for improved solubility of the impregnant material.⁶ This method is now deemed undesirable due to generation of NH₃ waste.² Among the samples tested, samples 2 and 5, which contain as much as 1.2 mmol CuCl₂/g AC and 1.2 mmol/g AC of either Cu or Zn oxides, offer adequate protection against SO₂ and HCN gases. The preparation of samples 2 and 5 involve the use of highly soluble salts which eliminates the need for ammonia or ammonium salts unlike that of the preparation of the URC product. Figure 4 indicates that these samples have a comparable SO₂ capacity with respect to commercially available URC and exceed the performance of URC in terms of dry NH₃ and dry OV adsorption. Overall, the samples containing 50% CuCl₂ showed the ability to remove SO₂, NH₃, HCN, and C₆H₁₂ (under dry conditions) and may potentially be useful as multigas adsorbents.

4. CONCLUSIONS

A fast and reliable method of screening for the gas adsorption properties of impregnated activated carbon materials has been established. The method was shown to be useful in assessing the adsorption capacity of the components of the ternary ZnO/CuO/CuCl₂ system of impregnants for SO₂ and NH₃. This

allowed potentially useful multigas formulations to be identified at a faster rate. The formation of the Cu₂Cl(OH)₃ phase was identified together with CuO and ZnO in samples initially impregnated with large amounts of CuCl₂ and the metal nitrates. The presence of large crystals of Cu₂Cl(OH)₃ did not compromise the SO₂, NH₃, and HCN gas adsorption.

The zinc and copper oxide IACs and their mixtures have good SO₂, NH₃, HCN, and dry C₆H₁₂ adsorption behaviors. The addition of the third CuCl₂ component in the impregnant mixture caused little effects on SO₂ adsorption and big improvements in NH₃ adsorption. The materials that were impregnated with as much as 50% CuCl₂ showed promising multigas adsorbent properties as evaluated using the combi method. Dynamic adsorption studies of bulk prepared materials with similar compositions as the best combi samples also confirmed their potential as multigas adsorbents. Bulk prepared samples containing 1.2 mmol CuCl₂/g AC and 1.2 mmol/g AC of either zinc or copper nitrates, out-performed a well-known universal carbon material in terms of NH₃ and dry OV gas adsorption while offering reasonable protection against SO₂ and HCN gases. The method successfully identified potential multigas adsorbent materials and also successfully pinpointed the presence of the Cu₂Cl(OH)₃ phase as the likely cause for the unexpected SO₂ adsorption behavior of the ternary ZnO/CuO/CuCl₂ system despite the presence of large crystallites. This phase is a potential multigas adsorbent which acts without the need to be fully dispersed on the surface of the carbon and merits further characterization. Further studies on the adsorption mechanism by Cu₂Cl(OH)₃ should be performed.

■ ASSOCIATED CONTENT

📄 Supporting Information

Detailed description of the combinatorial and screening method, dispense procedures, heat treatment, characterization, and dynamic adsorption testing. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jeff.dahn@dal.ca.

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