

Introduction.

In the manufacture of nitric acid, ammonia is oxidised by air using a platinum-rhodium catalyst. One of the processes is to dissolve the nitrogen peroxide in water, usually under pressure, when weak nitric acid is produced of around 60% strength. For many purposes this has to be concentrated to 96-98% HNO_3 . This is usually done by using sulphuric acid as dehydrating agent. Until fairly recently this has been done in a packed tower by passing the mixed acid down through it while blowing in steam at the bottom. This method requires a ratio of $\text{H}_2\text{SO}_4/\text{HNO}_3$ of some 3.5/1 to give even 96% HNO_3 at the top. It was later realised that it would be better to have a counter-current scrubbing section at the top of the plant so that the nitric acid would pass through a powerful dehydrating agent on its way from the plant and thus give a stronger nitric acid, and in this way reduce the ratio of H_2SO_4 to HNO_3 . Much work has been done on this in the Ordnance Factories during the recent war and ratios of 2.8/1 have been achieved and claims made for 2.5/1. It has also been realised that the addition of live steam to the plant to supply the heat for the denitration etc., is not a good thing as this means the addition of extra water to the sulphuric acid which in turn means more heat required to reconcentrate the weak sulphuric acid issuing from the base of the denitrator.

Messrs. Cyanamid Ltd. have tried to overcome this point and apply direct heat to a tubular heat exchanger at the base of their concentrator by which means the acid is heated by indirect contact with pressure steam. Their efforts do not appear to have been successful as the Cyanamid nitric acid concentration plant now has a denitration column heated by live steam following the heat exchanger, and the $\text{H}_2\text{SO}_4/\text{HNO}_3$ ratio has not been materially reduced.

By studying the overall heat balance in a system using the theoretical ratio of $\text{H}_2\text{SO}_4/\text{HNO}_3$, working on a counter-current principle without the injection of steam into the acids it becomes clear why the Cyanamid plant and other efforts made to achieve the theoretical ratio have failed, and it also becomes apparent how this ratio can be achieved.

Theoretical Considerations.

Calculation of minimum $\frac{\text{H}_2\text{SO}_4}{\text{HNO}_3}$ ratio.

Consider the production of 100 parts HNO_3 . This will require $100 \times \frac{10}{6} = 166.6$ parts 60% HNO_3 to produce it. \therefore wt of water = 66.6

Let x = weight of 100% H_2SO_4 required

i.e. $\frac{100x}{96}$ is weight of 96% H_2SO_4 required.

\therefore weight of water = $\frac{100x}{96} - x$

\therefore total water in the system = $66.6 + \left\{ \frac{100x}{96} - x \right\}$

All of this water must go into the sulphuric acid to give a weak sulphuric acid of 68% H_2SO_4 after denitration. 68% H_2SO_4 is chosen as it represents a good figure which is achieved in practice.

Heat Input to the system.

Heat of dilution of the acids has been determined by experiment. 167 parts 60% HNO_3 at 15°C . and 167 parts 96% H_2SO_4 at 15°C . were rapidly mixed and the temperature rise measured as 55°C . The specific heat of the mixture 30% HNO_3 , 48% H_2SO_4 is given in Trans. S.C.I. 62, 17 as 0.5.

$$\begin{aligned} \therefore \text{Heat of mixing of the acids} &= \text{mass} \times \text{sp.ht.} \times \text{temp. rise} \\ &= 334 \times .5 \times 55 \\ \therefore \text{m} &= 9190 \text{ cal.} \end{aligned}$$

Heat of Denitration of the Acid.

The heat required to denitrate the acid is not the heat required to drive off the concentrated nitric acid at the top as past workers seem to have assumed, but is the heat required to drive off the conc. nitric acid at the top plus the heat required to boil off the water which is distilled off along with the nitric acid during the denitration. Although this water plays no part in the material balance it supplies heat to the system and must be allowed for in the heat balance.

The mixture of the theoretical quantities of acids as above gives an analysis of approx. 30% HNO_3 , 48% H_2SO_4 . From the graph given in Trans. S.C.I. 62, 17 one finds that the strength of nitric acid boiling from this composition of acid is 93%. This point was plotted on a graph (Graph 1). Now after 5 gms. of HNO_3 have been distilled off, the composition of the acid can be calculated to be 26.35% HNO_3 , 50.5% H_2SO_4 which gives the strength of nitric boiling off it as 90%, which was also plotted. By a continuation of this method a graph has been drawn (Graph 1) of the variation of the composition of the nitric acid during the complete denitration process. Breaking up this graph into a number of straight line portions one finds that the first 5 gms. of nitric boil off at an average strength of 91.5%, the second 5 gms. at an average strength of 88.5% HNO_2 etc., the results being tabulated as follows:-

of	Average Comp. % HNO_3	Weight of WNA	Boiling Point	Heat Content	Heat Required
	91.5	5.47 gms.	95°C .		
	88.5	5.65 "	100°C .		
	85.5	5.85 "	105°C .		
	81.5	6.13 "	112°C		
	74.5	6.71 "	118°C .		
	55.5	4.50 "	119°C .		
	20.0	12.5 "	104.5°C		
gms.		46.81 "			14.765 cal.

$$\therefore \frac{(66.6 + \frac{x}{24}) 100}{x + 66.6 + \frac{x}{24}} = 32.$$

$$\therefore x = 160 \text{ approx.}$$

$$\therefore \text{Theoretical ratio } \frac{\text{H}_2\text{SO}_4}{\text{HNO}_3} = \frac{1.6}{1}$$

Heat Balance.

Suppose we consider the system, we have an input of 167 parts WNA at 60% HNO_3 and 167 parts 98% H_2SO_4 , an output of 100 parts approx. 100% HNO_3 at the top of the column and 234 parts of 68% sulphuric acid at the base since all of the water in the WNA is taken up by the sulphuric acid.

Now Let x = heat content of conc. nitric acid at the top of the plant.

Let y = heat content of weak sulphuric acid at the base of the plant.

Let r = radiation and convection losses.

Then heat output of system = $x + y + r$

Let z = heat required to denitrate the sulphuric acid

Let m = heat of mixing of the WNA and COV.

Then heat input of system = $z + m$.

For thermal equilibrium $x + y + r = z + m$ for the production of 100 gms. HNO_3 .

$$\begin{aligned} \text{Heat content of conc. nitric acid} &= \text{mass} \times \text{sp. ht.} \times \text{rise in temp.} \\ &\quad + \text{mass} \times \text{latent ht. of vapour-} \\ &\quad \text{isation.} \\ &= 100 \times .46 \times 65 + 100 \times 115 \\ &= 2990 + 11500 \\ &= 14490 \text{ cal.} \end{aligned}$$

$$\therefore x = 14490 \text{ cal.}$$

$$\begin{aligned} \text{Heat content of W.O.V.} &= \text{mass} \times \text{sp. ht.} \times \text{rise in temp.} \\ &= 234 \times .49 \times 150 \\ &= 17200 \text{ cal.} \end{aligned}$$

$$\therefore y = 17200 \text{ cal.}$$

Radiation losses.

Assuming an output of 20 tons/day of conc. nitric acid from a column 15 ft. high and 2 ft. diameter the radiation and convection losses have been calculated from a formula given in Chemical Engineers Handbook (Perry) 1st Edition p.863, giving a value of approx. 20 cal./gm. of HNO_3 produced.

$$\therefore \text{Radiation and convection losses} = 100 \times 20 = 2000 \text{ cal.}$$

$$\begin{aligned} \therefore \text{Total heat losses in system } x + y + r &= 14,490 + 17,200 + 2000 \\ &= 33,690 \text{ cal.} \end{aligned}$$

At the time of writing this report no data on the heat content of different strengths of nitric acid was available. We see from the above, however, that 46.81 gms. of WNA have to boil off at an average temperature of about 110°C . The heat required is therefore the sum of the heat required to raise 30 gms. of HNO_3 to 110°C . from 15°C ., the heat required to vapourise it, the heat required to raise 16.81 gms. of water to 110°C . and the heat required to vapourise it, i.e. $(30 \times .46 \times 95) + (30 \times 115) + (16.81 \times 500) + (16.81 \times 1 \times 95)$

$$\begin{aligned} &= 1310 + 3450 + 8405 + 1600 \\ &= 14,765 \text{ cal. for } 30 \text{ gms. } \text{HNO}_3 \\ &= 49,217 \text{ cal. for } 100 \text{ gms. } \text{HNO}_3 \end{aligned}$$

\therefore Total heat input $z + m = 49,217 + 9,190 = 53,407$ cal./100 gm.

We see, therefore, that with the ideal system of direct heat and a counter-current flow of acids at the top of the plant the heat input is 53,407 cal. and the heat output is 33,690 cal. for an output of 100 gms. HNO_3 . This means that there is excess heat of 19,717 cal. which must be removed from the system in some way.

Now in any process yet developed for concentrating nitric acid using sulphuric acid, there are only two ways of removing heat, one of these being in the nitric acid removed at the top of the plant and the other in the sulphuric acid at the bottom of the plant. For any given ratio of feeds the latter is a constant, since the weak sulphuric acid must be removed at its boiling point and can only be increased by increasing the sulphuric ratio. This has been the technique which has been employed in the past and obviously cannot give the theoretical ratio of $\text{H}_2\text{SO}_4/\text{HNO}_3$ of 1.6/1.

One possible method of removing the surplus heat, however, is to reflux conc. nitric acid at the top of the plant. Thus, for 100 gms. C.N.A. production there is an excess heat of 19,717 cal. If C.N.A. at 15°C . is refluxed at the top of the plant then we will have equilibrium when

$X \times .46 \times 70 + X \times 115 = 19,717$ where $x = \text{wt. of C.N.A. refluxed.}$

$$\therefore 32.2 x + 115 x = 19,717$$

$$\therefore 137.2 x = 19,717$$

$$\therefore x = 145.$$

The reflux ratio must therefore be 1.45/1.

The lack of appreciation of the need for reflux of C.N.A. explains why the Cyanamid plant, which employs direct heating of the acids at one stage without the addition of live steam, does not give the theoretical ratio of $\text{H}_2\text{SO}_4/\text{HNO}_3$. If we imagine the Cyanamid plant operating without reflux and without the addition of live steam with only the theoretical sulphuric acid, we see that there is excess heat in the system. The only way open for removal of the excess heat is at the top of the plant which, of course, means that steam must come over with the C.N.A. giving a more dilute product. For this reason more C.O.V. must be added to remove the excess heat at the base of the plant and when the quantity added causes a heat balance, C.N.A. is again produced. However, the addition of more C.O.V. would mean a considerably stronger spent acid at the base. Due to the presence of nitrosyl sulphuric in the acids there is a

maximum permissible strength of 70% H_2SO_4 in the spent acid. Thus on the higher C.O.V. input it is necessary to add water to the system which is done by adding live steam to denitrate the acid. The Cyanamid plant is indeed a combination of both methods and requires a 3/1 ratio of H_2SO_4/HNO_3 .

Recommendations.

It is suggested that a Cyanamid unit be modified to operate with a reflux ratio of 1.45/1 with the elimination of the injection of live steam when it should be possible to achieve the theoretical ratio of $\frac{H_2SO_4}{HNO_3} = \frac{1.6}{1}$. It may be necessary to alter the heat

exchanger system to give a temperature gradient throughout the denitrator and possibly a longer concentrator will be required. It is however suggested that the first trials should be made on an existing unit altered by fitting a nitric acid reflux. Should these trials show promise a really suitable plant could then be designed.