A STUDY OF THE CONVERSION EFFICIENCY
OF AN AMMONIA OXIDATION UNIT

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Massachusetts Institute of Technology, as partial
fulfillment of the requirements for the degree of
Bachelor of Science
in
Chemical Engineering.

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FOREWARD

The authors feel very grateful to Professor F.W. Adams of the Chemical Engineering Department of the Massachusetts Institute of Technology for his suggestions in working out the method of analysis. They also wish to thank Messrs Conklin and Healy of the Merrimac Chemical Company for their cooperation in arranging to run the test on the plant equipment, and the staff of the laboratory of the Everett plant for the helpful assistance they gave all during the time we were working there.
ABSTRACT

The method of analyzing nitrogen oxide gases leaving the convertor by absorbing them on asbestos covered with lead peroxide and regenerating the gases in a nitrometer, was found quite unsatisfactory. Absorption in a sodium peroxide solution followed by a permanganate bubbler, however, gave good results and furnishes a relatively simple method of plant analysis accurate to within about two per cent. On the two runs made on the plant equipment a conversion efficiency of about 95% was obtained.
Conversion Efficiency of Ammonia Oxidation.

This thesis was run on the ammonia oxidation unit in the Merrimac Chemical Company, Everett, Massachusetts.

The object of the thesis was to determine the conversion efficiency of the unit.

One of the most important chemicals in time of peace or war is nitric acid, as it is the basis of the fertilizer and munition industries. For this reason it is very important for a country to have a source of nitric acid which cannot be endangered by foreign powers. This led to the development of the ammonia oxidation process. Although the Merrimac Chemical Company does not use the process as a source of nitric acid - but as a source of nitrogen oxides for the sulphuric acid chambers - nevertheless the actual ammonia oxidation is the same as that used in the manufacture of nitric acid.

The principle of ammonia oxidation has been known for a long time, Kuhlman accomplishing the process by using platinum and other substances as catalyst in 1839. At that time, however, there was no commercial necessity for the process, and as a result, no development resulted from his discovery. As the demands for fertilizers and munitions became more pressing, the Germans realized the importance of a home supply of nitric acid.

To assure this supply, Ostwald developed the process on a commercial scale, establishing a small plant in 1909.
at Gerthe in Westphalia. Another plant was erected by the English at Velvorde, Belgium. In the process developed by Ostwald, the ammonia-air mixture passed thru an outer tube of silica, and then thru an inner tube of nickel containing the platinum catalyst. Thus it served as a preheater and a converter. This process was not used by the Germans during the war.

The next development in the oxidation of ammonia was the Kaiser process in which Dr. Kaiser of the University of Heidelberg constructed a plant using a platinum gauze in an iron pipe. This was in 1912 and 1913, and marked the first use of gauze for a catalyst. The process cannot compete with modern methods.

The process used by the Germans during the war was developed by Frank-Caro. In his method, an electrically heated platinum gauze was used. From this point on, the development became quite rapid. In 1916, the American Cyanamid Company erected a plant at Warners, New Jersey, to supply a 60,000 ton sulphuric acid plant with nitrogen oxides. In the same year, the Bureau of Mines started work on the process, and soon found that the electrical heating of the gauze was unnecessary if three layers of platinum were superimposed upon one another. This point marked the change from the flat gauze to the cylindrical basket type. It was found that iron pipe could be used after the converter so long as the temperature of the gases remained above 170-200°F. Before the converter,
it is necessary to use aluminum piping. Gauze temperature is another important feature in the proper operation of the plant, the best temperature being above 825°C, and it should never fall below 750°C.

The plant of the Merrimac Chemical Company has the latest development in ammonia oxidation units. The air is passed up thru a stripping column down which a carefully regulated stream of ammonia liquor descends. The bottom of the column is heated by the converted gases in a heat interchanger, thus driving out the last traces of ammonia. The ammonia-air mixture then passes thru a heat interchanger heated by the converted gases. This preheated mixture is then passed thru the converter, where it goes thru the platinum basket in the bottom of which is a silica plate. The converted gases then go thru the two heat interchangers mentioned above, and thus to the chambers. The platinum gauze used at the plant is made up of platinum wire 0.003 inches in diameter, containing not more than 0.1% iridium. The gauze is made up of 80 mesh wire in the form of a cylinder, the bottom being one layer, and the side four layers of wire superimposed on each other. Aluminum piping is used between the stripping column and the converter, the holder in the converter being made of nickel. After the converter, iron pipe is used. So it is seen that the plant uses the proper equipment as specified by the tests of the Bureau of Mines.
About a day before work was started at the plant, the platinum gauze burned out. Since the gauze had only been in operation two months, it was quite apparent that there was something wrong with the process. From a survey of the literature, it was readily seen that dust was very detrimental to the gauze, and would soon cause it to burn out. Mr. Conklin, who has charge of this unit, informed us that very dirty ammonia was being used in the process, due to storage of the ammonia in very dirty drums. It was quite logical to suppose that a similar destruction of the gauze would occur if this same ammonia were used. For this reason, the authors collaborated with Mr. Conklin in the development of a cleaning system. A settling tank followed by a filter was proposed, one filter for the clearer upper layer, and another for the dirty sludge in the bottom. The result was the installing of a settling tank, without a filter for the upper layer, but provision for filtering the sludge.

The most important and most difficult part of the test was soon seen to be the development of an accurate method of analyzing the converted gases. Several methods were suggested in the literature and in former theses, so it was necessary to investigate these in the laboratory. One method used in a previous thesis and also at the plant for the analysis of gases leaving the Gay Lussac tower was recommended for the authors use. In this method, the gases are passed thru tubes containing lead peroxide on asbestos. The nitrogen oxides react with the lead peroxide
to form lead nitrate. This is then leached out, and the solution introduced into a nitrometer. Upon the addition of concentrated sulphuric acid, and shaking, NO is formed. This gas is measured in the nitrometer, and thus the nitrogen oxide concentration of the gases determined. The method of operating the nitrometer was first checked by introducing a definite amount of lead nitrate into the nitrometer. This gave the required volume of NO. Several methods of generating a definite amount of NO and NO₂ from a weighed portion of Cu, were tried, but not all of the gas was absorbed by the lead peroxide. A definite volume of gas was next generated by using a weighed amount of sodium nitrite, which reacted with potassium ferrocyanide and sulphuric acid. This again would not give the proper amount of gas in the nitrometer to indicate complete absorption by the lead peroxide. Finally NO was generated in the nitrometer from lead nitrate as was done above, and this passed thru the absorption system, but complete absorption could not be obtained when the NO was passed thru pure or when the NO was first passed thru a bulb to dilute it with air. The asbestos sludge was leached again, but no gas was given off in the nitrometer from this washing, thus showing the method of leaching to be satisfactory. Two absorption bulbs were put in series, but the second bulb did not absorb any gas, which indicated that the first bulb was sufficient, no gas escaping into the second bulb.
Other methods suggested in the literature, although they
might have been satisfactory, were discarded because they
were not practical for plant operation. Finally a method
suggested by the British ministry of Munitions in a pamphlet "The Oxidation of Ammonia applied
to Vitriol Chamber Plants", published (revised edition)
March 1921 was tried. In this method, the gas is aspirated
thru two Drechsel absorption bottles containing sodium
peroxide solution, and then thru a ten bulb tube containing
acidulated potassium permanganate. The first two bottles
are titrated at the end of the run with standardized acid,
using litmus as an indicator, a light purple end-point
being obtained instead of the usual one. The potassium
permanganate is titrated with standardized oxalic acid to
a colorless end-point. When tests were made on this method
of analysis, by generating a definite volume of NO in the
nitrometer, 98.5 to 99% of the gas was accounted for in the
absorption train. To make the conditions similar to those
encountered in the plant, the pure NO was passed thru a
bulb placed in the system, thus bringing it into contact
with air, producing NO₂. This method of analysis having
been found sufficiently accurate, the plant investigation
was ready to be started.

The amounts of solution used in the various bottles
are as follows:-

(1) A Drechsel bottle containing:-
   100 cc. distilled water
   20 cc. Na₂O₂ solution
   40 cc. H₂O₂ solution (3%)
(2) A Drechsel bottle containing:-
50 c.c. distilled water
10 c.c. \( \text{N/Na}_2\text{O}_2 \) solution
20 c.c. \( \text{H}_2\text{O}_2 \) solution (3%)

The \( \text{N/Na}_2\text{O}_2 \) solution is prepared by adding 78 grams of sodium peroxide solution to 1 kilogram of powdered ice in small quantities with stirring, and then adding 1 liter of distilled water and filtering through glass wool. It is kept in a bottle with a capillary tube through the cork to allow the traces of \( \text{O}_2 \) given off to escape.

(3) A 10-bulb tube containing:-
5 c.c. \( \text{N/10 KMnO}_4 \) solution
10 c.c. 50% sulfuric acid

This train of three bottles is followed by the aspirator and graduate.

When the apparatus was installed in place in the plant several precautions were found necessary to obtain satisfactory results. Condensation in the gas sampling lines gave considerable trouble. The NO sampling pipe was lagged to prevent this until the gases which had entered the glass tubes from any condensate could be washed out at the end of a run. The ammonia percentage determination was carried out rapidly several times during an hour run with the same end in view, and an average of these taken. To correct for the partial vacuum present in the NO aspirator bottle, a manometer was installed to give a measure of this. In the titration of the \( \text{Na}_2\text{O}_2 \) solution, a light purple end-point was obtained with litmus rather than the usual one, but this was found quite satisfactory.
Although over half a dozen runs were made in the day and a half available for experimentation, only two of these were successful due to difficulties of a minor nature which were encountered. The first of these, which was run several hours after the new gauze had been installed gave an efficiency of 92.6% at the low rate of feed of 5.81#/ of ammonia per hour. The gas entering the convertor in this case had an ammonia content of 9.9%. In the second successful run, which took place the following day, an efficiency of 96.3% was calculated, feeding ammonia at the rate of 8.54#/hour and at a strength of 9.2%.

In the two runs mentioned the following data was recorded:

**Run #1**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Reading on air gauge</td>
<td>0.25</td>
</tr>
<tr>
<td>Ammonia feed</td>
<td>5.81#/hr.</td>
</tr>
<tr>
<td>Exit gas temperature</td>
<td>425 C</td>
</tr>
<tr>
<td>Gas aspirated thru ammonia absorber</td>
<td>1000c.c.</td>
</tr>
<tr>
<td>&quot; &quot; NO</td>
<td>945c.c.</td>
</tr>
<tr>
<td>M.e.'s of Na$_2$O$_2$ disappearing</td>
<td>4.45</td>
</tr>
<tr>
<td>M.e.'s of KMnO$_4$</td>
<td>0.263</td>
</tr>
<tr>
<td>M.e.'s of HCl neutralizing ammonia</td>
<td>4.423</td>
</tr>
</tbody>
</table>

**Run #2**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Reading on air gauge</td>
<td>0.55</td>
</tr>
<tr>
<td>Ammonia feed</td>
<td>8.54#/hr.</td>
</tr>
<tr>
<td>Exit gas temperature</td>
<td>520 C</td>
</tr>
<tr>
<td>Gas aspirated thru NO absorber</td>
<td>1010 c.c.</td>
</tr>
<tr>
<td>Pressure of gas aspirated</td>
<td>23mm vac.</td>
</tr>
<tr>
<td>Per cent ammonia in gas entering absorber</td>
<td>(a) 9.2 (b) 9.2</td>
</tr>
<tr>
<td>M.e.'s of Na$_2$O$_2$ disappearing</td>
<td>4.44</td>
</tr>
<tr>
<td>&quot; &quot; KMnO$_4$</td>
<td>0.514</td>
</tr>
<tr>
<td>Gauze Temp.</td>
<td>854°C</td>
</tr>
</tbody>
</table>
The results of the work done indicate that the sodium peroxide method of analysis is quite practicable if the proper precautions are taken, the method being simple enough for plant use. Its accuracy is within two percent. The experimental work performed on the plant equipment is too limited to warrant any general conclusions, although the two runs indicate a conversion efficiency of approximately 95%.

The ratio of ammonia to air in the gas entering the converter is given directly from the volume of air aspirated and the ammonia absorbed. If there were no change in volume of the air after the converter it would be possible to make a direct comparison of the weight of oxides of nitrogen corresponding to the volume of air aspirated, and the ammonia associated with an equal volume of air.

The aspirated volume after the converter, however, does not represent the volume of air which was associated with the ammonia corresponding to the oxides of nitrogen collected, because a portion of this air was used up in the oxidation. This consumed oxygen consist of two parts:

1) a portion used in burning the ammonia to NO in the converter, and
2) a further portion used in oxidizing the NO to higher oxides, which are then absorbed.

The first portion is the same in all cases, and is calculated as follows:

\[
4 \text{NH}_3 + 5 \text{O}_2 \rightarrow 4 \text{NO} + 6 \text{H}_2\text{O}
\]
25 volumes of air contain 20 vols. \( \text{N}_2 \)

the contraction of the air volume is here

\[
\frac{(25 - 20) \times 22.4}{4 \times 17} = 1.647 \text{ litres/gram NH}_3 \text{ burnt}
\]

The further contraction, due to secondary oxidation depends on which oxide is formed. It has been found by and by calculation (see p.11) previous experiments that between half and all of the NO is converted to NO\(_2\), 0.329 liters of \( \text{O}_2 \) disappearing per gram of NH\(_3\) in the first case, and twice that in the latter case. As a mean between these two values will be accurate within about a percent, this may be considered applicable for the purpose in hand.

The calculation for Run #2 is as follows:-

\[
4.44 \text{ milliequivalents } \text{Na}_2\text{O}_2 = 4.44 \times 0.017 = 0.075 \text{ g. NH}_3
\]

\[
0.514 \text{ g. K}_2\text{MnO}_4 = 0.514 \times \frac{1}{3} \times 0.017 = 0.0029 \text{ g. NH}_3
\]

Total gms. NH\(_3\) = 0.0783

Volume aspirated = 1010cc. \( \times \frac{760 - 23}{760 \times (273 + 25)} = 897 \text{ cc. S.C.} \)

(a) Gas assumed 50% to NO\(_2\)

Air volume correction:

\[
897 + 0.0754 \times (1.647 + 0.329) \times 1000 = 1046 \text{ c.c.; original air}
\]

If NH\(_3\) percentage is 9.2,

\[
\frac{0.092 \times 17 \times 1046}{(1 - 0.092) \times 22,400} = 0.0803 \text{ gms. NH}_3 \text{ corresponding to weight of nitrogen oxides absorbed.}
\]

Efficiency = 100 \( \frac{0.0783}{0.0803} = 97.5\% \)

(b) Gas assumed 100% to NO\(_2\)

Air volume correction:

\[
897 + 0.0754 \times (1.647 + .658) \times 1000 = 1071 \text{ cc.}
\]
If ammonia percentage is 9.2%:

\[ \frac{0.092 \times 17 \times \frac{1071}{22,400}}{1 - 0.092} = 0.0823 \text{ g. } \text{NH}_3 / 1071 \text{ cc. air} \]

Efficiency = \( 100 \times \frac{0.0783}{0.0823} = 95.1\% \)

Average efficiency = 96.3%

**NB.** By a consideration of the percentages of NO and O\(_2\) in the gas before it reached the first absorption bottle, and the time of contact of these at room temperature, a rough calculation of the amounts going to \( \text{NO}_2 \) was made. This showed that approximately 85% of the NO was transformed to \( \text{NO}_2 \). The time of contact of the gases was figured from the size and length of the glass tubing before the first absorption bottle. The rate of reaction constant was obtained from page 136 of Noyes and Sherrill's "Chemical Principles".
AMMONIA OXIDATION UNIT

Everett, Mass.
| 1. C.L.Parsons | Oxidation of Ammonia to Nitric Acid  
               | J.I.E.C., June 1919 |
| 6. --------    | British Ministry of Munitions Bulletin  
               | The Oxidation of Ammonia applied to  
               | Vitriol Chamber Plants  
| 7. Perley and Smith | Temperature Control in Ammonia Oxidation  
| 8. C.L.Parsons | Commercial Oxidation of Ammonia to Nitric Acid  
                | J.I.E.C., February, 1927 |
| 9. G.B.Taylor  | Oxidation of Ammonia  
                | J.I.E.C., November, 1927 |