A Neutralizer Condensate Recovery System

In addition to improving plant efficiency by increasing the recovery of ammonium nitrate, this recovery system has helped in solving a pollution problem.

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The Phillips Petroleum Co. solves a potential pollution problem at the Kennewick Wash., and Beatrice, Neb. SOL'N-32 plants, and makes a profit doing so. SOL'N-32 is Phillips' tradename for a mixture of urea, ammonium nitrate, and water in proportions such that the nitrogen content is 32%. The water content is about 20%. Urea is produced using a once-through process with the off-gas going to nitric acid and ammonium nitrate manufacture.

In the manufacture of ammonium nitrate, the heat generated by the reaction of ammonia and nitric acid vaporizes some of the water introduced with the nitric acid. The water vapor vented from the neutralization reactor contains some unreacted ammonia, nitric acid, and some entrained ammonium nitrate. These materials are present in sufficient quantities to become an air pollution problem if the stream is vented, and a possible water pollution problem if the stream is condensed and discarded to the sewer.

What can be done with this stream? Some possibilities are: inject the condensed stream to a disposal well, incinerate the stream, provide a surface collection pond for solar evaporation, use as cooling tower make-up, use as condensate feed to the remelt system if solid nitrate is produced, or use as water feed to the nitric acid absorber. All of these present special problems, and the application of any one method or combination depends on individual circumstances. Phillips is presently using all of these methods at our various locations where nitrate is produced.

Neutralizer condensate recovery system

Figure 1 is a flow diagram of the process used to recover neutralizer vapor for reuse as water feed to the nitric acid absorber. Starting at the neutralizer, the feed streams are nitric acid (50-to 57%), and urea plant off-gas containing about 50% ammonia, 25% CO_2 and 25% water vapor. The neutralizer operates at essentially atmospheric pressure, and at about 250-to 255°F. From the neutralizer the product nitrate overflows to the mix tank in the SOL'N-32 plant and the contaminated water vapor is taken to a wet scrubber. The scrubber is packed with Raschig rings. Weak nitrate solution is circulated over and through the scrubber
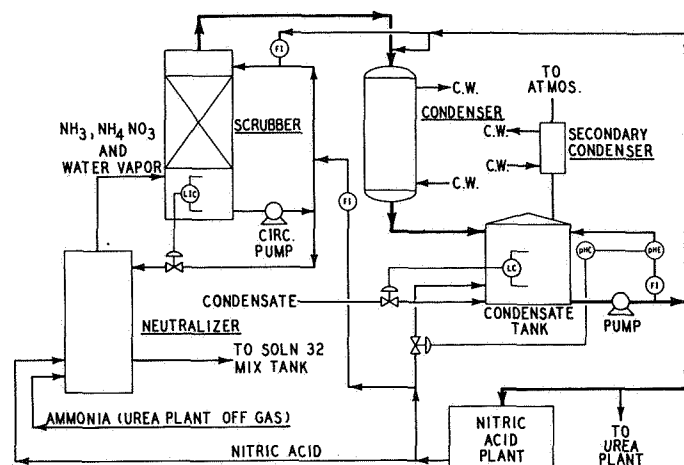

Figure 1. The neutralizer condensate recovery system.

by a pump, with the excess solution being recycled to the neutralizer on level control. The scrubber solution is circulated at about 220°F. A small amount of nitric acid is added to the circulating stream and a small amount of process condensate is added to control the nitrate concentration. Most of the entrained solids are removed in the scrubber, and most of the free ammonia is neutralized. The scrubbed vapor then flows to a condenser where the water vapor is condensed. The condenser is a shell and tube exchanger using cooling water. When the plant is down, condensate is sprayed into the inlet of the condenser to wash out solid nitrate which has collected. Condensate flows from the condenser, by gravity, into a collection tank. The pH of the collected condensate is controlled by the addition of nitric acid to the tank. CO_2 from the condensate tank is vented to the atmosphere through a secondary condenser. The net condensate produced is pumped to the nitric acid plant and urea plant.

Successful operation of this system depends on control of the pH. The CO_2 in the system, which is vented off the condensate tank, carries some water vapor with it which results in a white plume from the vent. The condition of this plume is a function of the pH in the tank. With a pH at, or near, 7.0, the plume is essentially free of ammonia and nitrate. The pH should be about 5.0 in the neutralizer,
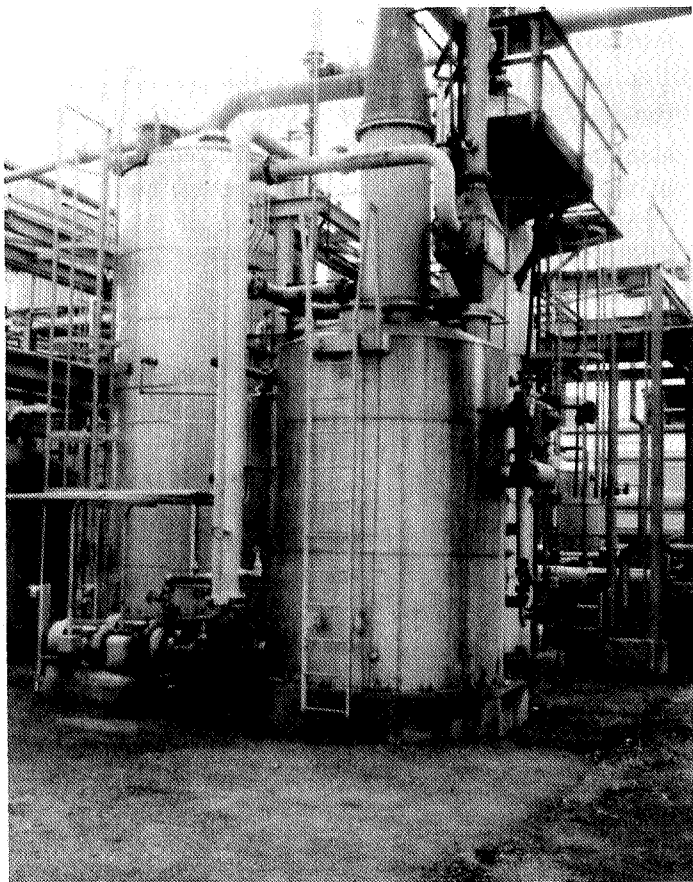
Figure 2. The neutralizer condensate recovery system at Phillips' SOL'N-32 plant in Beatrice, Neb.

6.0 in the scrubber, and 7.0 in the condensate tank.

Phillips has operated the plant at Kennewick, Wash. using this system since the summer of 1968, and the one at Beatrice, Neb. Figure 2, since the summer of 1969. Normal procedure is to start up the nitric acid plant using steam condensate and switch to neutralizer condensate when the pH of the condensate is in normal range. After initial start-up problems, the recovery system has operated essentially troublefree.

Normally, the ammonium nitrate content of the recovered condensate is between 1.5 and 2.5%. The nitrate concentration of the nitric acid from the absorber is about half of that of the water feed stream due to dilution by water made in the reaction, and water carried from the urea plant with the ammonia feed. During periods of upset operation we have recorded nitrate concentration in the 10-to 12% range in the recovered condensate.

$NH_4 NO_3$ decomposition studied

Before this system was put into operation the Phillips Research & Development Dept. investigated the possible decomposition of ammonia nitrate carried in the condensate under conditions prevailing in the nitric acid absorber. A literature search was made and a test program set up. No evidence was found in either the test work or in the literature that there would be a significant loss of ammonium nitrate in the nitric acid tower due to decomposition, or that any hazard exists from violent decomposition.

It is well known that ammonium nitrate decomposes at elevated temperatures, but the temperature at which the formation of N_2O begins, the lowest temperature of the various decomposition reactions, is about $410^{\circ}F$. Decompositions yielding nitrogen do not begin until considerably higher temperatures, 500-to $550^{\circ}F$, are reached. These temperatures pertain to reactions of the dry salt, although possibly the reactions could proceed at about the same temperature if an aqueous solution were heated under sufficient pressure to reach these temperatures. The only reaction which would be expected at the tower operating temperature of 150-to $175^{\circ}F$ would be a slight dissociation to ammonia and nitric acid. This does not become appreciable until $200^{\circ}F$, and would be suppressed by the 110 lb./sq. in. gauge absorber pressure.

A careful search of the literature served to document this information influences were found which it was believed might modify the nitrate decomposition reaction sufficiently to warrant further consideration. One was that the presence of nitric acid acts on the crystalline salt to accelerate the decomposition and, therefore, probably lowers the temperature at which the decomposition becomes detectable. If such an effect applies in the dilute solutions under consideration it would not be expected to be of the magnitude necessary to lower this temperature from $410^{\circ}F$ to the tower operating temperature of 150-to 175 $^{\circ}F$. However, laboratory tests were carried out to confirm this. A 5.5% solution of ammonium nitrate in 53% nitric acid was maintained at $150^{\circ}F$ at atmospheric pressure. After 2-and 8 hr. periods, analysis of the ammonium ion present showed absolutely no change from the initial ammonium ion concentration. Since contact time in the tower is relatively short, these tests confirm the feasibility from the safety standpoint of preneutralization of the incoming condensate stream.

The other influence noted in the literature was the effect of metallic catalysts on the decomposition reaction. Platinum is continuously lost from the gauze and a fraction of this material, carried in the process gas, may reach the absorber tower. Most experimental work described in the literature shows that metallic catalysts, including platinum, have no appreciable effect on the decomposition of solutions of ammonium nitrate. However, one reference, briefly cited in a comprehensive review of nitrate chemistry, claimed that almost complete decomposition of dilute solutions of ammonium nitrate occurred when heated with a platinum catalyst. Additional experiments were run with the 5.5% nitrate solution having a strip of bright platinum foil in the solution during the heating period. Again, no detectable decomposition occurred after 8 hr. heating at $150^{\circ}F$. The paper noted above showed that it had been possible to cause rapid decomposition of even relatively cool, dilute nitrate solutions by a very active, very carefully prepared platinum black catalyst. Many platinum black catalysts active for the usual reactions of hydrogenation, etc. were reported in the literature as

inactive in this nitrate decomposition, and even some prepared by the special procedure given in the paper were unaccountably inactive. Experimental work using a normally active platinum black catalyst prepared by a normal procedure failed to decompose the test nitrate solution in 5 hr. at 150°F.

The conditions under which a platinum black catalyst could be active for this nitrate decomposition apparently are in neutral solution and the complete absence of oxidizing agents. Since the absorber tower is highly acid and is under strongly oxidizing conditions, it is almost inconceivable that an active catalyst could be formed. If it were, it would be instantly deactivated by the strong oxidizing acid conditions in the tower.

In summary

Use of this recovery system improved operating efficiency by increasing the recovery of ammonium nitrate. It has aided in reducing or eliminating a pollution problem. No evidence from the literature or from our experimental work indicates any hazard in using neutralizer condensate as water feed to the nitric acid absorber.

O'BRIEN, George

Discussion

Q. Is there any problem with ammonia from dissociation going overhead into the tail gas recovery unit forming ammonium nitrate?
O'BRIEN: We have had some ammonium nitrate go overhead and collect on the catalytic combustor catalyst, and also collect in a heat exchanger in front of the combustor catalyst, but there's been no evidence that we have found of any ammonium nitrite. Now I won't say that we've run any extensive analytical work to determine this, but there has been nothing to indicate that this work should be done.
Q. At what pH do you keep your return condensate?
O'BRIEN: Near or at 7.0.
Q. That would be excess ammonia then.
O'BRIEN: Well, normally that would be right, but don't forget, this particular plant has in the feed, 25 per cent CO_2 which gives this pH the presence of CO_2 or alters the pH that you'd normally expect in ammonium nitrate as being on the basic side.
Q. Well, is it not then excess ammonia?
O'BRIEN: No. There's no excess ammonia.
Q. No excess ammonia in the condensate returning to the absorber?
It's on the acid side, then.
O'BRIEN: Right.
Q. You said the scrubber operated at 220 and the neutralizer at 250, and I didn't see any cooling in between. Is that just heat losses to the atmosphere in this case?
O'BRIEN: Yes, there's a continuous draw off and makeup of some cool condensate and there's a slightly lower pressure in the scrubber than in the neutralizer. And also the neutralizer is operating at a much higher nitrate concentration than the scrubber. The boiling point in the neutralizer is higher than the boiling point in the scrubber.

tower?
O'BRIEN: I don't know that we have set any maximum allowable. We have operated with as high as 13% ammonium nitrate in this water.
Q. I have an inconsistency in my notes here. You ran all your tests at low temperature. You have 13% nitrate in your tower condensate, and you're not considering (I know you're considering it but you didn't go into it in your paper) that this material goes to the reheater and in your catalytic combustor into areas of extremely high temperature. Now isn't that the basic question of using this material or did I miss something?
O'BRIEN: Well, the 13% is only on an upset situation.
Q. Well, okay, let's go back to one and a half per cent.
O'BRIEN: Okay. Now the one and a half per cent, the test work was done at five and a half per cent. And the water only goes through a cooler before it goes into the nitric acid absorber.
Q. No, what I'm speaking of, though, is the carry over from the absorber through the gas train, through the preheater and the reheater and then to the combustor.
O'BRIEN: We have noticed on shutdown on one occasion a heat exchanger in front of the catalyst combustor which had some nitrate deposit in it, but in this particular plant, the gas going off the top of the absorber goes right to a steam preheater and through a second heat exchanger into the combustor. It doesn't go through the regular nitric acid train heat exchange.

In another plant that does follow the normal heat exchange pattern, we have found a solid ammonium nitrate on the surface of the catalytic combustor catalyst. And apparently had no problem during operation. The catalytic combustor at that time was opened for another reason, not because of pressure drop or some other indication that

The temperature in the scrubber is controlled by the concentration in the scrubber.

Q. Now that the slide is back on, I think I see the answer to my other question. Normally, you couldn't take all the water from this reaction back to nitric acid or you'd have too much. I see some going to the urea plant and I guess some goes to the atmosphere.

O'BRIEN: Some goes to the atmosphere with the CO_2, but solution 32 contains roughly 20 per cent water and some is - the water is controlled in the concentration of the urea, and that's where this stream going to the urea plant is used for diluting the urea concentration to give a 20 per cent water concentration in the finished solution.

Q. What is the maximum concentration of ammonium nitrate you have in your condensate that you feed to the there was something wrong with it. The fact that it was coated with ammonium nitrate was discovered as kind of a side thing, after opening the vessel.

Q. That doesn't bother you to have ammonium nitrate on that catalyst at, say, 1100 degrees?

O'BRIEN: No. Well, ammonium nitrate cannot exist at 1100 degrees. It decomposes.

Q. Right, but it's heating up to get to that point.

O'BRIEN: I'm not talking about a large quantity of this material. It is possible to get this deposit on start-up and shutdown. On a shutdown you get some deposited on the catalyst. So when the plant is started up and the temperature gets back up, the nitrate has decomposed, and it is swept out with the rest of the gas.