

1994 NASA/ASEE SUMMER FACULTY FELLOWSHIP PROGRAM 111 760

JOHN F. KENNEDY SPACE CENTER  
UNIVERSITY OF CENTRAL FLORIDA

59-25  
33969  
P. 28

INVESTIGATION OF NEW HYPERGOL SCRUBBER TECHNOLOGY

PREPARED BY:	Dr. Barbara H. Glasscock
ACADEMIC RANK:	Associate Professor
UNIVERSITY AND DEPARTMENT:	California State Polytechnic University, Pomona Chemical and Materials Engineering
NASA/KSC	
DIVISION:	Materials Science
BRANCH:	Materials and Chemical Analysis
NASA COLLEAGUE:	Gale Allen
DATE:	August 19, 1994
CONTRACT NUMBER:	University of Central Florida NASA-NGT-60002 Supplement: 17



### ACKNOWLEDGMENTS

I would like to express my sincere appreciation to the Office of Educational Affairs, NASA Headquarters, Washington, D.C. and the American Society for Engineering Education (ASEE) for their sponsorship of the 1994 NASA/ASEE Summer Faculty Fellowship Program at Kennedy Space Center. My summer research experience at KSC has been stimulating and rewarding and I know that I will carry with me to my home university many of the new ideas I have gained here.

The program was well organized and ran smoothly, thanks to the administrative efforts of the folks at the University of Central Florida, in particular Dr. Loren A. Anderson and Ms. Kari Stiles.

A special thanks to Gale Allen, my NASA Colleague, for suggesting this work as a summer project and for her enthusiasm along the way. I am grateful to Lee Underhill and Orlando Melendez, both of the Chemical Analysis Section, for their collaboration on several aspects of the project, especially to Orlando for his work on Stability Study #2. I would like to acknowledge all of the members of the Chemical Analysis Section and thank them for their stimulating discussions in the lab, the lunchroom, and over a computer screen.

**ABSTRACT**

The ultimate goal of this work is to minimize the liquid waste generated from the scrubbing of hypergolic vent gases. In particular, nitrogen tetroxide, a strong oxidizer used in hypergolic propellant systems, is currently scrubbed with a sodium hydroxide solution resulting in a hazardous liquid waste. This study investigated the use of a solution of potassium hydroxide and hydrogen peroxide for the nitrogen tetroxide vent scrubber system. The potassium nitrate formed would be potentially usable as a fertilizer. The hydrogen peroxide is added to convert the potassium nitrite that is formed into more potassium nitrate. Small scale laboratory tests were conducted to establish the stability of hydrogen peroxide in the proposed scrubbing solution and to evaluate the effectiveness of hydrogen peroxide in converting nitrite to nitrate.

## SUMMARY

Small scale laboratory tests were conducted to evaluate the stability of hydrogen peroxide ( $H_2O_2$ ) in alkaline mixtures, some of which included nitrate and nitrite salts, and which were adjusted to different pH levels. These mixtures simulated the proposed scrubber liquor for removing nitrogen tetroxide ( $N_2O_4$ ) from the scrubbing of hypergolic vent gases. Currently the  $N_2O_4$  vent gas is scrubbed with a sodium hydroxide (NaOH) solution resulting in a hazardous liquid waste. This study investigated the use of a solution of potassium hydroxide (KOH) and hydrogen peroxide ( $H_2O_2$ ) for the nitrogen tetroxide vent scrubber system with a goal of producing a solution of potassium nitrate ( $KNO_3$ ) that could be used as a fertilizer.

A series of three different stability studies were conducted. In the first study a  $2^4$  factorial experimental design was used to compare the effect of four variables (pH, nitrite concentration, nitrate concentration, and sodium ( $Na^+$ ) or potassium ( $K^+$ ) as the cation) on the response variable, % $H_2O_2$  decomposed. It was found that the most significant effect was the pH; an average of 65% of the  $H_2O_2$  disappeared at pH = 9 and only 4% disappeared at pH = 6 after 68 hours at room temperature. The potassium salts may have a slight stabilizing effect over the sodium salts. It also appears that when there was nitrite present in the original solution, a significant portion of the nitrite reacted with the hydrogen peroxide to yield nitrate.

The second stability study considered the effect of pH on the stability of  $H_2O_2$  in the absence of any salts. The decomposition rate of  $H_2O_2$  at pH = 9 and pH = 13 was comparable, but surprisingly pH = 11 exhibited a higher decomposition rate. Thus the decomposition rate as a function of pH appears to go through a maximum at a pH around 11. The decomposition rate was very high initially and then leveled off with time when expressed as %decomposed/hour.

The third stability study was a  $2^3$  factorial experimental design to compare the effect of three variables (pH,  $H_2O_2$  concentration,  $Na^+$  or  $K^+$ ), with levels of nitrate and nitrite held constant, on the response variable, % $H_2O_2$  decomposed. It again appears that some of the nitrite is converted to nitrate.

In addition, preparations were made to conduct small scale scrubbing experiments to measure the efficiency of the solutions on removing  $N_2O_4$  from gaseous nitrogen, but time limitations prevented the completion of this part of the work.

In conclusion, a mixture of potassium hydroxide and hydrogen peroxide shows promise as a scrubbing liquor for  $N_2O_4$  because of its ability to convert the nitrite in solution to nitrate, thus producing a solution that may be useful as a feed stream to a fertilizer manufacturer.

## TABLE OF CONTENTS

<b>ACKNOWLEDGEMENTS .....</b>	<b>2</b>
<b>ABSTRACT .....</b>	<b>3</b>
<b>SUMMARY .....</b>	<b>4</b>
<b>LIST OF FIGURES.....</b>	<b>6</b>
<b>LIST OF TABLES .....</b>	<b>7</b>
<b>ABBREVIATIONS .....</b>	<b>8</b>
<b>1. INTRODUCTION.....</b>	<b>9</b>
1.1 BACKGROUND .....	9
1.2 SCRUBBER SYSTEM.....	9
1.3 CHEMISTRY .....	10
<b>2. PROPOSED SCRUBBER LIQUOR.....</b>	<b>12</b>
2.1 COMPOSITION.....	12
2.2 CONCERNS .....	12
2.2.1 PRESENCE OF NITRITES.....	12
2.2.2 STABILITY OF HYDROGEN PEROXIDE .....	12
2.2.3 EFFICIENCY OF SCRUBBER LIQUOR .....	12
2.2.4 SOLUBILITY OF POTASSIUM NITRATE.....	13
2.2.5 CAPACITY OF SCRUBBER LIQUOR.....	13
<b>3. MATERIALS AND METHODS .....</b>	<b>15</b>
3.1 STABILITY STUDIES .....	15
3.1.1 STABILITY STUDY #1 .....	15
3.1.2 STABILITY STUDY #2 .....	16
3.1.3 STABILITY STUDY #3 .....	16
3.2 SCRUBBER EFFICIENCY EXPERIMENTS .....	17
<b>4. RESULTS AND DISCUSSION.....</b>	<b>18</b>
4.1 STABILITY STUDY #1.....	18
4.2 STABILITY STUDY #2.....	20
4.3 STABILITY STUDY #3.....	23
<b>5. CONCLUSIONS.....</b>	<b>26</b>
<b>APPENDIX A. SEPARATION OF THE H<sub>2</sub>O<sub>2</sub> AND NO<sub>2</sub><sup>-</sup> INTERACTIONS WITH   KMNO<sub>4</sub> .....</b>	<b>27</b>
<b>REFERENCES.....</b>	<b>28</b>

## LIST OF FIGURES

FIGURE 1. VENT GAS SCRUBBER SYSTEM .....	10
FIGURE 2. SCRUBBER EFFICIENCY EXPERIMENTS.....	17
FIGURE 3. TABULAR DISPLAY OF STABILITY STUDY #1.....	19
FIGURE 4. RESPONSE PLOT FOR STABILITY STUDY #1 .....	20
FIGURE 5. DISTRIBUTION OF H <sub>2</sub> O <sub>2</sub> AFTER 68 HOURS IN STABILITY STUDY #1 ...	20
FIGURE 6. STABILITY STUDY #2 - EFFECT OF PH ON DECOMPOSITION RATE OF H <sub>2</sub> O <sub>2</sub> .....	21
FIGURE 7. STABILITY STUDY #2 - DECOMPOSITION RATE VS. TIME .....	22
FIGURE 8. TABULAR DISPLAY OF STABILITY STUDY #3.....	24
FIGURE 9. RESPONSE PLOT FOR STABILITY STUDY #3 .....	25
FIGURE 10. DISTRIBUTION OF H <sub>2</sub> O <sub>2</sub> AFTER 68 HOURS IN STABILITY STUDY #3. ....	25

## LIST OF TABLES

TABLE 1. SOLUBILITY OF $\text{NaNO}_3$ AND $\text{KNO}_3$ IN WATER AT $25^\circ\text{C}$ .....	13
TABLE 2. MAXIMUM CAPACITY OF SCRUBBING LIQUORS.....	14
TABLE 3. STABILITY STUDY #1 - $2^4$ DESIGN MATRIX .....	15
TABLE 4. STABILITY STUDY #3 - $2^3$ DESIGN MATRIX .....	16
TABLE 5. STABILITY STUDY #1 RESULTS .....	19
TABLE 6. STABILITY STUDY #2 RESULTS .....	21
TABLE 7. STABILITY STUDY #3 RESULTS .....	24

## ABBREVIATIONS

cc	cubic centimeter
cfm	cubic feet per minute
g	grams
gpm	gallons per minute
H <sub>2</sub> O	water
H <sub>2</sub> O <sub>2</sub>	hydrogen peroxide
K <sup>+</sup>	potassium ion
KMnO <sub>4</sub>	potassium permanganate
KNO <sub>2</sub>	potassium nitrite
KNO <sub>3</sub>	potassium nitrate
KOH	potassium hydroxide
mg	milligram
ml	milliliter
MMH	monomethyl-hydrazine
N	Normality (equivalents/liter)
NO	nitric oxide
NO <sub>2</sub>	nitrogen dioxide
NO <sub>2</sub> <sup>-</sup>	nitrite ion
NO <sub>3</sub> <sup>-</sup>	nitrate ion
N <sub>2</sub> O <sub>3</sub>	dinitrogen trioxide
N <sub>2</sub> O <sub>4</sub>	nitrogen tetroxide (dinitrogen tetroxide)
Na <sup>+</sup>	sodium ion
NaNO <sub>2</sub>	sodium nitrite
NaNO <sub>3</sub>	sodium nitrate
NaOH	sodium hydroxide
ppm	parts per million
wt%	weight percent
[ ]	concentration



## 1. INTRODUCTION

### 1.1 BACKGROUND

Hypergolic fuels are used at Kennedy Space Center (KSC) and Cape Canaveral Air Force Station (CCAFS) for propulsion in Space Shuttle Orbiters, satellites, etc. During on-ground servicing involving hypergols, such as transfer between storage tank and orbiter, the excess hypergols are purged and flushed from tanks and transfer lines using gaseous nitrogen. There is no storage capability for this vent gas mixture of nitrogen and hypergol and it must be scrubbed, i.e. the hypergol removed, before being released to the atmosphere. This scrubbing is accomplished by bubbling the gaseous stream through a liquid that will react with the hypergol to convert it into a water soluble species, thus removing it from the gas stream. The liquid waste stream can then be disposed.

The two primary hypergols currently used in the space program are monomethylhydrazine (MMH) as the fuel and nitrogen tetroxide ( $N_2O_4$ ) as the oxidizer. The MMH vent gas is scrubbed with a citric acid solution and the  $N_2O_4$  vent gas is scrubbed with a sodium hydroxide (NaOH) solution. The spent scrubber solution for the  $N_2O_4$  vent gas constitutes the second largest hazardous waste stream at the Kennedy Space Center and is the subject of this study.

### 1.2 SCRUBBER SYSTEM

The currently used scrubber solution for the  $N_2O_4$  vent gas is 25 wt.% NaOH. Because there is no storage capability for the vent gas, a scrubber system is required at each location where the  $N_2O_4$  gas is handled and as a result, there are at least ten separate scrubbing systems in the KSC/CCAFS complex. Figure 1 shows the schematic for one such system.

The scrubber liquor is held in a 750 gallon tank and is pumped at a rate of 80 to 200 gpm to a distributor in the piping which divides the flow equally to the tops of four gas scrubbing columns. The liquor flows in parallel, downward through the columns and is returned to the tank. The  $N_2O_4$  vent gas flows in series through the four gas scrubbing columns, entering from the bottom and exiting the top of each column. The vent gas only passes through the gas scrubbing train once, but the scrubbing liquor is recirculated until the scrubbing capacity has been determined to be sufficiently exhausted. The gas scrubbing columns are packed with polypropylene Pall rings to enhance the contact between the gas and liquid.

The concentration of  $N_2O_4$  in the vent gas and the flow rate before entering the scrubbing system can vary widely depending on the conditions and the operation that generated the vent gas. Typically the vent gas associated with loading  $N_2O_4$  on the shuttle orbiter when it is on the launch pad results in high levels of  $N_2O_4$  and high volumes of vent gas because of the large quantity of  $N_2O_4$  being handled. Concentrations of  $N_2O_4$  in the vent gas can range from 100,000 ppm to 900,000 ppm at flow rates of 10 to 400 cfm.

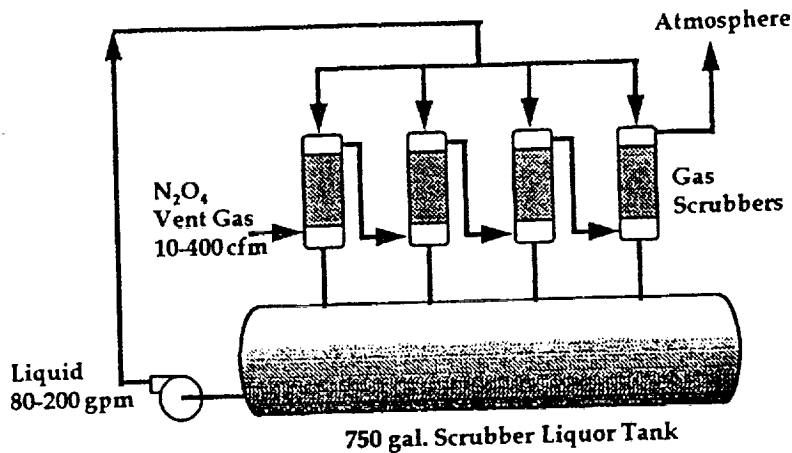


Figure 1. Vent Gas Scrubber System.

The efficiency of the vent gas scrubber system can be calculated as shown in equation (1).

$$\text{Efficiency} = 100\% \times ([\text{N}_2\text{O}_4]_{\text{in}} - [\text{N}_2\text{O}_4]_{\text{out}}) / [\text{N}_2\text{O}_4]_{\text{in}} \quad (1)$$

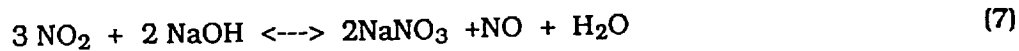
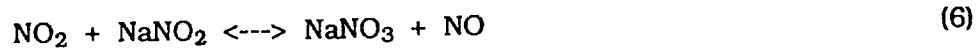
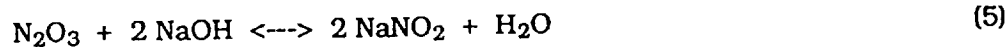
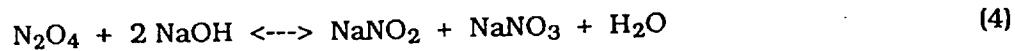
where  $[\text{N}_2\text{O}_4]_{\text{in}}$  represents the concentration of  $\text{N}_2\text{O}_4$  in the feed gas and  $[\text{N}_2\text{O}_4]_{\text{out}}$  represents the concentration of  $\text{N}_2\text{O}_4$  in the exit gas released to the atmosphere.

### 1.3 CHEMISTRY

The reaction chemistry of nitrogen tetroxide gas reacting with aqueous solutions of alkali is extremely complex when one considers all of  $\text{NO}_x$  species that may be present in the gas phase and their varying solubilities and reactivities in the liquid phase. Nitrogen tetroxide ( $\text{N}_2\text{O}_4$ ) is a dimer of nitrogen dioxide ( $\text{NO}_2$ ) and both exist in equilibrium, the amounts determined by the temperature, pressure, and concentration of the system. Nitric oxide ( $\text{NO}$ ) will also be present as a byproduct of the liquid phase reactions. Some of the more important chemical reactions in the gas phase and in the liquid phase for the current  $\text{NaOH}$  system are shown below, although others are known to occur also.

#### Gas Phase Reactions



Liquid Phase Reactions

Reaction #4 is the primary liquid phase reaction and if it were the only reaction occurring, equal moles of  $\text{NaNO}_2$  and  $\text{NaNO}_3$  would be formed. However because of the other liquid phase reactions occurring, the moles of  $\text{NaNO}_3$  is always greater than the moles of  $\text{NaNO}_2$ .

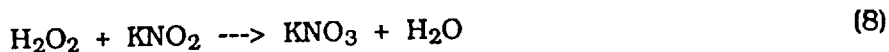
The reactions for a solution of  $\text{KOH}$  instead of  $\text{NaOH}$  are expected to be similar to the above reaction for  $\text{NaOH}$ , however the rates and equilibrium concentration may be different.

## 2. PROPOSED SCRUBBER LIQUOR

### 2.1 COMPOSITION

The proposed scrubber solution would utilize potassium hydroxide (KOH) rather than sodium hydroxide (NaOH) because the potassium nitrate ( $\text{KNO}_3$ ) produced is more attractive to the fertilizer industry than the corresponding sodium salt.

In addition, hydrogen peroxide will be explored as an additive in the hopes of converting the nitrites to nitrates according to the following reaction.



Thus, the new scrubbing liquor under study would contain 10 to 25 wt.% KOH and 0 to 10 wt.%  $\text{H}_2\text{O}_2$ .

### 2.2 CONCERNS

As promising as this proposed scrubbing liquor appears, there are a number of concerns that will need to be addressed before it could be adopted.

#### 2.2.1 PRESENCE OF NITRITES

In order for the spent scrubbing liquor to be successfully used in the fertilizer industry, it needs to be essentially free of nitrites and contain only nitrates. As shown previously (equations 2 to 7) it is expected that a mixture of nitrite and nitrate will be produced. Molar ratios of  $\text{NaNO}_3 / \text{NaNO}_2$  in the range of 2 to 16 are typical in the absence of  $\text{H}_2\text{O}_2$ . It is hoped that the hydrogen peroxide can drive this ratio even higher. This will be a key evaluation criteria for the proposed scrubbing liquor.

#### 2.2.2 STABILITY OF HYDROGEN PEROXIDE

Hydrogen peroxide undergoes homogeneous decomposition in the presence of catalysts and alkali as shown in the following reaction.



Solutions of  $\text{H}_2\text{O}_2$  are most stable at a pH of about 4.0 to 5.0. Thus, it will be of major concern whether the  $\text{H}_2\text{O}_2$  will last long enough in a basic solution to react with the nitrites.

The stability usually increases with increasing concentration of  $\text{H}_2\text{O}_2$  and decreases with temperature as would be expected.

#### 2.2.3 EFFICIENCY OF SCRUBBER LIQUOR

As previously discussed, the efficiency of the vent gas scrubber system is calculated as was shown in equation (1).

$$\text{Efficiency} = 100\% \times ([N_2O_4]_{in} - [N_2O_4]_{out}) / [N_2O_4]_{in} \quad (1)$$

Any scrubber liquor must be able to meet the requirements for reducing the emissions of  $N_2O_4$ .

#### 2.2.4 SOLUBILITY OF POTASSIUM NITRATE

One possible constraint of the potassium system that may not be readily apparent is the solubility limit of potassium nitrate. The solubilities of  $NaNO_3$  and  $KNO_3$  in water at  $25^\circ C$  are shown in the table below in the standard units of g./100 ml. saturated solution, and using the densities of the solutions, have been converted to wt%.

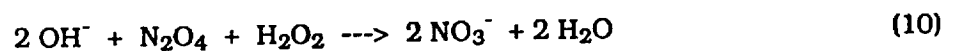
Table 1. Solubility of  $NaNO_3$  and  $KNO_3$  in Water at  $25^\circ C$ .

at $25^\circ C$	Solubility, g./100 ml	Density, g./cc	Solubility, wt%
$NaNO_3$	92.1	1.5	61.4
$KNO_3$	27.7	1.16	23.8

It can be seen that  $NaNO_3$  is almost three times more soluble than  $KNO_3$  in water. It is not known what the effect of the other species in the scrubbing system might have on solubility or if concentrations approaching the solubility limits would be reached. Nonetheless, this concern warrants further consideration as it would be extremely undesirable to have solids precipitating in the scrubbers or piping.

#### 2.2.5 CAPACITY OF SCRUBBER LIQUOR

The capacity of the scrubbing liquor can be described as how much  $N_2O_4$  could be absorbed by one tank batch of liquor. Assuming the limiting factor is the solubility of the nitrate and that we have been successful in converting all of the nitrite to nitrate, then one can calculate how much hydroxide would have reacted to reach that limit as shown in equation (10). In addition, one can calculate how much  $N_2O_4$  would have been absorbed or reacted to reach that limit. Using the solubilities presented in the previous section and assuming a batch size of 650 gallons, the numbers shown in Table 2 are generated.



As shown in Table 2, the  $NaOH$  solution can theoretically hold over three times as much  $N_2O_4$  as the  $KOH$  solution, due to the solubility differences in their nitrate salts and the difference in molecular weights. It is interesting to note that the solubility limit for the sodium system would be reached if 28 wt%  $NaOH$  reacted to form  $NaNO_3$ , which is greater than the 25 wt%  $NaOH$  currently used as a scrubbing liquor. Thus all of the  $NaOH$  in the current solution of 25 wt% could form  $NaNO_3$  with no precipitate forming. In actuality not all of the  $NaOH$  is consumed and currently the more soluble  $NaNO_2$  is also formed so the system is far from the solubility limit. However, the proposed potassium system could operate near the solubility limit for  $KNO_3$ , limiting the overall capacity.

*Table 2. Maximum capacity of scrubbing liquors.*

at 25°C	Wt% hydroxide reacting to reach NO <sub>3</sub> solubility limit	Maximum capacity kg. N <sub>2</sub> O <sub>4</sub> absorbed at solubility limit
NaOH	28 wt% NaOH	940 kg N <sub>2</sub> O <sub>4</sub>
KOH	13 wt% KOH	310 kg N <sub>2</sub> O <sub>4</sub>

This concern will be somewhat mitigated if the spent scrubbing liquor containing KNO<sub>3</sub> can be used as a fertilizer rather than being classified as a hazardous waste. So that even if more scrubbing liquor must be used, this increased cost will be partially offset by not incurring a disposal fee and perhaps by income from the fertilizer company.

### 3. MATERIALS AND METHODS

#### 3.1 STABILITY STUDIES

The goal of the stability studies was to measure the stability or the rate of decomposition of hydrogen peroxide as a function of time, at different pH levels and with different levels of salts present. The nitrate and nitrite salts serve to simulate a partially used scrubbing liquor.

##### 3.1.1 STABILITY STUDY #1

In the first study a  $2^4$  factorial experimental design was used to compare the effect of four variables (pH,  $[\text{NO}_2]$ ,  $[\text{NO}_3]$ ,  $\text{Na}^+$  or  $\text{K}^+$ ), each at 2 levels, on the response variable, % $\text{H}_2\text{O}_2$  decomposed. The design matrix for this study is shown below in Table 3.

Table 3. Stability Study #1 -  $2^4$  Design Matrix.

Test #	Cation - = $\text{Na}^+$ + = $\text{K}^+$	pH - = 6 + = 9	$\text{NaNO}_2$ or $\text{KNO}_2$ - = 0 wt% + = 5 wt%	$\text{NaNO}_3$ or $\text{KNO}_3$ - = 0 wt% + = 5 wt%
1	-	-	-	-
2	-	-	-	+
3	-	-	+	-
4	-	-	+	+
5	-	+	-	-
6	-	+	-	+
7	-	+	+	-
8	-	+	+	+
9	+	-	-	-
10	+	-	-	+
11	+	-	+	-
12	+	-	+	+
13	+	+	-	-
14	+	+	-	+
15	+	+	+	-
16	+	+	+	+

To prepare the solutions, first the appropriate quantities of nitrite and nitrate salts were weighed on a Metler balance and then added to a 250ml Erlenmeyer flask. Next a small amount of deionized water was added to dissolve the salts. Then 9 ml of nominally 50 wt%  $\text{H}_2\text{O}_2$  stock solution was added to the flask. The  $\text{H}_2\text{O}_2$  stock solution had a density of 1.1935 g/ml and was determined to contain 48.3 wt%  $\text{H}_2\text{O}_2$  by standard titration with 0.1N  $\text{KMnO}_4$ . Thus 5.173 g. of  $\text{H}_2\text{O}_2$  was added to each flask. The pH of each solution was adjusted by the addition of  $\text{NaOH}$  or  $\text{KOH}$  solutions as appropriate and/or addition of  $\text{H}_2\text{SO}_4$  solution. Simultaneously while achieving the desired pH, the final total net weight was made to total 100 g. The pH was measured with a glass electrode pH probe,

calibrated at pH = 7. The starting weights of all of the solutions were noted and aluminum foil was placed loosely on the top of each flask to keep out contaminants and minimize evaporative water losses, yet allow the O<sub>2</sub> from the decomposition of the H<sub>2</sub>O<sub>2</sub> to escape. A "blank" was also prepared that contained only 100 g. of water, and capped in the same manner, to measure the weight loss due to water evaporation.

After 68 hours the flasks were all weighed again, the weight loss corrected for the water evaporation, and the remaining weight loss being due to O<sub>2</sub> escape from decomposition of H<sub>2</sub>O<sub>2</sub>. Using stoichiometry, the quantity of H<sub>2</sub>O<sub>2</sub> that decomposed can be calculated from the O<sub>2</sub> lost as was shown in equation (9). Samples were taken from each flask and titrated with 0.1N KMnO<sub>4</sub> to determine the quantity of H<sub>2</sub>O<sub>2</sub> remaining. The H<sub>2</sub>O<sub>2</sub> that is unaccounted for by these methods is postulated to have reacted with the nitrite as expressed in equation (11).

$$[\text{H}_2\text{O}_2]_{\text{reacted}} = [\text{H}_2\text{O}_2]_{\text{initial}} - [\text{H}_2\text{O}_2]_{\text{decomposed}} - [\text{H}_2\text{O}_2]_{\text{remaining}} \quad (11)$$

The one difficulty encountered in this method was the discovery that the KMnO<sub>4</sub> used in the titration analysis for H<sub>2</sub>O<sub>2</sub> also reacted with any nitrites that were still present. This was corrected for mathematically as explained in the appendix.

### 3.1.2 STABILITY STUDY #2

The second stability study considered the effect of pH on the stability of H<sub>2</sub>O<sub>2</sub> in the absence of any salts. Solutions were prepared similarly to Study #1, except that no salts were added. Erlenmeyer flasks of 125ml capacity were used to prepare solutions totaling 30 g. in weights. To each flask was added 3ml of the stock H<sub>2</sub>O<sub>2</sub> solution, netting 1.73g H<sub>2</sub>O<sub>2</sub> in each solution. The pH was then adjusted with KOH solutions or pellets. For measuring pH levels at 11 and 13, the probe was calibrated at pH = 10. The flasks were loosely capped with aluminum foil and samples withdrawn at different time intervals for titration with 0.1N KMnO<sub>4</sub> for determination of H<sub>2</sub>O<sub>2</sub> remaining.

### 3.1.3 STABILITY STUDY #3

The third stability study was a 2<sup>3</sup> factorial experimental design to compare the effect of three variables (pH, [H<sub>2</sub>O<sub>2</sub>], Na<sup>+</sup> or K<sup>+</sup>), with levels of nitrate and nitrite held constant, on the response variable, %H<sub>2</sub>O<sub>2</sub> decomposed. The design matrix for this study is shown below in Table 4.

Table 4. Stability Study #3 - 2<sup>3</sup> Design Matrix.

Test #	Cation - = Na <sup>+</sup> + = K <sup>+</sup>	pH - = 9 + = 11	H <sub>2</sub> O <sub>2</sub> - = 2.3 wt% + = 5.2 wt%
1	-	-	-
2	-	-	+
3	-	+	-
4	-	+	+
5	+	-	-
6	+	-	+
7	+	+	-
8	+	+	+



The quantity of nitrate and nitrite salts added was that necessary to achieve (40 mg ion)/ml, which roughly corresponds to 5 wt.% salt. It was felt that a better comparison could be achieved if the ions were present in equal concentrations rather than the salts being in equal concentration. PH levels of 9 and 11 were chosen for this study. Two levels of  $H_2O_2$  were used as indicated in Table 4, the lower value being approximately just enough to react with the nitrite present. Solutions were prepared and handled in a manner similar to the procedure described for Stability Study #1.

### 3.2 SCRUBBER EFFICIENCY EXPERIMENTS

In addition, preparations were made to conduct small scale scrubbing experiments to measure the efficiency of the solutions on removing  $N_2O_4$  from gaseous nitrogen. A gas mixture of  $N_2$  and  $N_2O_4$  flowed from a pressurized cylinder, with the flow controlled by a needle valve and the flowrate monitored by a rotameter. Next the gas passed through the scrubbing liquor contained in a midget impinger. After the impinger it was possible to capture a sample of the exit gas in glass sampler for later analysis. A simplified diagram of the equipment is shown in Figure 2.

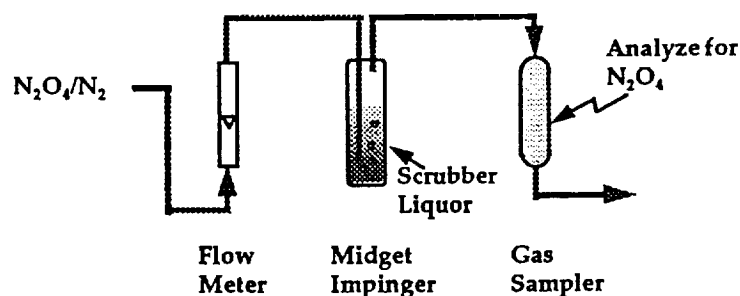


Figure 2. Scrubber Efficiency Experiments

This arrangement was to allow comparison of the efficiency of different scrubbing liquors and at different gas flow rates, but time limitations prevented the completion of this part of the work.

## 4. RESULTS AND DISCUSSION

### 4.1 STABILITY STUDY #1

In the first study a  $2^4$  factorial experimental design was used to compare the effect of four variables (pH,  $[\text{NO}_2]$ ,  $[\text{NO}_3]$ ,  $\text{Na}^+$  or  $\text{K}^+$ ) on the response variable, % $\text{H}_2\text{O}_2$  decomposed. The design matrix was presented earlier in Table 3 and the data and overall results are presented in Table 5. The weight lost was measured after 68 hours at room temperature.

The fraction  $\text{H}_2\text{O}_2$  decomposed was determined from the weight loss, attributable to the  $\text{O}_2$  escaping and was assumed to be more accurate than the fraction  $\text{H}_2\text{O}_2$  remaining as determined by titration with 0.1N  $\text{KMnO}_4$ . Thus, for example, in Run #1 originally there was 5.17 g.  $\text{H}_2\text{O}_2$  with 0 g.  $\text{H}_2\text{O}_2$  lost as determined by weight loss, therefore it is assumed that 5.17 g.  $\text{H}_2\text{O}_2$  remain, even though the titration gave a value of 5.02 g.  $\text{H}_2\text{O}_2$  remaining.

Figure 3 contains a tabular display of the response factor for Stability Study #1, expressed as percent  $\text{H}_2\text{O}_2$  decomposed. Each cell in the table corresponds to a specific combination of the factors and aids in the analysis of the data. The effect of various factors can be compared by comparing different columns or rows. For example the percent decomposed is significantly higher at pH 9 as shown in the two rightmost columns. An average of 65% of the  $\text{H}_2\text{O}_2$  disappeared at pH = 9 and only 4% disappeared at pH = 6.

A response plot shown in Figure 4 illustrates the effect of pH on the percent  $\text{H}_2\text{O}_2$  decomposed. Each data point in the response plots represents an average response from four runs, obtained by holding two of the factors constant. For example for  $\text{Na}^+$  as the cation and at a pH = 6, runs #1, 2, 3, and 4 can be averaged together. The first response plot in Figure 4 suggests that potassium salts may have a slight stabilizing effect over the sodium salts, i.e. less decomposed.

The distribution of the fate of the  $\text{H}_2\text{O}_2$  is shown graphically in Figure 5. The values shown for each set of conditions is the average of the four runs which satisfy those conditions, similar to the treatment for the response plot. It appears that when there was nitrite present in the original solution, a significant portion of the nitrite reacted with the hydrogen peroxide to yield nitrate.

Table 5. Stability Study #1 Results. Runs 1 to 8 contain sodium salts, Runs 9 to 16 contain potassium salts.

Run #	Orig. NaNO3 or KNO3 g.	Orig. NaNO2 or KNO2 g.	Orig. H2O2 g.	Total weight	pH	Weight lost g. O2	H2O2 decomp. g.	H2O2 remain, wt% (titration)	H2O2 remain, g.	H2O2 rx w/ NO2, g.	Fraction of H2O2 of rx	Fraction of H2O2 decomp	Fraction of H2O2 remain
1	0.00	0.00	5.17	99.9	6.1	0.0	0.00	5.02	5.01		0.00	0.00	1.00
2	5.01	0.00	5.17	99.9	6.0	0.1	0.21	5.11	5.10		0.00	0.04	0.96
3	0.00	5.01	5.17	102.9	6.1	0.3	0.64	2.39	2.45	2.08	0.40	0.12	0.47
4	5.01	5.00	5.17	100.1	6.1	0.1	0.21	2.42	2.42	2.54	0.49	0.04	0.47
5	0.00	0.00	5.17	100.0	9.2	2.1	4.46	0.43	0.42		0.00	0.86	0.14
6	5.01	0.00	5.17	101.3	9.0	1.7	3.61	1.15	1.15		0.00	0.70	0.30
7	0.00	5.02	5.17	100.0	9.0	1.6	3.40	0.27	0.27	1.50	0.29	0.66	0.05
8	5.00	5.00	5.17	100.0	9.0	1.6	3.40	0.16	0.16	1.61	0.31	0.66	0.03
9	0.00	0.00	5.17	101.0	5.9	0.0	0.00	4.94	4.99		0.00	0.00	1.00
10	5.01	0.00	5.17	100.7	5.9	0.2	0.43	4.91	4.93		0.00	0.08	0.92
11	0.00	5.01	5.17	100.1	6.0	0.0	0.00	2.99	2.99	2.18	0.42	0.00	0.58
12	5.00	5.01	5.17	100.0	5.9	0.1	0.21	2.99	2.99	1.97	0.38	0.04	0.58
13	0.00	0.00	5.17	100.0	9.1	1.3	2.76	2.20	2.17		0.00	0.53	0.47
14	5.01	0.00	5.17	101.6	9.1	1.5	3.19	1.89	1.89		0.00	0.62	0.38
15	0.00	5.01	5.17	101.1	9.1	1.4	2.98	0.15	0.15	2.04	0.40	0.58	0.03
16	5.00	5.00	5.17	99.6	9.1	1.4	2.98	0.04	0.04	2.15	0.42	0.58	0.01

		Nitrite		pH			
				6		9	
				Nitrate		Nitrate	
Cation	Na <sup>+</sup>	Nitrite	0%	5%	0%	5%	
					0% <td>0</td> <td>4</td> <td>86</td> <td>70</td>	0	4
		5%	12	4	66	66	
Cation	K <sup>+</sup>	Nitrite	0%	8	53	62	
			5%	0	4	58	58

Figure 3. Tabular Display of Stability Study #1. Response is the percent H<sub>2</sub>O<sub>2</sub> decomposed.

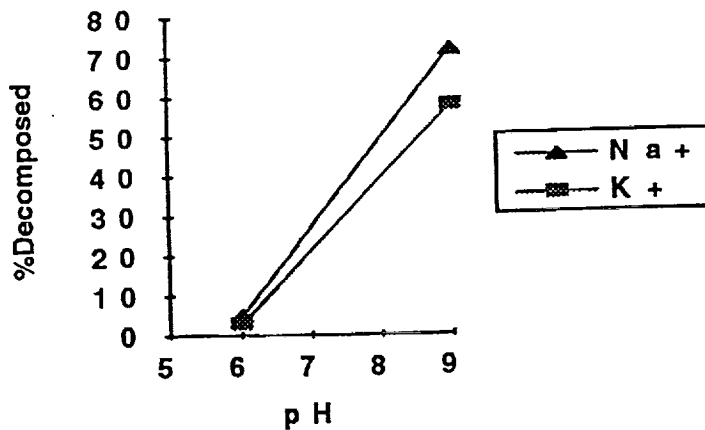


Figure 4. Response Plot for Stability Study #1.

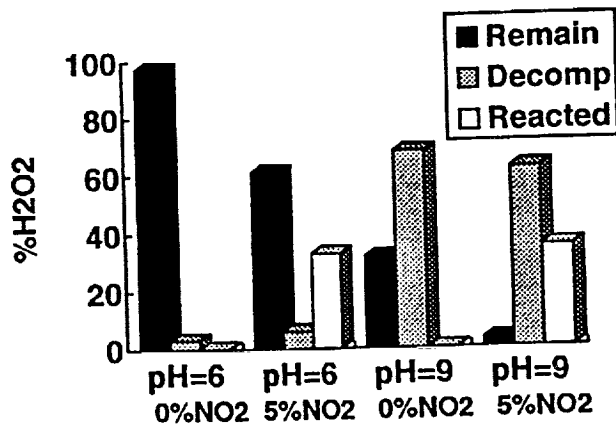


Figure 5. Distribution of H<sub>2</sub>O<sub>2</sub> after 68 hours in Stability Study #1.

#### 4.2 STABILITY STUDY #2

The second stability study considered the effect of pH on the stability of H<sub>2</sub>O<sub>2</sub> in the absence of any salts. Solutions for this study were prepared at two different times, first a set of three solutions at pH = 9, 11, and 13; later a set of six samples were prepared consisting of duplicates at each of the pHs. Samples were withdrawn from the solutions at various times and titrated with KMnO<sub>4</sub> to determine the H<sub>2</sub>O<sub>2</sub> concentration. The starting concentration was assumed to be the calculated concentration based on weighed and pipetted amounts. The rate of decomposition can be calculated as the percent decrease in concentration divided by the elapsed time. This data is presented in Table 6.

Table 6. Stability Study #2 Results.

ph	time	H2O2	rate
	hours	wt%	%dec/h
9	0	5.66	
9	1	3.71	34.45
9	2	3.57	18.46
9	5	3.21	8.66
9	22	2.32	2.68
9	24	2.25	2.51
11	0	5.66	
11	1	1.95	65.55
11	2	1.38	37.81
11	5	1.18	15.83
11	22	0.94	3.79
11	24	0.86	3.53
13	0	5.66	
13	1	3.52	37.81
13	2	3.34	20.49
13	22	2.17	2.80
13	24	2.03	2.67
9.04	0	5.73	
9.04	1	5.22	8.90
9.04	48	2.87	1.04
9.04	72	1.74	0.97
9.24	0	5.73	
9.24	18	2.26	3.36
9.24	48	1.248	1.63
9.24	72	0.47	1.27
10.96	0	5.71	
10.96	1	2.12	62.87
10.96	18	1.08	4.50
10.96	48	0.79	1.80
10.96	72	0.34	1.31
11.09	0	5.75	
11.09	1	2.09	63.65
11.09	18	1.34	4.26
11.09	48	0.86	1.77
12.97	0	5.72	
12.97	18	3.18	2.47
12.97	48	2.39	1.21
12.97	72	1.79	0.95
13.1	0	5.35	
13.1	1	4.5	15.89
13.1	48	2.03	1.29
13.1	72	1.99	0.87

An interesting observation during this work was that when all of the samples at pH = 11 were titrated soon after preparation, over 60% of the H<sub>2</sub>O<sub>2</sub> had already disappeared. In Figure 6 all of the data is plotted as decomposition rate vs. pH. The decomposition rate of H<sub>2</sub>O<sub>2</sub> at pH = 9 and pH = 13 was comparable, but surprisingly pH = 11 exhibited a higher decomposition rate. Thus the decomposition rate as a function of pH appears to go through a maximum at a pH around 11.

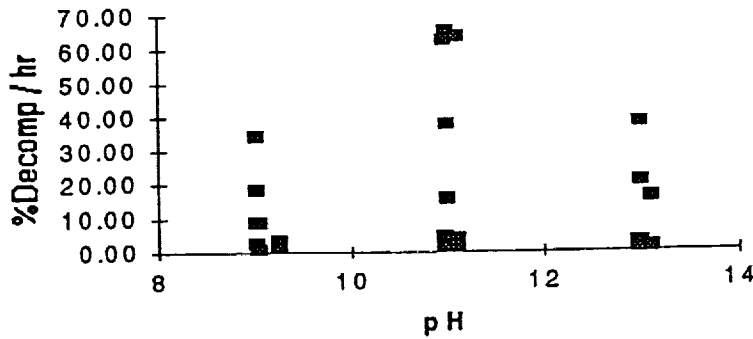


Figure 6. Stability Study #2 - Effect of pH on Decomposition Rate of H<sub>2</sub>O<sub>2</sub>.

The highest values for the decomposition rates at all pH values occurred at the shortest intervals of time. This can be seen better in Figure 7, decomposition rate as a function of time. The decomposition rate was very high initially and then leveled off with time when expressed as %decomposed/hour.

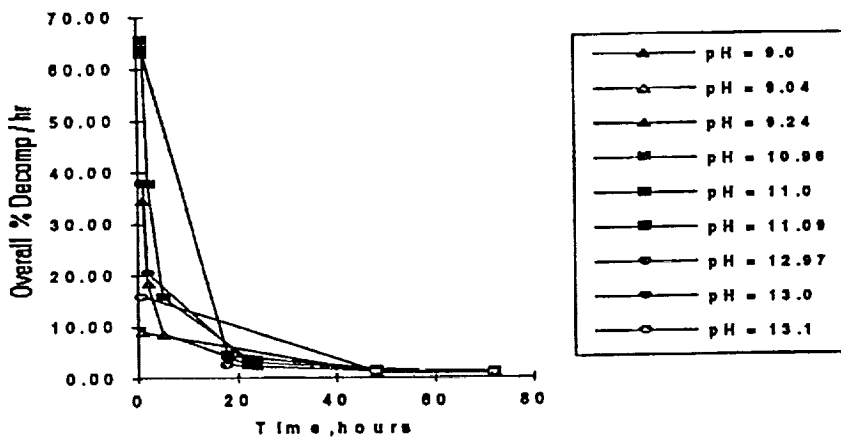


Figure 7. Stability Study #2 - Decomposition Rate vs. Time

### 4.3 STABILITY STUDY #3

The third stability study was a  $2^3$  factorial experimental design to compare the effect of three variables (pH,  $[H_2O_2]$ ,  $Na^+$  or  $K^+$ ), with levels of nitrate and nitrite held constant, on the response variable, % $H_2O_2$  decomposed. The design matrix was presented earlier in Table 4 and the data and overall results are presented in Table 7. The weight lost was measured after 68 hours at room temperature. As in Stability Study #1, the fraction  $H_2O_2$  decomposed was determined from the weight loss, attributable to the  $O_2$  escaping and was assumed to be more accurate than the fraction  $H_2O_2$  remaining as determined by titration with 0.1N  $KMnO_4$ . Both the  $H_2O_2$  and the nitrite react with the  $KMnO_4$  during the titration, but this has been corrected for, as explained in the appendix.

Figure 8 contains a tabular display of the response factor for Stability Study #3, expressed as percent  $H_2O_2$  decomposed. Each cell in the table corresponds to a specific combination of the factors. The effect of various factors can be compared by comparing different columns or rows. There does not appear to be any strong trends in this data.

A response plot shown in Figure 9 illustrates the effect of pH on the percent  $H_2O_2$  decomposed. Each data point in the response plots represents an average response from two runs, obtained by holding two of the factors constant. No explanation is obvious as to why the two lines in Figure 9 cross..

The distribution of the fate of the  $H_2O_2$  is shown graphically in Figure 10. The values shown for each set of conditions is the average of the two runs which satisfy those conditions. It does appear that a significant portion of the hydrogen peroxide reacted with the nitrite to yield nitrate.

Table 7. Stability Study #3 Results. Runs 1 to 4 contain sodium salts, Runs 5 to 8 contain potassium salts.

Run #	g. NaNO3 or KNO3	g. NaNO2 or KNO2	Initial weight	Orig. g. H2O2	pH	Weight lost g. O2	H2O2 decomp. (g)	Titration sample g.	ml titrate	g. H2O2 rx w/NO2	% H2O2 Decomp	% H2O2 React	% H2O2 Remain
1	5.00	5.45	100.12	2.31	9.28	0.547	1.16	0.835	7.95	0.856	50.4%	37.1%	12.4%
2	5.00	5.45	100.15	5.19	9.02	2.031	4.32	0.885	9.5	0.579	83.2%	11.2%	5.6%
3	5.00	5.46	101.41	2.31	10.89	0.618	1.31	0.673	5.05	0.968	57.0%	42.0%	1.1%
4	5.00	5.46	100.34	5.19	10.93	1.055	2.24	0.662	4.75	2.131	43.2%	41.1%	15.7%
5	5.93	6.73	99.50	2.31	9.03	0.417	0.89	0.733	6.2	1.385	38.4%	60.1%	1.5%
6	5.93	6.73	100.05	5.19	9.11	1.867	3.97	0.709	6.45	1.206	76.5%	23.2%	0.3%
7	5.93	6.73	100.23	2.31	10.96	0.545	1.16	0.742	7.1	1.119	50.2%	48.5%	1.2%
8	5.93	6.73	101.52	5.19	10.93	1.084	2.30	0.759	6.5	2.223	44.4%	42.9%	12.7%

		pH			
		9		11	
Cation		H <sub>2</sub> O <sub>2</sub>		H <sub>2</sub> O <sub>2</sub>	
		2.3%	5%	2.3%	5%
Na <sup>+</sup>	Na <sup>+</sup>	50	83	57	43
	K <sup>+</sup>	38	76	50	44

Figure 8. Tabular Display of Stability Study #3. Response is the percent H<sub>2</sub>O<sub>2</sub> decomposed.



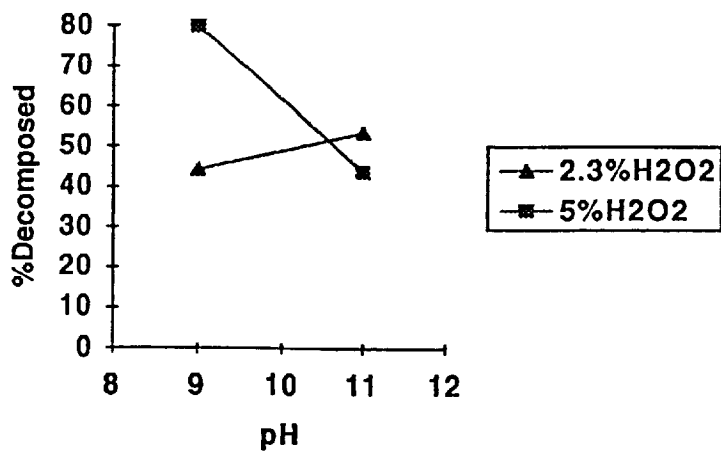


Figure 9. Response Plot for Stability Study #3.

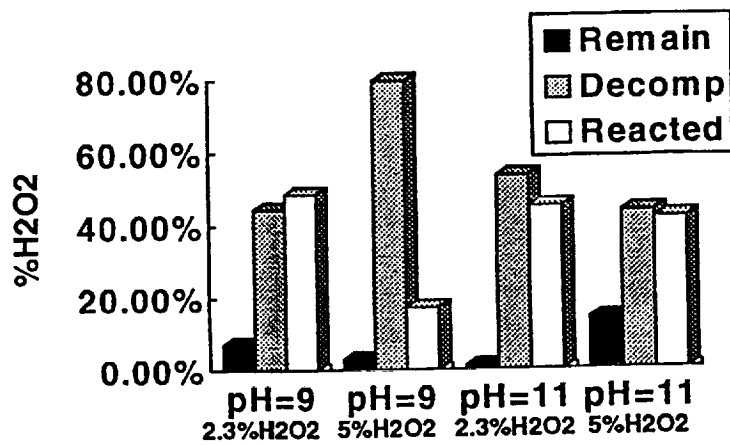


Figure 10. Distribution of H<sub>2</sub>O<sub>2</sub> after 68 hours in Stability Study #3.

## 5. CONCLUSIONS

Small scale laboratory tests were conducted to evaluate the stability of  $H_2O_2$  in alkaline mixtures, some of which included nitrate and nitrite salts, and which were adjusted to different pH levels. These mixtures simulated the proposed scrubber liquor for removing  $N_2O_4$  from the scrubbing of hypergolic vent gases. Currently the  $N_2O_4$  vent gas is scrubbed with a sodium hydroxide (NaOH) solution resulting in a hazardous liquid waste. This study investigated the use of a solution of potassium hydroxide (KOH) and hydrogen peroxide ( $H_2O_2$ ) for the nitrogen tetroxide vent scrubber system with a goal of producing a solution of  $NO_3$  that could be used as a fertilizer.

A series of three different stability studies were conducted. In the first it was found that the most significant effect was the pH; an average of 65% of the  $H_2O_2$  disappeared at pH = 9 and only 4% disappeared at pH = 6 after 68 hours at room temperature. It also appears that when there was nitrite present in the original solution, a significant portion of the nitrite reacted with the hydrogen peroxide to yield nitrate. The second stability study found that the decomposition rate of  $H_2O_2$  as a function of pH appears to go through a maximum at pH 11. In the third stability study it again appears that some of the nitrite is converted to nitrate.

In conclusion, a mixture of potassium hydroxide and hydrogen peroxide shows promise as a scrubbing liquor for  $N_2O_4$  because of its ability to convert the nitrite in solution to nitrate, thus producing a solution that may be useful as a feed stream to a fertilizer manufacturer.

### Appendix A

#### Appendix A. Separation of the $\text{H}_2\text{O}_2$ and $\text{NO}_2^-$ Interactions with $\text{KMnO}_4$ .

The following two material balances can be used to solve for the  $\text{H}_2\text{O}_2$  remaining and the  $\text{H}_2\text{O}_2$  that reacted with  $\text{NO}_2^-$ .

##### Hydrogen Peroxide Material Balance:

$$\text{g. H}_2\text{O}_2 \text{ initial} - \text{g. H}_2\text{O}_2 \text{ decomp.} = \text{g. H}_2\text{O}_2 \text{ remain} - \text{g. H}_2\text{O}_2 \text{ reacted w/ NO}_2^- \quad (\text{A.1})$$

##### KMnO<sub>4</sub> Material Balance:

$$\text{total ml. titrate} = \text{ml. titrate for NO}_2^- + \text{ml. titrate for H}_2\text{O}_2 \quad (\text{A.2})$$

Let the two unknowns be expressed as

$$x = \text{g. H}_2\text{O}_2 \text{ remain} \quad (\text{A.3})$$

$$y = \text{g. H}_2\text{O}_2 \text{ reacted w/ NO}_2^- \quad (\text{A.4})$$

Now developing equation for (ml. titrate for  $\text{NO}_2^-$ ):

$$\text{g. NO}_2^- \text{ remain} = \text{g. NO}_2^- \text{ initial} - \text{g. NO}_2^- \text{ reacted} \quad (\text{A.5})$$

and the (g.  $\text{NO}_2^-$  reacted) can be related to "y" (g.  $\text{H}_2\text{O}_2$  reacted w/  $\text{NO}_2^-$ ) from the reaction stoichiometry:

$$\text{g. NO}_2^- \text{ reacted} = y (\text{MW NaNO}_2) / (\text{MW H}_2\text{O}_2) \quad (\text{A.6})$$

Expressions can also be developed to relate the (g.  $\text{NO}_2^-$  remain) to the (ml. titrate for  $\text{NO}_2^-$ ) and to relate the (g.  $\text{H}_2\text{O}_2$  remain) to the (ml. titrate for  $\text{H}_2\text{O}_2$ ) based on the titration sample size.

Thus the two material balances, equations (A.1) and (A.2), can be written with only the two unknowns "x" and "y", all other values being known. It is just a matter of algebraic manipulation to solve for "x" and "y".

The one problem with this correction is that the  $\text{NO}_2^-$  does not react completely with the  $\text{KMnO}_4$ , but most of it does. It was determined by titration without  $\text{H}_2\text{O}_2$  that 68% to 78% of the  $\text{NO}_2^-$  reacts with the  $\text{KMnO}_4$ , thus a correction factor was used to account for the partial reaction of  $\text{NO}_2^-$  with  $\text{KMnO}_4$ .

## References

- Ardon, Michael, *Oxygen, Elementary Forms and Hydrogen Peroxide*, W. A. Benjamin Publ, New York, 1965.
- Chopp, R. J., H. Dev, P. Condorelli, B. J. Jody, "Effects of Packing Material, Caustic Strength, By-Product Level, and Temperature on an Oxidizer Scrubber", Report IITRI C06567-TR2, IIT Research Institute, 1984.
- "Evaluation of Hypergolic Emissions Control Technologies", Report NAS 10-10715, Research Triangle Institute, 1984.
- Felts, W. Keith, "Air Pollution Testing of Hypergolic fuel - Vapor Scrubbers at Cape Canaveral Air Force Station, Florida", Report ESL-TR-80-58, Engineering Science, 1981.
- "Hypergolic Nitrogen Tetroxide Vapor Scrubber, Phase 1 Test Report", Report KSC-DD-777, Planning Research Corporation, 1983.
- "Hypergol Oxidizer Vapor Scrubber Report, Phase IV and Phase V Test Results", Report KSCE-824-0014, EG&G Florida, 1989.
- "Hypergolic Vapor Scrubber, Phase II (N<sub>2</sub>O<sub>4</sub>) & Phase III (MMH), Modification and Test Project", Report KSC-E-3084, EG&G Florida, 1986.
- Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd edition, volume 18, John Wiley and Sons, New York, 1982.
- Moen, Ronald D., Thomas W. Nolan, LLOYD P. Provost, *Improving Quality Through Planned Experimentation*, McGraw-Hill, New York, 1991.
- Schumb, W. C., et al., *Hydrogen Peroxide*, Reinhold Publishing Corp., New York, 1955.
- Thomas, J., et al., "Improved Hypergolic Vapor Removal Systems", Report NAS 10-10106, Florida Institute of Technology, 1982.
- Weast, Robert C., ed., *Handbook of Chemistry and Physics*, The Chemical Rubber Co., Cleveland, Ohio, 1965.