RECOVERY AND REUSE OF AQUEOUS EFFLUENT FROM A MODERN AMMONIA PLANT

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Production of synthetic anhydrous ammonia is a large industry in the United States. Production in 1969, for example, was about 12½ million tons. While the ammonia industry did not expand between 1968 and 1969, ammonia production has nevertheless increased at a substantial rate in the last twenty years. Production in the U.S. in 1950 was about 1½ million tons, and so the industry has increased its production at an annual rate of about 11 or 12% for two decades. Ammonia production, based on data published by TVA, is illustrated on Figure 1.

Patterns of production

There is presently an excess of production capacity in the United States; installed capacity in 1969 was estimated to be about 17 million tons, and this will rise to something over about 19 million tons in the next two years, based on known projects in construction. While a substantial portion of the excess capacity consists of small plants, or plants which are technologically obsolete, it is significant to note that plant capacity is available for continued growth in production.

Currently, ammonia is produced by approximately eighty companies in the United States, in as many as one hundred separate plants. There has been a change in the pattern of the industry in the last five years in that large-scale plants now produce most of the ammonia, and it is interesting to note that the number of plants in operation is actually decreasing. It is the older small-scale plants which are being phased out. In the ammonia industry, the term "large-scale" generally applies to plants of capacity of 600 tons/day or larger.

The importance of the new large-scale plants is indicated by the fact that approximately 60% of today's capacity, and probably more than 80% of production, is of the new large-scale variety.

Ammonia plants are located in most parts of the United States, except for New England and the mountain states. There is one large plant in Alaska, but none so far in Hawaii. Figure 2 indicates location of plants in 1969. The location of the new large plants has tended to center on the Gulf Coast area, with a sprinkling of plants in the midwest farm belt. These plants are located either near the source of low cost natural gas, or near the heavy agricultural marketing area. The historic pattern of small ammonia plants serving a local market seems to be changing. We have seen a significant increase in long distance transport of ammonia, and expect to see more.

New technology

The new large-scale plants feature some new technology, such as use of centrifugal compressors, new and improved catalysts, and a system for efficient utilization of energy derived from waste heat. The process is briefly described below, and a flow sheet of a typical plant is shown on Figure 3.

Natural gas feedstock is partially reacted with an excess of steam in a primary reformer to produce hydrogen and carbon monoxide, which is then mived with air, the source of nitrogen, and further reacted in a secondary reformer. The carbon monoxide in the gas is reacted with excess steam in a two-stage shift converter to produce carbon dioxide and additional hydrogen. This stream is colled, and most of the unreacted steam is condensed and separated as process condensate, one of the waste streams under consideration.

The synthesis gas is next scrubbed to remove carbon dioxide and remaining trace amounts of carbon oxides are catalytically reacted with hydrogen to form methane. The purified synthesis gas contains hydrogen and nitrogen and small amounts of methane and argon.

The gas is compressed to the synthesis pressure by a centrifugal compressor. The fresh gas is joined with recycle gas from the converter, and is chilled with refrigerant so that liquid ammonia is condensed. The separated gas is heated and enters the ammonia converter where the synthesis of ammonia occurs over an iron catalyst. Only a fraction of the feed is converted into ammonia, and so a large amount of unreacted gas is recycled. The inerts, which tend to accumulate in the synthesis loop are regulated by purging some gas. Liquid ammonia product is chilled and delivered to storage.

The steam system of an ammonia plant is closely integrated with the process. Process heat is recovered and used for BFW preheating, steam generation, and superheat duty. Steam is used in driving the pumps and compressors, and is used in the reforming and shift reactions. The high pressure steam system used in modern ammonia plants, over 1,000 lb./sq. in., requires a high purity boiler feed water. This is provided by demineralization utilizing ion exchange.

An aerial view of an ammonia plant is shown in Figure 4. The process equipment and control room occupy an area about 200 feet by 400 feet. Also shown is the cooling tower

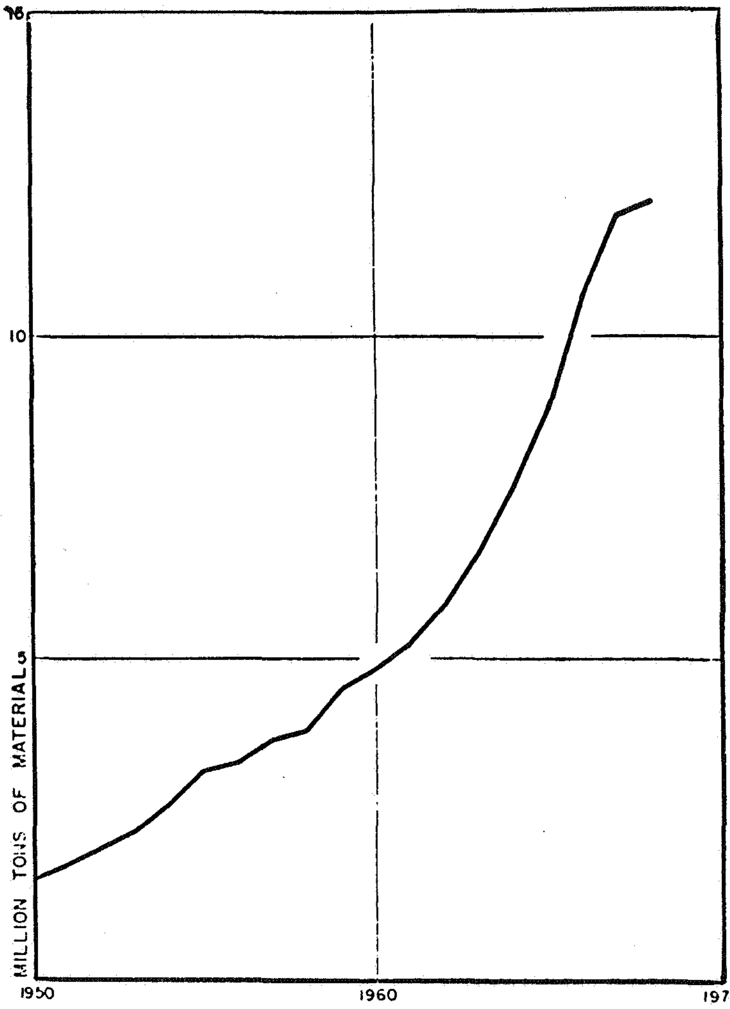

Figure 1. Anhydrous ammonia production in the United States.

and product storage area.

Aqueous effluent

The aqueous effluent from this type of chemical plant can be grouped into two general categories: (1) spill and purge. Spill includes effluents which occur as a result of operating upsets or mechanical failures. The occurrence is not predictable, and in a well-built and well-operated plant spills occur rarely if at all. It is not the intent of this report to discuss the various engineering and operating practices which are intended to prevent or contain spills.

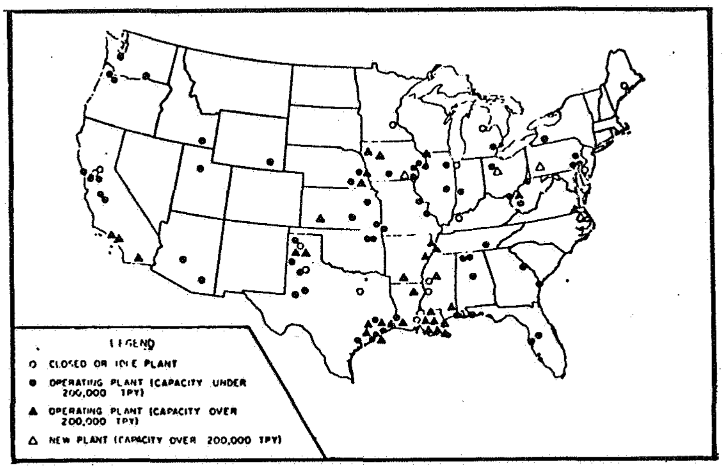

Figure 2. Ammonia plant locations.

The purse from a chemical plant, and specifically from an ammonia plant, is a continuous, twenty-four hour per day, flow of material from the plant. It is a sort of valueless byproduct, materials which derive from the process unit and which have been discarded because (a) recovery of the chemical content is not economic and (b) discharge of these materials into a convenient body of water has been, in the past, considered acceptable practice.

The purge from an ammonia plant, say a typical modern 1,000 ton/day plant, is comprised of the following:

1. Process Condensate—the stream of water, resulting from unreacted steam introduced into the steam-methane reformer. It is approximately 200 gal./min., or 290,000 gal./day, containing approximately 1,000 ppm of ammonia in the form of ammonium bicarbonate, and approximately 2,000 ppm of organic matter, principally methanol. Other organic compounds are also present in lesser quantities. Small amounts of various metals are also present.

The ammonia is formed in the first stage of shift conversion, where, in the presence of the iron-containing shift catalyst, a small amount is formed, not intentionally, and some of it is dissoved in the process condensate. The condensate is saturated with carbon dioxide from the gas; the ammonia and carbon dioxide are principally in the form of ammonium bicarbonate. The condensate contains small amounts of sodium, iron, copper, zinc, calcium, magnesium, and silica, which impurities enter the process stream through contact with catalysts, internal refractory, vessel walls, and piping. The organic matter is principally methanol, formed in the second state of shift conversion which contains a copper catalyst.

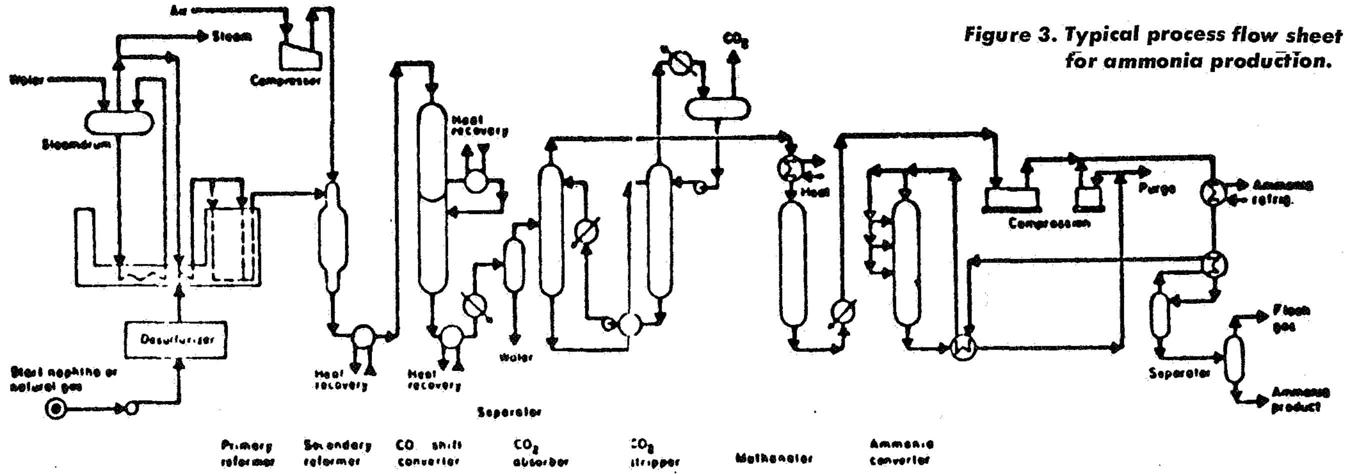

Figure 3. Typical process flow sheet for ammonia production.

Table 1. Effluent aqueous purge from an ammonia plant.

	Process condensate	Water treating effluent	Total
Quantity, gal./day	290,00	700,000	990,000
Suspended solids, ppm	—	170	120
Ammonia, ppm	1,000	—	290
Dissolved solids, ppm	—	1,200	850
Organics, ppm	2,000	—	580

Table 2. Ion exchange feed and product.

	Ion exchange feed, ppm	Ion exchange product, ppm
Ammonia	20	—
Carbon dioxide	40	—
Organic material	50	—
Metals	0.6	0.05
Silica	0.01	0.01

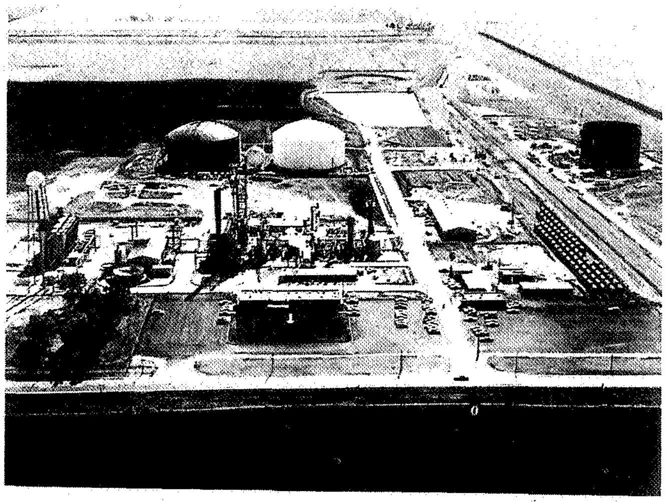

Figure 4. Aerial view of an ammonia plant.

2. Other aqueous effluent streams which originate in the water treatment plant, the steam boilers, and the recirculating cooling water system. It is not of particular interest here to discuss these systems, except to repeat that the water treatment plant generally includes a demineralizer to purify boiler feed units, and that the water treatment effluent is therefore relatively high in both water quantity and solids content.

As mentioned above, the demineralizer ion exchange resins become saturated and are regenerated periodically. A strong acid, usually sulfuric, is used to regenerate the cation exchange resin, and anion exchange resin is regenerated with sodium hydroxide. The effluent from the demineralization plant contains the dissolved ions removed from the raw water plus the chemicals used in regeneration. Other streams comprising the water treating effluent are the cooling tower blowdown and the boiler blow down.

The combined water treatment effluent from a typical 1,000 ton/day ammonia plant is about 500 gal./min., or 700,000 gal./day, containing about 170 ppm of suspended solids and about 1,200 ppm dissolved solid.

The quantities of aqueous effluent are summarized on Table 1.

Recovery of the process condensate is at best only marginally justified on the basis of plant economics alone. It is generally more convenient to install a demineralizer adequate to provide all the makeup boiler feedwater from a raw water source. Given an incentive to reduce aqueous effluent, we believe that recovery and reuse of the process condensate by removing most of its impurities can be accomplished at a relatively small cost.

Treating system

A system of treating process condensate is suggested in which this stream, which is normally discarded, is recovered, purified and used as boiler feedwater. This system would reduce the plant effluent in two ways. Firstly, the process condensate is recovered and used and secondly, the demineralizer effluent is reduced since the need for demineralization of raw water is decreased. The aqueous effluent from the plant is reduced in both volume and in quantity of solids.

The flow sheet of the proposed system is shown in Figure 5. The system consists of a stripper and an ion exchange unit. The process condensate is fed to a stripping tower to remove the volatile gases—ammonia, carbon dioxide, and methanol. The stripper overhead is condensed to recover aqueous ammonia. The stripper is expected to reduce the ammonia, carbon dioxide and methanol concentration to about 20, 40 and 50 ppm, respectively.

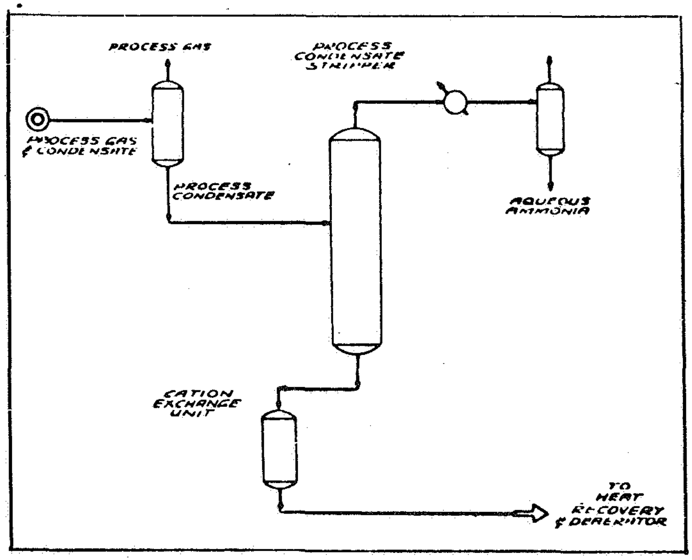

Figure 5. Process condensate recovery.

The stripped water is sent to an ion exchanger where the heavy metal ions are removed and replaced with ammonium ions. The amount of ammonia added to the water is very small compared to the amount removed in the stripper. The ion exchange unit produces boiler feedwater of comparable quality to the demineralizer with respect to heavy metals. Regeneration of the resin is expected to be very infrequent, and would be accomplished with an acid followed by ammonium hydroxide to convert the resin to the ammonia form. The water from the ion exchanger joins the fresh demineralized water, and is used as boiler feedwater.

The proposed system would introduce small quantities of ammonia, carbon dioxide, and organics, which are not removed in the stripper, to the steam system. No adverse effects are expected. The ammonia, carbon dioxide and most of the organics are expected to leave the steam drum with the steam, based on experience with a somewhat lower pressure boiler in a commercial ammonia plant. The ammonia, carbon dioxide and organics would leave the steam system via the process steam, which is about one-third of the total flow. The presence of small amounts of these extraneous gases in the process steam is not expected to present a problem. In the primary and secondary reformers ammonia is dissociated into its elements, and carbon dioxide is already present in large amounts. It is anticipated that the high temperature in the reformers will dissociate the organics also.

The presence of organic materials in the steam may contribute slightly toward a tendency to foam. Experience with lower pressure boilers, but with much higher concentrations or organic material, indicates that such tendency will not be troublesome.

Evaluation

Process condensate strippers have been in commercial service for some time. In order to evaluate the proposed system that stripped water from one of these units, which normally was discarded, was further treated with cation resin in a pilot study. Typical analyses of the ion exchange feed, and the ion exchange effluent are shown in Table 2.

The ion exchange was successful in removing most of the heavy metals, as expected. The total solids of the treated condensate was less than 0.1 ppm, which is about the same purity as demineralized water.

The organic matter in the treated process condensate could not be distilled with atmosphereic distillation; the residue was found to be soluble in water. No oily film could be detected and no organic carbon compounds could be extracted from the aqueous phase with carbon tetrachloride, a solvent normally used for this purpose. The residual organic compounds, principally alcohols and aldehydes, will probably be released from the boiler water at its operating temperature.

Because the proposed system would recycle the process condensate within the process, this stream would be eliminated as an effluent, and of course ammonia content of the plant purge would be eliminated. In addition, because the recycled process condensate serves as feedwater to the high pressure steam system, it would reduce the requirement for demineralized water by a proportionate amount, and thereby reduce the effluent attributed to the demineralizer.

Over-all effect

The over all effect of the proposed system on acueous purge from the ammonia plant is illustrated in Table 3. As can be seen, the quantity of aqueous effluent is reduced by about 35%. While the concentrations of suspended solids and dissolved solids increase slightly, the absolute quantities are reduced by about 10% and 30% respectively. The greatest benefit, of course, is in the elimination of ammonia and organics as components of the effluent. The possibility of adverse effects of reusing process condensate within the plant is considered to be remote.

Table 3. Overall effect of condensate recovery.

	Without condensate recovery	**With condensate recovery**
Quantity, gal./day	990,000	640,000
Suspended solids, ppm	120	170
Ammonia, ppm	290	—
Dissolved solids, ppm	850	920
Organics, ppm	580	—

The authors are pleased to acknowledge that the recovery system discussed herein is the result of a team effort within The M.W. Kellogg Co., and that particularly the work of Mr. Frank Jester, of Kellogg's Design Engineering Department, has contributed most effectively toward the development of this system.

DISCUSSION

SCHIEBER—Universal Interloc: I assume that steam will be used for stripping of the process condensate. What are the data on which column design is based? What are temperatures, pressures, reflux raio and theoretical number of plates?

FINNERAN: It is correct that steam will be used for stripping the process condensate. The process condensate contains ammonia, carbon dioxide and organic material; the vapor-liquid equilibria for this system is fairly complex in that chemical equilibrium, as well as physical vapor-liquid equilibrium, is involved. Some experimental data are available, but the concentration range involved is so low that published experimental data are not extensive. For these reasons, the design basis for the stripping tower is empirical. As we mentioned in the paper, process condensate strippers, based on this empirical design, have been in service in commercial ammonia plants for some time.

The operating pressure for this type of tower is generally quite low, say 10 to 15 lb./sq. in. gauge, and the temperature is essentially the boiling point of water at this pressure.

Towers have been designed with sieve trays, say up to 30 trays, as well as with raschig ring packing. Reflux ratio varies widely, dependent upon how the tower overhead is handled.