To my beloved parents,
Baoling Luo and Tianxiao Zhou
ACKNOWLEDGMENTS

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<td>Water activity</td>
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<td>$a_{wa}$</td>
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<td>$y_{gly-water-Na_2CO_3}$</td>
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<td>$RH_E$</td>
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<td>$C_i$</td>
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<td>$F$</td>
<td>Sampling flow rate (Lpm)</td>
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<td>$k$</td>
<td>Dimensionless constant of proportionality</td>
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<tr>
<td>$k'(min^{-1}) = \frac{k C_i F}{S_T}$</td>
<td>Lumpsum proportionality constant</td>
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<td>$\tau$</td>
<td>Time for 50% breakthrough</td>
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LIMITATIONS AND MODIFICATIONS OF IMPREGNATED FILTER METHOD FOR SAMPLING SULFUR DIOXIDE GAS

By
Chufan Zhou
August 2017

Chair: Chang-Yu Wu
Major: Environmental Engineering Sciences

Collection of sulfur dioxide gas (SO$_2$) using a filter impregnated with a solution containing sodium carbonate (Na$_2$CO$_3$) and glycerol is a popular and convenient method to assess SO$_2$ concentration in the occupational setting. However, this method performs poorly under low relative humidity (RH), and breakthrough as a function of time cannot be predicted. To improve the collection and to predict the breakthrough, the collection mechanism and sorption kinetics were investigated.

Firstly, a family of filters treated by solutions with an increasing amount of glycerol (0 – 20% v/v) and a constant amount of sodium carbonate (2.5% w/v) was tested under medium (45%) RH condition. The theoretical and experimental SO$_2$ sorption capacities were determined by the coated Na$_2$CO$_3$ amount and breakthrough curves, respectively. The results showed no correlation between these two capacities and these treated filters did not have enough capacity for sampling 10 ppm of SO$_2$ under both the 200-minute sampling and 8-hour occupational exposure conditions. The breakthrough curve illustrated that filters coated with less glycerol had earlier 50% breakthrough, indicating that increasing the coated glycerol amount on the filter built up
the water content, leading to the dissolution and dissociation of Na$_2$CO$_3$. Consequently, Na ion transport was enhanced in the mixture that helped increase the utilization of the coated Na$_2$CO$_3$.

Secondly, two modified protocols to coat filters with more Na$_2$CO$_3$ and glycerol were proposed and evaluated. The results demonstrated that the new filters worked well in 45% RH condition for 8-hr tests, while their performance was not ideal in dry (25%) RH condition due to low utilization of Na$_2$CO$_3$ resulting from the scant amount of absorbed water and the weak ion transport in the concentrated mixture. The results suggest that incorporating more Na$_2$CO$_3$ and glycerol in the coating protocol may further improve performance. Finally, a kinetic model was proposed to describe SO$_2$ sorption behavior on the impregnated filter. This model gave a good prediction when impregnated filter working in medium RH range or holding sufficient glycerol amount, i.e., when the ion diffusion rate in liquid phase was high and the coated Na$_2$CO$_3$ could be utilized fully.

This study provides a comprehensive understanding of the role of each coating component and reveals the sampling mechanism of the impregnated filter. The kinetic model can predict the breakthrough of filters with high Na$_2$CO$_3$ utilization rate, allowing users to determine the optimal working duration. In addition, this study illustrates a low-cost, predictable and reliable industrial hygiene tool for sampling not only SO$_2$ but also potentially other similar workplace gas contaminants.
CHAPTER 1
INTRODUCTION

Sulfur Dioxide Health Effect

As a health hazard listed in National Fire Protection Association NFPA 704 [1] and the European Union (EU) Dangerous Substances Directive [2], sulfur dioxide (SO₂) is a widespread toxic that can be easily absorbed in the humid respiratory tract due to its high water-solubility. Exposure to SO₂ is associated with adverse health effects on both upper and lower airways, which because of their location and function in the body consist of a wet environment. Additionally, children and adults with asthma are most susceptible to adverse health effects caused by exposure to SO₂ in their airways. Research studies have shown that SO₂ acts as a promoter to cause serious residual injury to people who are exposed to it. If the exposure to SO₂ is through the nasal system, the resistance in respiratory tract to the airflow increases [3]. At 5 ppm, studies reported most people complained dryness in both the throat and the upper respiratory airway. The smell of 6 – 8 ppm is perceptible [4]. Workers who are chronically exposed to SO₂ are more likely to develop chromosomal aberrations than those in the SO₂-free environment [5]. Thus, sulfur dioxide warrants more attention, considering its significant concentration-dependent adverse health effects [6].

Emission Sources and Exposure Regulations in Workplace

Sulfur dioxide is a useful chemical commonly used in treating wood pulp, paper manufacturing, extraction of lubricating oils, and ore and metal refining, as a fumigating, bleaching and disinfecting, reducing agent and food additive and preservative [7]. On the other hand, sulfur dioxide is also a deleterious air pollutant, especially near smelters and thermal electrical power plants when burning high sulfur oil or soft coal [8]. Workers
risk their health in the environment with high exposure probability of SO$_2$, which makes them more likely to suffer from SO$_2$-related health issues. To protect workers, the Occupational Safety and Health Administration (OSHA) has mandated an exposure limit. Permissible Exposure Limit (PEL) for SO$_2$ is set as 5 ppm (time weight average: TWA) [9], while American Conference of Governmental Industrial Hygienists (ACGIH) sets even more stringent 0.25 ppm as short-term exposure limit (STEL) [10]. Therefore, a reliable sampling method is necessary to determine human exposure level to SO$_2$.

**Sampling Methods**

OSHA originally employed a midget impinger containing 0.3 N hydrogen peroxide to sample SO$_2$ [11]. However, the inconvenience and safety issues associated with impinger sampling in workplace triggered OSHA to develop a new solid-sorbent method, OSHA Method ID-200. This method, which applied impregnated beaded activated carbon as sorption medium, suffered from mass-dependent or lot-dependent extraction efficiency, inconvenient analysis and low SO$_2$ sorption capacity [12]. Another method, OSHA Method 1011 [7], which demanded a glass tube sampler within impregnated glass fiber depth filter (GFF) and treated silica gel, had difficulty of separating and extracting samples from the sampler tube. An impregnated filter method, NIOSH Method 6004 [13], which requires a sampler consisting of one 0.8 µm pore size MCE pre-filter with one support pad and one impregnated backup cellulose filter coated with a mixture of Na$_2$CO$_3$ and glycerol, is widely used nowadays. Sulfuric acid, sulfate salts, and sulfite salts aerosols are collected on the pre-filter and are quantified as total particulate sulfate. SO$_2$ gas is then collected on the back impregnated filter. The advantages of coating Na$_2$CO$_3$ along with glycerol is that glycerol, serving as a humectant, would absorb water moisture from the ambient, helping the dissolution and
dissociation of coated $\text{Na}_2\text{CO}_3$ [14]. Due to its hydroxyl groups, glycerol has solubility characteristics like water and simple aliphatic alcohols. Moreover, glycerol is a stable solvent that can be stored for a long period of time and withstand baking at 100 °C without degradation due to its high boiling point (290 °C) and low volatility [15, 16].

This kind of impregnated filter method is feasible for the collection of $\text{SO}_2$ when the environment relative humidity (RH) is higher than 30%. However, it has been reported that the collection efficiency decreases as RH decreases, especially when RH is lower than 30% [7, 17-20]. Table 1-1 summarizes the performance of various impregnated filter methods for $\text{SO}_2$ collection. Outdoor RH being lower than 30% is common in some dry places in America, such as Wyoming, Nebraska, Southern California, and Alabama during winter time [21]. RH also considerably decreases if the indoor air becomes warmer after air conditioning [18]. When sampling in such a scenario, the indoor workplace $\text{SO}_2$ concentrations and the human exposure level may be underestimated by the impregnated filter method. In addition, there are no current tools to predict its breakthrough because the sorption kinetic which allows prediction of the performance has not been fully investigated. Users may have concerns using the established method to sample at lower RH condition. Thus, the goal of this thesis was to study the mechanism and kinetics of $\text{SO}_2$ sorption on impregnated filters for 1) improving their sampling efficiency through modification of the coating protocol and 2) predicting the breakthrough through kinetic modeling.

The specific objectives of this study were 1) to reveal the roles of $\text{Na}_2\text{CO}_3$ and glycerol in the $\text{SO}_2$ collection mechanism on treated filter; 2) to predict the breakthrough
of filters treated by given protocols in a specific working condition; 3) to validate a reliable remedy to eliminate the breakthrough of the filter in low RH condition.
Table 1-1. Summary of the performances of different impregnated filter methods for SO₂ collection from several publications and standard methods

<table>
<thead>
<tr>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Filter type/ filter area</td>
<td>Whatman cellulose No. 1/16 cm²</td>
<td>S&amp;S Fast Flow Cellulose No.2W/516 cm²</td>
<td>Whatman cellulose No. 40/11 cm²</td>
<td>Millipore membranes filter/17 cm²</td>
<td>Glass fiber filter/1.3 cm²</td>
<td>Whatman cellulose No. 40/11 cm²</td>
</tr>
<tr>
<td>Alkali amount (mg/cm²)</td>
<td>2.26</td>
<td>1.53</td>
<td>NA</td>
<td>0.63</td>
<td>NA</td>
<td>0.33</td>
</tr>
</tbody>
</table>

**Operation**

- Filter linear velocity (cm/s): < 15, < 65, < 70, 0.96, 0.63, 1.55 (1 Lpm)
- SO₂ sampling range (ppm): < 3.8, < 6, 0.02 – 0.08, 0.1 – 10, < 11.1 (or 22.1) *, 19
- Total SO₂ mass collected (mg): < 10% alkali, > 10% alkali, 1.100, 0.785, 0.348 (or 1.390), 1.1
- RH (%): > 30, > 30, > 30 – 35, NA, 20 (or 78), > 30

*11.1 ppm SO₂ in a relatively dry atmosphere with 20% RH at 22 °C; 22.1 ppm SO₂ with 78% RH at 23 °C.
CHAPTER 2
METHODOLOGY

Experiment Set-up

The experiment set-up is shown in Figure 2-1. 100 ppm SO\textsubscript{2} from a certified standard-spec grade cylinder (CISA 2729, Airgas) flowing at 0.7 liter per minute (Lpm) controlled by a mass flow controller (FMA5400/5500 FMA5516, Omega) was diluted by breathing quality compressed air (AI B 300, Airgas) flowing at 0.7 Lpm controlled by a rotameter. The mixture was then injected into a closed stainless-steel cylinder chamber with 41 cm in diameter, 71 cm in length, and 9374 cm\textsuperscript{3} in volume for more than 30 minutes of conditioning. The temperature was monitored by a sanitary bimetal thermometer (LL-40, Omega). The chamber RH was controlled by another flow of compressed air going through a water-filled sparger and monitored by a relative humidity/ambient temperature transmitter (HX94B, Omega). Herein, RH smaller than 35\% was designated as “low RH condition”, RH between 35\% and 55\% was “medium RH condition”, and RH higher than 55\% was defined as “high RH condition”. The 10-mL absorption solution in the impingers (Cat# 225-36-4, SKC) was 0.3N H\textsubscript{2}O\textsubscript{2} solution prepared by adding 0.25 mL 35 wt.\% H\textsubscript{2}O\textsubscript{2} solution (CAS# 7722-84-1, Acros) into 9.75 mL deionized (DI) water (18.2 M\textOH-cm, Barnstead D11911 Water Purification Systems) following the instruction of OSHA ID-104 [22]. The sampling flow rate was fixed at 1 Lpm by a personal pump (AIRCHEK sampler model 224-PCXR4, SKC) to comply with the sampling flow rate denoted in the NIOSH Method 6004, which was treated as the reference protocol in this experiment. Teflon tubing was employed because Tygon, stainless steel, and other tubing materials were reported to react with SO\textsubscript{2} during sampling [23].
The study was carried out in three tasks. Task 1 was to identify SO<sub>2</sub> collection mechanism. In Task 2, sorption kinetics of impregnated filters were determined. In Task 3, modified coating protocol to improve sorption performance was validated. The treatment protocols to impregnate the filter of each task are listed in Table 2-1. Details for each task are discussed as follows.

**Table 2-1. Treatment protocols of each task for the test filters**

<table>
<thead>
<tr>
<th>Protocol names</th>
<th>Filter type</th>
<th>Na&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt; (% w/v)</th>
<th>Glycerol (% v/v)</th>
<th>Baking Temperature (°C)</th>
<th>Baking Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Task 1 &amp; 2</td>
<td>N2.5, G2&lt;sup&gt;*&lt;/sup&gt;, G10 &amp; G20</td>
<td>37 mm Whatman Grade 40</td>
<td>2.5</td>
<td>0, 2, 10 &amp; 20</td>
<td>100</td>
</tr>
<tr>
<td>Task 3</td>
<td>N10G20 &amp; N20G20</td>
<td>37 mm Whatman Grade 40</td>
<td>10 &amp; 20</td>
<td>20</td>
<td>100</td>
</tr>
</tbody>
</table>

<sup>*</sup>G2: Filter treated by NIOSH Method 6004 representing as reference.

N: Na<sub>2</sub>CO<sub>3</sub>; G: glycerol; the following numbers stand for Na<sub>2</sub>CO<sub>3</sub> and glycerol amount in the units of (% w/v) and (% v/v) in coating solution.
Task 1: SO₂ Collection Mechanism

All the impregnated filters in this task were tested under medium RH condition (~45%), since most of the sampler test conditions specified by OHSA fell into the medium RH range. An impinger was hooked right after the test filter and was replaced in pre-set time intervals. SO₂ breakthrough concentration was calculated by the mass of SO₂ collected in that impinger divided by the sampling air volume during that time interval. Impregnated filters treated by a family of coating solutions with an increasing amount of glycerol (G0-G20) but constant amount of sodium carbonate (N2.5) were tested in medium RH condition. The 200-minutes breakthrough curve, which is the SO₂ percentage breakthrough versus time, was generated for each tested filter. The mass loss of the glycerol can be considered as negligible, because 1) glycerol is not a volatile organic compound. The vapor pressure of the glycerol at both 100 °C (baking temperature) and 25 °C (experimental condition) is around 0.2 and 0.001 mmHg [16], respectively; 2) the rate of the weight loss by free evaporation is directly proportional to the vapor pressure of the glycerol [24]. As a reference, the vapor pressure of water at 0 °C is 0.54 mmHg. When vapor pressure is low, the weight loss is negligible. Na₂CO₃ is not volatile either. Therefore, the amount of coated components was considered as constant during the entire experiment. The role of each coated component, Na₂CO₃ and glycerol, was experimentally investigated and is discussed in the following subsections.

Role of Na₂CO₃: SO₂ Sorption Capacity

The absorbed SO₂ reacts with Na₂CO₃ on the filter. Thus, the gas contaminant capacity is directly related to the coated Na₂CO₃ amount (N, mg). The experimental SO₂ sorption capacity (Sₑ, mg) was derived from the collected SO₂ amount on the tested filter at 95% breakthrough or the total collected SO₂ amount on the tested filter at the
end of the test if the tested filter had not reached the 95% breakthrough. Each tested filter was soaked in DI water overnight to extract the Na ion and then to determine $N$ by ion chromatography (IC). The theoretical SO$_2$ sorption capacity ($S_T$, mg) was calculated stoichiometrically based on $N$ by the following equation,

$$S_T = \frac{N \cdot MW_{SO_2}}{MW_N}$$  \hspace{1cm} (2-1)

where $MW_{SO_2}$ and $MW_N$ are the molecular weight of SO$_2$ and Na$_2$CO$_3$, respectively.

Paired t-test was applied to determine if there was significant difference between $S_T$ of each type of tested filter, N2.5, G2, G10, and G20.

**Role of Glycerol: Water Content on the Impregnated Filter**

For the treated filters, N2.5, G2, G10, and G20, which were designed to have the same $N$, the Na$_2$CO$_3$ concentration (mg/mg) on the filter could be estimated by $N$ (mg) divided by the amount (mg) of glycerol-water-Na$_2$CO$_3$ mixture (GWN) on the filter. The amount of GWN is the sum of the coated glycerol amount ($G$, mg), the absorbed water amount ($W$, mg), and the coated Na$_2$CO$_3$ amount ($N$, mg). Without the exact $G$, a simple comparison of the Na$_2$CO$_3$ concentration for each kind of treated filter was conducted using the following equations.

Since $W$ varies with different ambient RH, coated Na$_2$CO$_3$ and glycerol amount, the relationship of water mole fraction in the GWN mixture and the ambient RH is expressed as Equation 2-2 [25], which is based on the condition that water activity ($a_w$) in a known solution is proportional to the water mole fraction ($x_{water}$) in that solution with a constant factor,

$$x_{water} = \frac{a_w}{y_{gly-water-Na_2CO_3}}$$  \hspace{1cm} (2-2)
where $x_{\text{water}}$ in the GWN mixture is obtained by moles of water divided by the total moles of ingredients in the mixture; $y_{\text{gly-water-Na}_2\text{CO}_3}^{\text{Water}}$ is the activity coefficient of water in the GWN mixture. Na$_2$CO$_3$ is hygroscopic and glycerol with three hydroxyl groups is also hygroscopic. For simplification, $y_{\text{gly-water-Na}_2\text{CO}_3}^{\text{Water}}$ is assumed to be close to unity and will keep the same value within our experimental RH condition from 25% to 45%.

When the chamber RH is a constant (45%), any hygroscopic chemical or chemical mixture in that ambient would keep absorbing water moisture from air until the entire system reaches equilibrium, i.e., the water activity of the mixture ($a_w$) finally equates to water activity of air ($a_{wa}$). The water activity of air ($a_{wa}$) has the relation of

$$a_{wa} = \frac{R_{HE}}{100\%},$$

where $R_{HE}$ as the equilibrium relative humidity of ambient is 45%.

Consequently, the mole fraction of water in the mixture is finally equal to 0.45 as shown in Equation 2-3. The time to reach equilibrium RH for the entrie system can be considered as instant due to the small amount of the GWN mixture and the sufficient amount of ambient moisture. Also, by the preliminary test, the newly baked impregnated filter reached the equilibrium condition and the weight kept stable on the balance under room condition (RH = 40%) in less than one minute.

$$x_{\text{water}} = \left(\frac{R_{HE}}{100\%}\right) / \left(y_{\text{gly-water-Na}_2\text{CO}_3}^{\text{Water}}\right) = 0.45$$  \hspace{1cm} (2-3)

Representing $x_{\text{water}}$ by the amount of each component in the mixture, Equation 2-4 is obtained by using the linear relationship between $W$, $G$ and $N$ at 45% RH.

Equation 2-5 is the general function of the absorbed water amount, the coated glycerol and Na$_2$CO$_3$ amount at specific $R_{HE}$. In medium RH condition when $R_{HE} = 45\%$, Equation 2-4 is the simplification of Equation 2-5. As $G$ increases, $W$ increases, which in turn will help the dissociation and dissolution of the Na$_2$CO$_3$. Similarly, as $N$ increases,
$W$ increases as well, although it in turn will weaken the dissociation and dissolution because the increased amount of salt is much larger than the increased amount of water (1 vs. 0.14 at 45% RH).

$$\frac{W/18}{G/92+W/18+N/106} = x_{water} = \frac{RH_E}{100\%} = 0.45$$

$$W = 0.16G + 0.14N \tag{2-4}$$

$$W = \frac{RH_E}{1-RH_E} (0.2G + 0.17N) \tag{2-5}$$

It can be seen in Equation 2-5, the absorbed water amount is proportional to the coated glycerol and the Na$_2$CO$_3$ amount. In other words, the more the glycerol is coated, the more the water is absorbed from ambient, and the larger amount of GWN mixture is generated on the filter. In this case, the amount of GWN mixture of the G20 would be much larger than that of the N2.5, resulting in the larger denominator, i.e., lower Na$_2$CO$_3$ concentration. In short, the Na$_2$CO$_3$ concentration would decrease as $G$ increases.

Furthermore, Equation 2-5 tells that when the ambient has lower RH, it would become harder for the treated filter to absorb water from the ambient. $\frac{RH_E}{1-RH_E}$ starts to be smaller than unity at 50% RH and keeps shrinking faster as $RH_E$ decreases. For example, when sampling under 45% RH, $W$ will be the sum of 1/6 $G$ and 1/7 $N$; while sampling under 25% RH, $W$ will be the sum of 1/15 $G$ and 1/18 $N$, which will be around 1/3 of $W$ under 45% RH, resulting in a significant decrease of $W$ in 25% RH condition, i.e., an increase of the Na$_2$CO$_3$ concentration.

Sha et. al. [26] pointed out that in the highly concentrated solution, the ion dynamics could not be depicted by the Debye–Hückel equation and the free ion would
be localized in a multicandidate ion cage, which could be specified as ion cage effect. Such an effect might increase the resistance of the ion transport, reduce the number of free-moving ions, thus weakening the ion diffusion rate. Therefore, for the same tested filter when the RH decreases, \( W \) will be smaller; the amount of GWN will drop, and the Na ion concentration will be higher, thus resulting in a stronger ion cage effect and lower ion diffusion rate in GWN. On the other hand, for the same RH condition, filters coated with more glycerol is expected to have more \( W \) and more GWN amount; the Na ion concentration will be lower, bringing about a weaker ion cage effect and higher ion diffusion rate.

**Task 2: Sorption Kinetics of Impregnated Filters**

**Verification of Assumption for Kinetic Model**

The breakthrough behaviors of the four types of tested filters were examined to determine whether the rate of change in SO\(_2\) breakthrough concentration \( \left( \frac{dC_b}{dt}, \text{ppm/min} \right) \) is proportional to the product of SO\(_2\) breakthrough concentration \( (C_b, \text{ppm}) \) and absorbed SO\(_2\) concentration \( (C_i - C_b, \text{ppm}) \) as shown in Equation 2-6 [27]. The plots of the linearity were generated, and the adjusted \( R^2 \) was obtained to evaluate the linearity. This relationship was firstly observed by Yoon and Nelson [28] by using respirator cartridge to collect methyl acetate and vinyl chloride at varied concentration from 50 ppm to 2000 ppm under medium RH condition, and was the foundation for further deriving the equation to relate the initial concentration and the breakthrough concentration with the breakthrough time in a sorption system. Such an equation could serve to predict the breakthrough as a function of time.

\[
\frac{dC_b}{dt} \propto C_b(C_i - C_b) \tag{2-6}
\]
Hence, the breakthrough data of N2.5, G2, G10, and G20 were analyzed to verify the proportionality.

**Kinetic Model**

The following steps were constructed to derive the SO\(_2\) sorption kinetic model for the impregnated filter for systems that meet the condition of Equation 2-6. There are only two probable fates of SO\(_2\) molecule in the system: it is either removed or it penetrates. Hence, the sum of breakthrough probability \((B)\) and the removal probability \((R)\) is equal to one, i.e., \(B = 1 - R\). As \(C_b\) is proportional to \(B\) and \((C_i - C_b)\) is proportional to \(R\) for each molecule, Equation 2-7 could be constructed based on the rearrangement of Equation 2-6. Yoon and Nelson [28] proposed an explicit model to predict gas contaminant sorption kinetics for a respirator cartridge.

\[
-\frac{dR}{dt} \propto BR
\]  
(2-7)

Besides, the rate of decrease of removal probability \(-\frac{dR}{dt}\) is also proportional to the incoming SO\(_2\) concentration, \(C_i\) (ppm), and the sampling flow rate, \(F\) (Lpm), but inversely proportional to the sorbent capacity, \(S_T\) (milligram of theoretical SO\(_2\) sorption capacity per piece of impregnated filter). By introducing a dimensionless constant of proportionality, \(k\), to obtain the equality of both sides and lumping \(\frac{kC_iF}{S_T}\) as another proportionality constant, \(k'\) (min\(^{-1}\)), Equation 2-7 can be rewritten as Equation 2-8.

\[
-\frac{dR}{dt} = \frac{kC_iF}{S_T} BR = k'BR
\]  
(2-8)

Since \(k'\) is independent of time \((t)\), solving Equation 2-8 can lead to Equation 2-9.

\[
ln \frac{R}{1-R} = -k't + Constant
\]  
(2-9)
Herein, applying $t = \tau$, i.e., the time for 50% breakthrough, where $R = B = 0.5$, the constant in Equation 2-9 can be determined as $k' \tau$. Thus, Equation 2-10 is obtained.

$$\ln \frac{R}{1-R} = k'(\tau - t) \quad (2-10)$$

As the breakthrough fraction ($\frac{C_b}{C_i}$) is equal to the breakthrough probability ($P$), i.e., $\frac{C_b}{C_i} = B$, and $B = 1 - R$, $R$ can be expressed as $\frac{C_i - C_b}{C_b}$. Equation 2-10 can be rearranged as Equation 2-11 or Equation 2-12.

$$\ln \frac{C_b}{C_i - C_b} = -k'(\tau - t) \quad (2-11)$$

$$t = \tau + \frac{1}{k'} \ln \frac{C_b}{C_i - C_b} \quad (2-12)$$

When the utilization of Na$_2$CO$_3$ is high in which the high-water content could be obtained due to either high ambient RH or sufficient coated glycerol amount, a simpler model, Equation 2-13 could be conducted. Since the breakthrough curve is centrally symmetric [28], the quantity of SO$_2$ penetrating the treated filter within the period from $t = 0$ to $t = \tau$ is equal to the quantity of SO$_2$ removed within the period from $t = \tau$ until the treated filter is saturated. Thus, the theoretical SO$_2$ sorption capacity ($S_T$) is the product of three parameters, i.e., 50% breakthrough time ($\tau$), incoming SO$_2$ concentration ($C_i$) and sampling flow rate ($F$). In short, $\tau$ can be expressed as the following Equation 2-13.

$$\tau = \frac{S_T}{C_i F} \quad (2-13)$$

**Task 3: Validation of Modified Coating Protocol**

Coating with more Na$_2$CO$_3$ will increase the SO$_2$ sorption capacity of the treated filter. In addition, coating with more glycerol will promote the dissolution, dissociation and the ion transport of the Na$_2$CO$_3$ in the GWN mixture. In Task 3, N10G20 and
N20G20 treated filters, which represent the higher concentration of \( \text{Na}_2\text{CO}_3 \) and glycerol in the coating solution, were tested in both medium RH and low RH working conditions. The breakthroughs were experimentally verified by 8-hour sampling time, 1 Lpm sampling flow rate and 10 ppm \( \text{SO}_2 \). The tested \( \text{SO}_2 \) concentration, 10 ppm, is twice the PEL concentration, 5 ppm, specified by OHSA. The 8-hour breakthrough curves were constructed to identify the optimal operation time based on the instruction denoted in the OSHA Validation Guideline for Air Sampling Method Utilizing Chromatographic Analysis [29]. The linearity of Equation 2-6 was observed to verify the feasibility of the model at first. Then both Equation 2-12 and Equation 2-13 were applied to evaluate the performance of the model.
CHAPTER 3
RESULTS AND DISCUSSIONS

SO₂ Collection Mechanism

As shown in Table 3-1, the mean theoretical SO₂ sorption capacity ($S_T$) of N2.5, G2, G10, and G20 was very close to each other, which was 3.5 mg, 3.6 mg, 3.6 mg, and 3.6 mg, respectively. The results of paired t-test showed that there was no significant difference between $S_T$ of each pair of the tested filters in 95% confidence interval for mean difference. This family of filters were treated by the solution with the same Na₂CO₃ concentration (2.5% w/v) but different glycerol concentrations from 0% to 20% v/v. The $S_T$ listed in Table 3-1 indicates that the glycerol concentration in the coating solution did not influence the coated Na₂CO₃ amount ($N$). The solutions with the same Na₂CO₃ concentration coated the same amount of Na₂CO₃ onto the treated filter, proving that the volume of coating solution left on the filter after soaking was similar. As specified in NIOSH Method 6004, the maximum sampling volume limit is 200 L, meaning that in our test condition, 10 ppm SO₂, the total incoming SO₂ amount was 4.1 mg, which was larger than $S_T$ of this family of filters. It is obvious that the coated Na₂CO₃ amount was not enough. The sorption capacity of the treated filter has to be increased and more coated Na₂CO₃ is needed.

The experimental SO₂ sorption capacity ($S_E$) for 200-minute, medium RH test showed that only G20 reached the theoretical SO₂ sorption level, while others, N2.5, G2, and G10 didn’t. These four kinds of treated filter held the same coated Na₂CO₃ amount and the same $S_T$, but presented different sorption behaviors, meaning that there should have been a mass transfer barrier in the GWN mixture so that the absorbed and reacted SO₂ gas molecule on the mixture surface could not go deeper. In other words,
parts of the coated Na$_2$CO$_3$ were unused. When considering one standard deviation, similar value of $S_E$ for N2.5 and G2 was found. G2, the standard method treated filter designated in the NIOSH Method 6004, didn’t absorb more SO$_2$ under medium RH condition. However, G10 and G20 did have a significant increase of $S_E$ as the glycerol concentration in the coating solution increased. Thus, it can be concluded that the different $S_E$ among these four impregnated filters is controlled by the utilization rate of the coated Na$_2$CO$_3$. Without quantifying the glycerol amount for filters, it is rational to deduce that after baking the filter treated by more concentrated glycerol solution should have more glycerol amount left, and helps to increase the Na$_2$CO$_3$ utilization.

Table 3-1. Comparison of $S_T$ and $S_E$ of different tested filters under medium RH condition

<table>
<thead>
<tr>
<th>Filter type</th>
<th>ST ± 1SD (mg) (n = 3)</th>
<th>SE ± 1SD (mg) (n = 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2.5</td>
<td>3.5 ± 0.1</td>
<td>3.0 ± 0.4</td>
</tr>
<tr>
<td>G2</td>
<td>3.6 ± 0.3</td>
<td>2.7 ± 0.2</td>
</tr>
<tr>
<td>G10</td>
<td>3.6 ± 0.1</td>
<td>3.4 ± 0.1</td>
</tr>
<tr>
<td>G20</td>
<td>3.6 ± 0.3</td>
<td>4.0 ± 0.3</td>
</tr>
<tr>
<td>N10G20</td>
<td>13.6 ± 2.7</td>
<td>10.6 ± 0.5</td>
</tr>
<tr>
<td>N20G20</td>
<td>25.0 ± 3.9</td>
<td>12.1 ± 0.1</td>
</tr>
</tbody>
</table>

The data of N2.5, G2, G10, and G20 are based on 200-minute (200-L) test; the data of filters (N10G20 and N20G20) treated by the modified protocol are based on 8-hour test.

The breakthrough curves of N2.5, G2, G10, and G20 filters are shown in Figure 3-1. The 50% breakthrough time of N2.5, G2, G10, and G20 protocol treated filters were around 66, 72, 109, and 148 minutes, respectively. It is obvious that the 50% breakthrough time increased for the filter treated by the solution with higher glycerol concentration. Before each curve started to flatten, the slopes of them were similar. We could define this zone as active mass transfer zone where the liquid mass transfer was active and the rate was limited by the gas phase transfer rate, which was controlled by
the incoming SO₂ concentration and the sampling flow rate, which in our case were both constant.

Figure 3-1. Breakthroughs of N2.5, G2, G10, and G20, RH = 45%, SO₂ = 10 ppm, Temperature = 74 °F, 4.5 hours sampling time

At around 200 minutes, G20 reached the saturation capacity. However, N2.5, G2, and G10 with the same coated Na₂CO₃ amount (N) didn’t saturate at this point but kept absorbing SO₂ even at the end of the test for 200-minute, medium RH condition. The results further support that the glycerol played a key role of fast absorption in the GWN mixture by 1) increasing the absorbed water amount; 2) increasing the GWN amount; 3) decreasing the Na ion concentration that helped Na ion diffusion in the mixture. It could be expected that N2.5, G2, and G10 would keep absorbing SO₂ slowly after 4 hours and the penetration would keep increasing until $S_E$ would be finally equal to $S_T$. One possible reason of different sorption behaviors was that the glycerol assisted the dissolution and dissociation of Na₂CO₃ in the GWN mixture, thus promoting ion transportation and freeing ions from the ion cage in the concentrated GWN mixture. The
Na ion on the surface of the more dilute mixture (G20) reacted with the incoming SO$_2$ molecule and was fast transported into the deeper layers of the mixture. Then the mixture surface could keep absorbing incoming SO$_2$ molecules until this “active site” became saturated, which in turn prolonged the active mass transfer zone. In contrast, in the concentrated mixture (i.e., N2.5, G2, and G10), it was harder for the dissociated Na ion on the mixture surface to diffuse deep because of the resistance of ion transportation by the ion cage effect, resulting in the faster depletion of the surface Na$_2$CO$_3$ and earlier 50% breakthrough time shown in Figure 3-1. The earlier the depletion happened, the lower the glycerol amount was coated.

G2 served as a reference filter, which was treated by 2.5% w/v of Na$_2$CO$_3$ and 2% v/v of glycerol coating solution designated in the NIOSH Method 6004. It didn’t have better sampling performance under medium RH condition than N2.5, which was treated only by 2.5% w/v of Na$_2$CO$_3$ solution. After working in the medium RH condition for 30 minutes of sampling, the penetration already reached 20%. In dry working condition (RH < 30%), where the GWN mixture amount is supposed to be less, Na$_2$CO$_3$ in the mixture may be more concentrated and the ion cage effect is thus stronger than it is in medium RH condition. The 50% breakthrough would occur earlier than 72$^{th}$ minute. In that case, the SO$_2$ concentration measured by the NIOSH Method 6004 will be underestimated.

In conclusion, using 2.5% w/v Na$_2$CO$_3$ and 2% v/v glycerol solution treatment of the filters was not enough to meet the Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis [29] under both medium and dry conditions. Higher concentration of Na$_2$CO$_3$ and glycerol coating solution is needed. So, N10G20 and N20G20 were proposed for testing under medium and low RH conditions in Task 3.
Sorption Kinetics of Impregnated Filters

Figure 3-2 illustrates the relationship between the rate of change in SO\textsubscript{2} breakthrough concentration ($\frac{dc_b}{dt}$, ppm/min) and the product of SO\textsubscript{2} breakthrough concentration ($C_b$, ppm) and absorbed SO\textsubscript{2} concentration ($C_i - C_b$, ppm) for three replicates of N2.5, G2, G10 and G20 in subsection (a), (b), (c), and (d), respectively under medium (~45%) RH condition. Relatively strong proportionality was observed for both G10 and G20 with $R^2$ being equal to 0.88 and 0.85, respectively, thus validating the assumption of Equation 2-6. Relatively worse linearity was observed from N2.5 and G2 with less coated glycerol as shown in subsection (a) and (b). However, the proportionality of both existed plausibly, so the model was applied and the fitting was evaluated. The linearity became stronger as coated glycerol increased. Equation 2-12 was accordingly validated to predict the breakthrough of the impregnated filters.

![Figure 3-2. Proportionality of rate of change in breakthrough concentration and the product of breakthrough concentration and removal concentration for 3 replicates of N2.5 (a), G2 (b), G10 (c), and G20 (d) in medium RH (45%) condition](image-url)
Figure 3-2. Continued

Equation 2-12 of $\ln \frac{C_b}{C_i - C_b}$ versus time ($t$) in Figures 3-3 was generated from the data points before breakthrough curve starting to flatten out, which were defined as active mass transfer zone. Na$_2$CO$_3$ was still well utilized in this zone, but the limiting step is if Na$_2$CO$_3$ is no longer accessible where liquid phase transfer occurs and the model will not work anymore. Figure 3-3 displays a relatively better linear relationship for G20 than that for N2.5, G2, and G10 with the $R^2$ of 1 versus 0.93, 0.85, and 0.93, respectively. It shows that the proposed kinetic model fitted well for each of the tested filters in the active mass transfer zone. Figure 3-4 displays each of the fitted curves for the four types of tested filters based on Equation 2-12 to help visualize the agreement. As shown, before the experimental breakthrough starts to flatten out, i.e., in the active mass transfer zone, the model fits the experimental data relatively well for N2.5 and G2. However, after the curve flattened out, the model did not fit anymore which echoes the model assumption that the model works only when the Na$_2$CO$_3$ utilization is high. For G10 and G20, the model curve and the experimental data agreed well, telling that the model is a useful and reliable tool to describe the filters with high Na$_2$CO$_3$ utilization.
The 50% breakthrough time usually appears before the turning point of active mass transfer zone. Thus, the estimation of the 50% breakthrough time by the proposed model for both N2.5 and G2 is possible.

![Graph showing kinetic model fitting for different filters](image)

**Figure 3-3.** Proposed kinetic model fitting for N2.5, G2, G10, and G20, RH = 45%, SO₂ = 10 ppm, Temperature = 74 °F, 4.5 hours sampling time

![Comparison between experimental and model predicted breakthrough](image)

**Figure 3-4.** The comparison between the experimental breakthrough and the model predicted breakthrough for each tested filter, (a) N2.5, (b) G2, (c) G10, and (d) G20 in medium RH (45%) condition
Figure 3-4. Continued

Table 3-2 shows the comparison between the 50% breakthrough time determined from experiment and the 50% breakthrough time estimated by Equation 2-12. In Figure 3-3, the fitting of N2.5 and G2 was not good. The relative error between experimental and Equation 2-12 predicted $\tau$ for N2.5 and G2 showed a relatively larger error than 10%, indicating that the proposed kinetic model could not offer a reliable prediction of the filter coated with relatively less glycerol amount. In comparison, G10 and G20 had smaller relative errors, 1.8% and 0.7%, respectively, with a clear trend that the experimental error will be lowest when the more glycerol is coated onto the filter. Thus, Equation 2-12 provides an accurate tool to describe the breakthrough time for G10 and G20 which are coated with a relatively higher amount of glycerol.

Table 3-2. Comparison between the 50% breakthrough time conducted by experiment ($\tau_{exp}$) and the 50% breakthrough time calculated by Equation 2-12 ($\tau_{2-12}$)

<table>
<thead>
<tr>
<th>Filters</th>
<th>N2.5</th>
<th>G2</th>
<th>G10</th>
<th>G20</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_{exp}$ (min)</td>
<td>66</td>
<td>72</td>
<td>109</td>
<td>148</td>
</tr>
<tr>
<td>$\tau_{2-12}$ (min)</td>
<td>81</td>
<td>82</td>
<td>111</td>
<td>147</td>
</tr>
<tr>
<td>Relative Errors ($\frac{</td>
<td>\tau_{2-12}-\tau_{exp}</td>
<td>}{\tau_{exp}} \times 100%$)</td>
<td>22.7%</td>
<td>13.9%</td>
</tr>
</tbody>
</table>
Table 3-3 shows the comparison between the 50% breakthrough time determined by experiment and the 50% breakthrough time calculated by Equation 2-13. Equation 2-13 was derived for predicting the 50% breakthrough time for the filter with high Na₂CO₃ utilization, which was supposed to be better for G20 than for N2.5, G2, and G10. As shown in Table 3-3, even though the relative error for G20 was 15.5%, there was still a trend that when the coated glycerol increased, i.e., more water was captured during the sampling, more Na₂CO₃ on the filter was utilized, and the relative error tended to be smaller. In one word, the filters treated by the glycerol solutions with a higher concentration have better predictability and agree with the model better.

### Table 3-3. Comparison between the 50% breakthrough time conducted by experiment ($τ_{exp}$) and the 50% breakthrough time calculated by Equation 2-13 ($τ_{2-13}$)

<table>
<thead>
<tr>
<th>Filters</th>
<th>N2.5</th>
<th>G2</th>
<th>G10</th>
<th>G20</th>
</tr>
</thead>
<tbody>
<tr>
<td>$τ_{exp}$ (min)</td>
<td>66</td>
<td>72</td>
<td>109</td>
<td>148</td>
</tr>
<tr>
<td>$τ_{2-13}$ (min)</td>
<td>123</td>
<td>124</td>
<td>128</td>
<td>125</td>
</tr>
<tr>
<td>Relative Errors ($\frac{</td>
<td>τ_{2-13}-τ_{exp}</td>
<td>}{τ_{exp}} \times 100%$)</td>
<td>86.4%</td>
<td>72.2%</td>
</tr>
</tbody>
</table>

The inability to accurately predict both N2.5 and G2 indicates that the breakthrough of N2.5 and G2 is more susceptible to the environmental factors, i.e., fluctuations of ambient RH, SO₂ concentration, and sampling flowrate, due to scant amount of the GWN mixture and the poor diffusion rate of the Na ion in the mixture resulting from the high concentration.

**Validation of Modified Coating Protocol**

In order to increase $S_E$ and release the Na ions from the ion cage in the concentrated GWN mixture, coating more Na₂CO₃ and glycerol onto the filter is needed. Thus, N10G20 and N20G20 which were the filters treated by the 10% w/v Na₂CO₃, 20% v/v glycerol solution and 20% w/v Na₂CO₃, 20% v/v glycerol solution were tested. As
shown in Table 3-1, $S_T$ of N10G20 and N20G20 is around 4 and 8 folds of the reference filter, G2. The Na$_2$CO$_3$ concentration of coating solution for N10G20 and N20G20 is accordingly 4 and 8 folds of that for G2. The result confirms the hypothesis that the volume of solution left on the filter was similar after soaking with different coating solutions, resulting in the coated Na$_2$CO$_3$ amount ($S_T$) being proportional to the Na$_2$CO$_3$ concentration of the coating solution. The coated glycerol amount and the glycerol concentration in the coating solution likely followed the same relationship.

The filters treated with the modified protocol were then tested under 45% RH condition and 25% RH condition. Figure 3-5 shows the breakthrough over time for both N10G20 and N20G20 under 45% and 25% RH working conditions. The breakthrough for both modified protocols in 45% RH condition did not exceed 5% when the sampling volume was less than 200 liters of air. However, in occupational health sampling condition, 8-hour sampling was preferred in most of the cases. In this case, only the breakthrough of the N20G20 was below 5% in medium RH condition, while N10G20 almost reached the 50% breakthrough point at the end of 8 hours. The $S_E$ of N10G20, 10.6 mg, was getting close to its $S_T$, 13.6 mg, listed in Table 3-1, indicating that N10G20 was almost exhausted in the 8-hour medium RH test. On the other hand, the $S_E$ of N20G20, 12.141 mg, was about half of its $S_T$, 24.981 mg, showing that the capacity of N20G20 was still sufficient in 8-hour test. Thus, N20G20 is more reliable in both 8-hour test and 200-minute (200-L) sampling volume test under medium RH condition.

In some of the dry areas in America, the indoor RH after air conditioning can get close to 25%. It is therefore important to verify that the modified protocol treated filter still has satisfactory performance. The breakthrough plot of the N10G20 and N20G20
under low RH (25%) condition is shown in Figure 3-5, where their trend of the breakthrough curves is very similar. When the absorbed water amount is in shortage, there is not much difference between N10G20 and N20G20 based on the amount of free Na ions in the mixture. The coated Na$_2$CO$_3$ was partially utilized with relatively high concentration in the mixture, generating the high resistance of the ion transport and low ion diffusion rate. Thus, the breakthrough of both modified protocol treated filters tended to be similar. Before 40 minutes, there was a sharp increase of the breakthrough under low RH, then the breakthrough curve acquired the similar trend of that in the medium RH condition. One possible explanation is that the time for the GWN mixture grabbing water moisture from ambient to reach equilibrium state was no longer instantaneous at the 25% RH condition. In other word, the water activity in the GWN mixture reaching the ambient water activity might take time. At the very beginning, the absorbed water amount in the mixture was too scarce for Na$_2$CO$_3$ dissolution and dissociation. Thus, the free Na ion in the mixture was scant and only the surface of the mixture was available for SO$_2$ removal, causing the sharp increase of the breakthrough during this period. Afterward, the increase of the breakthrough decreased when the mixture obtained enough water from ambient approaching equilibrium.

As shown in Table 3-1, the capacity of 20% w/v Na$_2$CO$_3$ coating solution treated filter (N20G20) was enough for both 200-L and 8-hour sampling. For 200-minute sampling, $S_T$ (24.981 mg) was around 5 folds larger than the incoming SO$_2$ amount, 4.12 mg. For 8-hour sampling, $S_T$ was around 2 folds larger than the incoming SO$_2$ amount, 9.89 mg. Both modified protocol treated filters, N10G20 and N20G20, had a much larger sampling capacity and slower breakthrough compared with the reference
protocol, G2. However, they still could not cover 200-minute sampling volume within 5% breakthrough at 25% RH condition, implying that more coated glycerol amount is needed.

![Graph](image)

**Figure 3-5.** Breakthrough curve for N10G20 and N20G20, RH = 45% & 25%, SO2 = 10 ppm, Temperature = 74 °F, 8 hours sampling time

**Figure 3-6** illustrates the relationship between the rate of change in SO$_2$ breakthrough concentration \(\frac{dC_b}{dt}, \text{ ppm/min}\) and the product of SO$_2$ breakthrough concentration \(C_b, \text{ ppm}\) and absorbed SO$_2$ concentration \((C_i - C_b, \text{ ppm})\) for both N10G20 and N20G20 under both medium (~45%) and dry (~25%) RH conditions. Good proportionality was observed from subsections (a), (c), and (d), indicating the model could be conducted to describe the breakthrough. However, due to the early-stage breakthrough curve for N20G20 under medium RH condition as shown in (b), the data points are still in the fresh zone that do not generate good linearity for the model. Since
the breakthrough of N20G20 under medium RH didn’t exceed 5% at the end of the 8-hrs test, and the sampling performance was fully satisfactory, there is no need to conduct model further to describe the breakthrough behavior.

Figure 3-6. Proportionality of rate of change in breakthrough concentration and the product of breakthrough concentration and removal concentration for 3 replicates of (a) N10G20 and (b) N20G20 in medium (45%) RH condition, and single replicate of (c) N10G20 (d) and N20G20 in dry RH (25%) condition

Model fitting of both N10G20 and N20G20 shown in Figure 3-7 displays a good linear relationship with unity of R², which illustrates its good ability to predict the 50%
breakthrough time based on Equation 2-12. For N10G20 under medium RH condition, the experimental 50% breakthrough time of N10G20 was around 470 min. The theoretical 50% breakthrough time calculated by Equation 2-12 was 444 minutes, which had a similar value with a 6% relative error towards the experimental value. As shown, Equation 2-12 gives a reliable tool to describe the breakthrough of N10G20. For N20G20, the theoretical 50% breakthrough time calculated by Equation 2-12 was 1616 min. This value could not be experimentally confirmed since the breakthrough curve was incomplete, but 1616 minutes of N20G20 greatly exceeded the possible 50% breakthrough time. If sampling at 10 ppm SO\textsubscript{2} for 1616 min, the incoming SO\textsubscript{2} amount would be 42 mg, which was much larger than \(S_T\) of N20G20, 24.98 mg shown in Table 3-1. Therefore, without a complete breakthrough curve, using Equation 2-12 to describe the breakthrough is significantly inaccurate. When the experimental breakthrough is very incomplete, Equation 2-13 may be more reliable to directly predict the breakthrough for the filter with high Na\textsubscript{2}CO\textsubscript{3} utilization, i.e., \(S_T \approx S_E\).

In dry conditions, as shown in Figure 3-7, good agreement between the theoretical 50% breakthrough time calculated by Equation 2-12, 453 minutes and 467 minutes for N10G20 and N20G20, and the experimental 50% breakthrough time, was about 460 minutes for both tested filters. As illustrated, Equation 2-12 works well for both N10G20 and N20G20 under dry condition. Due to the low ambient RH and the less amount of absorbed water, the breakthrough curve shifted towards left for both tested filters, indicating that the Na\textsubscript{2}CO\textsubscript{3} utilization was lower than under medium RH condition. Therefore, in the case of \(S_T > S_E\), Equation 2-13 is not suitable, but Equation 2-12 can still give a good prediction of the breakthrough.
In conclusion, when the coated glycerol is insufficient or ambient RH is low to bring about the scant amount of absorbed water on the tested filter (i.e., Na ion transport is low), the Na$_2$CO$_3$ is partially available to fix the incoming SO$_2$ (i.e., $S_T > S_E$), and accordingly the simplified model, Equation 2-13 is not suitable. Equation 2-13 only works for an impregnated filter which has a relatively high Na$_2$CO$_3$ utilization rate, i.e., Na$_2$CO$_3$ is dissolved in dilute solution and the exhausted surface ion can easily diffuse into deeper layers of the mixture. On the other hand, Equation 2-12 gives a relatively good description of the breakthrough behavior, unless the filter cannot hold sufficient water and the RH is like the performance in describing N2.5 and G2.

![Graph showing kinetic model fitting for G20, N10G20 and N20G20, RH = 25% and 45%, SO$_2$ = 10 ppm, Temperature = 74 °F, 8 hours sampling time](image)

From Figure 3-7, the intercept of the linear fitting is controlled by the coated Na$_2$CO$_3$ amount, which is directly related to the SO$_2$ sorption capacity. In the same working condition and coated glycerol amount, when coated with more Na$_2$CO$_3$, the
intercept tends to be bigger and the curve will become more flatten, which means the later 50% breakthrough. Furthermore, the slope of the fitting represents the ambient RH condition and the coated glycerol amount, both being strongly related to the utilization and liquid phase mass transfer rate of Na$_2$CO$_3$. Within the same RH condition, the higher ratio of coated glycerol and Na$_2$CO$_3$ amount indicates lower Na$_2$CO$_3$ concentration in the mixture, which in turn increases the liquid phase mass transfer rate, generating a higher slope as shown in the comparison of the purple, black and red line.

The experimental data and the model predicted curve are compared in Figure 3-8. Except N20G20 at 45% RH condition, good agreement was observed for both modified protocol in dry and medium RH condition, demonstrating that the model is a useful tool to describe the breakthrough of the filter treated by modified protocol.

Figure 3-8. The comparison between the experimental breakthrough and the model predicted breakthrough for (a) N10G20 under medium RH condition and (b) N10G20 and N20G20 under dry RH condition
Figure 3-8. Continued
CHAPTER 5
SUMMARY AND CONCLUSIONS

To eliminate the shortage of $S_E$ in N2.5, G2, G10, and G20 for 200-minute sampling volume and 8-hour sampling, coating more Na$_2$CO$_3$ onto the filter is preferred. In Na-ion concentrated mixture, the ion cage effect has a strongly negative influence on the transport of the exhausted Na ion in Na concentrated GWN mixture, resulting in the 50% breakthrough of the N2.5 and G2 happening earlier. Coating more glycerol helps to increase the amount of absorbed water moisture. Accordingly, the increased GWN mixture amount in G10 and G20 in turn decreased the Na ion concentration in the GWN mixture, freeing the Na ion from the ion cage, strengthening the liquid phase mass transfer rate. In other words, coated Na$_2$CO$_3$ is better utilized by the more active ion in the mixture.

The proposed kinetic model has better predictability for G10 and G20 than for N2.5 and G2, which had less coated glycerol. The filters treated by the modified protocol, N10G20 and N20G20, performed well under medium RH condition (RH = 45%). N20G20 had the best performance as its breakthrough did not exceed 5% at the end of the 8-hour test, demonstrating the reliability and feasibility of the N20G20 protocol. At 25% RH condition, the 5% breakthrough was reached much earlier for both N10G20 and N20G20 than under 45% RH, indicating that the proposed protocol needs to be further modified to face the tougher low RH sampling condition. The model predicts well the 50% breakthrough time of both modified protocol treated filters under both dry and medium RH condition, while the simplified model only works when ambient RH is high, and the Na$_2$CO$_3$ utilization of the tested filter is high, i.e., $S_T \approx S_E$. It does not
perform well under low RH condition when ion transport is weak and Na$_2$CO$_3$ cannot be fully utilized.
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BIOGRAPHICAL SKETCH

Chufan Zhou was born in Zhengzhou, Henan, China. He graduated with a master’s degree in summer 2017 from the Department of Environmental Engineering Sciences, University of Florida, USA. He joined Dr. Chang-Yu Wu’s aerosol research group from fall 2015 after he was admitted by University of Florida. During the years of the study and research, he participated several research projects, such as development of a thoracic personal sampler for co-sampling gas and aerosol contaminant and feasibility testing cellulose filter for sampling sulfuric acid mist, which achieved the winner of the poster competition at the 35th AAAR annual conference. He was also a 2-month visiting scholar at Texas A&M University at Qatar in Dr. Bing Guo’s research group and conducting the study of dust motion on the Electronic Dynamic Shield by high speed camera and image processing.