MINED UNDERGROUND STORAGE FOR ANHYDROUS AMMONIA

The trend to large volume shipments which must be quickly handled dictates use of mined storage for anhydrous ammonia if such caverns can be provided.

S. E. Scisson
Fenix & Scisson
Tulsa, Okla.

Current planning for use of pipelines and unitized trains for the transportation of anhydrous ammonia offers a good example of the technological advances made today. As advantageous as these developments are, however, they create problems. In this case, large volumes of economical storage must be developed or these new methods of transportation cannot be fully effective.

There are three types of storage now used for ammonia. They are: (1) Conventional steel storage tanks that are capable of containing the product under pressure, (2) refrigerated storage tanks that allow the product to be stored at near atmospheric pressure, and (3) mined underground storage caverns.

The large volumes of storage required for these new operations cannot be economically provided by conventional steel tanks so they may be eliminated from further consideration.

High delivery rates a problem

Traditionally, anhydrous ammonia has been stored successfully and economically by means of refrigerated storage tanks. The problem encountered by this type of storage when dealing with pipelines or unitized trains is the high rate at which the ammonia must be received into storage.

As an example, consider a pipeline delivery rate of 450 bbl./hr. This means that the terminal must receive 50 tons/hr. of product and refrigerate it to —28° F. Assuming a delivery temperature of 50° F., this would require a refrigeration plant of almost 1,800 hp. at an investment cost of approximately $550,000. This represents only the cost of cooling the product to storage temperature and does not include cost of the actual storage. It should also be noted that the efficient and economical operation of a pipeline could result in rates much higher than this example.

The third type of storage to be considered is mined underground caverns. Those who are familiar with the pipelining of LP-Gas know that similar problems encountered by that industry were successfully solved by constructing mined caverns. Since 1950, some 60 of these facilities have been constructed and successfully operated, with individual units having storage capacities ranging from 20,000 to 800,000 bbl.

As an outgrowth of this success, it is natural that the concept would be considered when problems involving large volume storage of other volatile liquids are encountered. In the case of ammonia, not only has this type storage been considered, it has been used, and two such caverns have already been constructed. The first of these, a 50,000-ton unit, was constructed for Norsk-Hydro at its Herya, Norway plant, and has been in successful operation for approximately one year. The second cavern, a 20,000-ton unit, was recently completed for the DuPont company at its Rapauno Works near Gibbstown, N.J.

Advantages and problems of caverns

A mined cavern is essentially a pressure storage vessel. The product is stored as a liquid at the normal earth temperature—usually about 60° F. and refrigeration equipment is not required. The product can be placed into storage at nearly any desired rate. LP-Gas storage caverns have received product at rates as high as 8,000 bbl./hr. without difficulty.

It is difficult to visualize a safer method for storage of a toxic product. Storage caverns are constructed at a depth that is sufficient to provide a hydrostatic water head exceeding the vapor pressure of the product. If there is leakage, it is water into the cavern rather than the product leaking out. As a container or vessel, a cavern would probably have four exposed connections, each being no more than two ft. above the ground. Even in the event of rupture of one of these four points, the stored product is 300 ft. below the surface and spillage is eliminated completely. The ammonia that would escape from a broken aboveground connection would be the vapors caused by the loss of pressure. Even in that event, there are well established procedures from the petroleum and the pipeline industries for controlling the loss until repairs are made.

Underground storage of anhydrous ammonia is not without problems, and one of them is both complex and difficult. It concerns the possible or probable contamination of the product by water. Water in a cavern may be in two forms. It can be water flowing into the cavern from natural fractures in the surrounding rock. Water of this type ordinarily can be greatly reduced and in some cases eliminated by grouting with Portland cement or chemical grouting materials. The water that cannot economically be eliminated, may in some cases be conducted to a sump for removal without contaminating the stored product.

The second source of moisture in a cavern is the dehydration of certain rocks. Some rocks, notably shales, although classified as impermeable by normal laboratory analysis, are porous and have water filled pore space. It has been observed that ammonia has the ability to dehydrate these formations, resulting in a displacement of water into the cavern. Indications are that the entry of ammonia into the rock pores will decrease as the invasion progresses outward and will ultimately reach an equilibrium point where the exchange ceases. Laboratory tests have also indicated that the structural stability and strength of the rock are not affected as a result of this exchange.

Solutions to moisture problems

The economics of underground storage, at this time, must be based on the assumption that the stored ammonia will be water contaminated and must be processed in order to meet current agricultural specifications.

The separation of the ammonia from ammonium hydroxide or aqua ammonia, the water-contaminated product, is a simple and well known process. It consists of heating the mixture and then condensing the ammonia gas. The quality of the resulting anhydrous ammonia will meet specification requirements and the remainder can either be marketed as aqua ammonia or fractionated to reclaim the remaining ammonia, depending, of course, upon the market conditions and the economics.

Geological investigations are not precise enough to determine before the underground construction has started the exact amount of aqua ammonia that might be produced in a cavern. However, tests during the construction period should provide such design criteria. It will require about the equivalent in BTU's of 1,000 cu. ft. of natural gas to recover one ton of ammonia. There will be only a minor variation of fuel needed whether the contaminated ammonia has 2% or 20% of moisture. Based on emptying a cavern within a 30-day period, the capital cost for the equipment to treat all of the stored product will be about $10 to $12 per ton of storage capacity.

Recent developments and experiments have given industry new and interesting information on stratification and diffusion of moisture when the ammonia is stored under pressure, at a constant temperature, and with a relatively small amount of water in a large volume of ammonia. At some locations, it may be possible to collect the contaminating water as aqua ammonia, remove it on a regular schedule, and keep the remaining ammonia in storage as a specification product. In such a case, the cost of the process equipment would be only a fraction of that required if all of the product would need to be processed as it is removed.

Another solution for the water contamination problem would be to sell the ammonia on the basis of nitrogen content. This would be a radical departure from the custom of the United States agricultural industry. However, a similar procedure has been common in the petroleum industry for almost 100 years. So the solution is not without precedent.

Geological requirements for caverns

The first requirement for the storage of ammonia underground is suitable geology. Locations must have a structurally sound, impervious rock strata, at a feasible depth that meets the normal requirements for a storage site. In addition to all of the geological requirements for an LP-Gas storage cavern, there must not be a chemical reaction between the ammonia and the rock in the proposed storage strata. Also, it is necessary to be more selective in locating sites where the underground water problems will be minimum. Figure 1 illustrates the areas of the United States which are generally suitable for mined caverns.

Figure 1. Potentialities for mined storage. Shaded area not favorable for mined cavities.

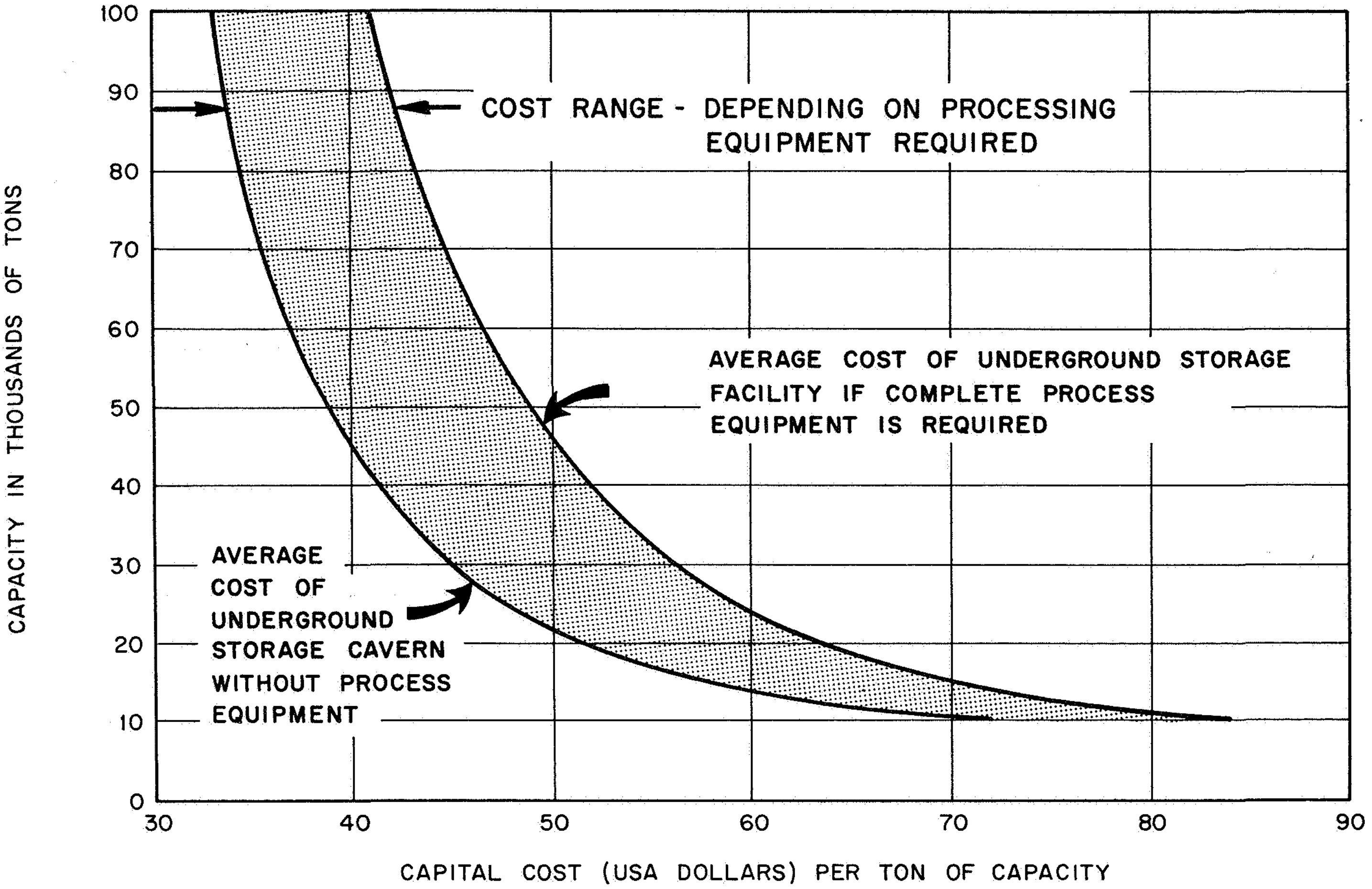

Figure 2. Average capital costs for mined underground storage facility, at average location, for anhydrous ammonia.

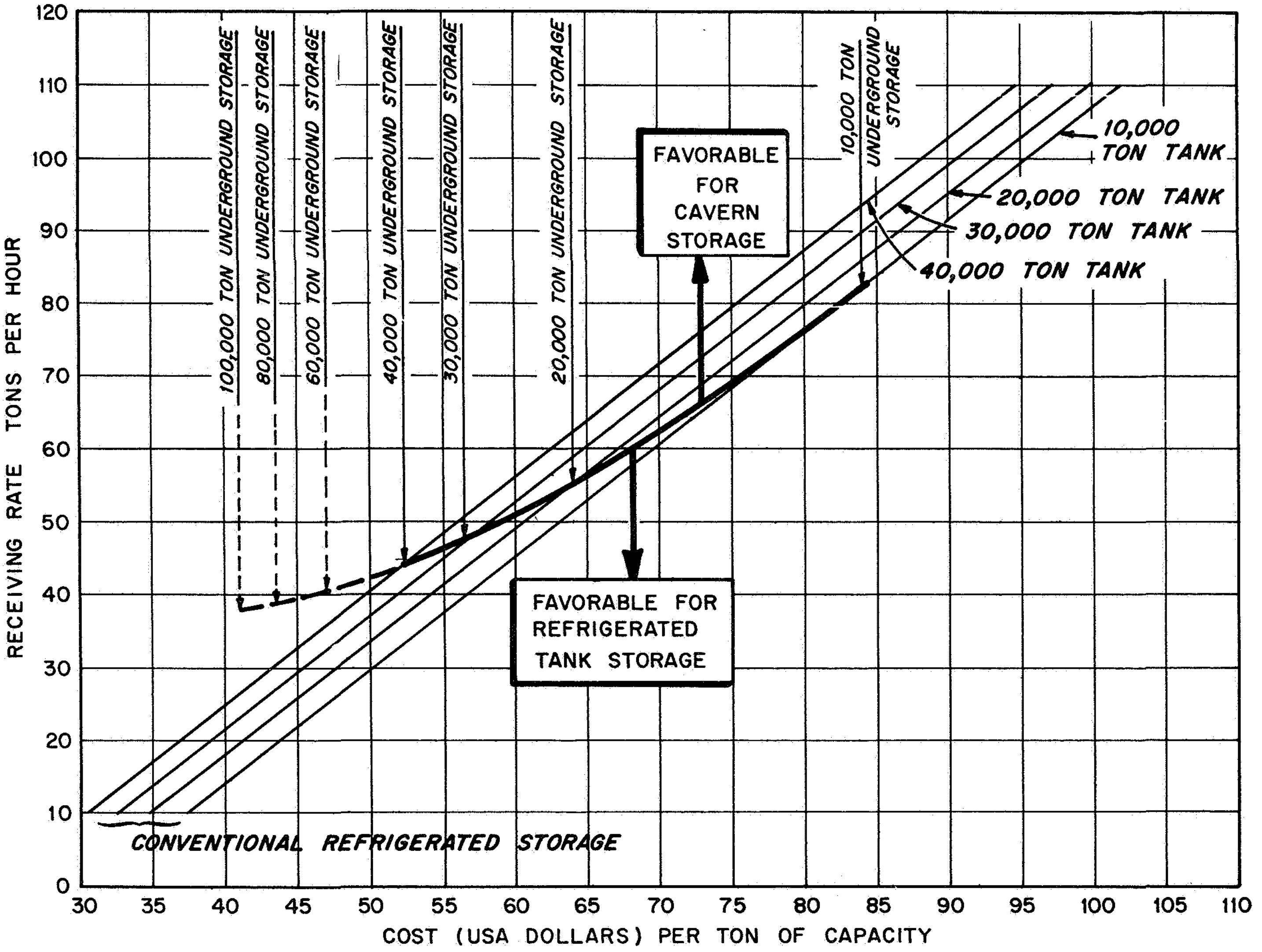

Figure 3. Average capital costs of anhydrous ammonia storage facilities as a function of the rate of filling.

Figure 2 shows estimates for the construction costs of underground storage facilities, both as to the bare cavern facility and as to cases in which reprocessing equipment is required to remove moisture as the ammonia comes out of the storage cavern. Hopefully, most cases would be somewhere between these estimates. Even though these estimates are for average locations, they should be within a plus or minus 10% for nearly all areas where underground storage is possible.

Figure 3 shows the cost of various sized underground and refrigerated storage facilities in relation to their filling rates. It also shows the general relationship between sizes and fill rates where each type of storage will usually be more economical.

Generalizations and conclusions can be both difficult and misleading, but we feel that mined underground storage caverns should be considered for anhydrous ammonia providing:

1. You have a need for 40,000 tons or more of storage facilities in an area that is designated in Figure 1 as a desirable area.
2. If it would improve your operations to have a fill rate in excess of 40 tons/hr.
3. If you can sell your product on the basis of its nitrogen content and avoid the cost of most, if not all, of the reprocessing equipment.
4. If your operations require more than the normal safety requirements.

Discussion

Q. How do you handle inerts that are sometimes in the ammonia, and what pressures do you maintain?

SCISSON: We store the product at natural ground temperature. It is stored under pressure at equilibrium and you will have your liquid phase with whatever space is left in the cavern filled with vapor. As you put in additional fill, vapors condense; as you withdraw liquid vaporization occurs to maintain equilibrium. This means that for a typical installation with a ground temperature of about 60 degrees you would have a pressure around 90-95 pounds gauge. As you fill with liquids the pressure will increase about five pounds and as you withdraw liquids there will be a drop of about five pounds.

The venting of inerts is somewhat of a problem and I'm not fully capable of telling you what the operators have been doing on that. The inerts must be vented and withdrawn. There are high points in the caverns for venting and, of course, with the LPG caverns, we have a problem of lighter components mixed with the propanes and butanes which must be collected, and they are usually burned.

Q. Will pre-existing caverns serve the purpose? If you have dry salt mines which are at a reasonable depth below surface, would this be a sufficiently impervious material for containment as well as be generally suitable?

SCISSON: The salt itself is impervious and would be suitable. The only actual underground storage of ammonia that I know of in salt was an experiment that Phillips Petroleum made out in West Texas some years ago. I assume from what I've heard that it was not successful and do know they haven't continued it or gone into it in other places.

Q. The cavern costs you quoted which were approximately $50/ton installed, is this for excavation in rock or in lesser materials?

SCISSON: All of this is based on excavation in rock that is structurally capable of holding an opening that is impervious, impermeable, and is hard material. The cost figures quoted would include everything for the storage from the fill line on top to a discharge flange on withdrawal pumps.

Q. On your map you indicated quite an area in California which would be suitable for this type of storage. Can you predict the earthquake activity in these fringe areas sufficiently to guarantee the integrity of this type of storage?

SCISSON: Even though the map shows California as being suitable for mined underground storage and we have found one or two locations that did appear good, most of our efforts in finding locations in California have not been successful, and there have been no installations of this nature built in California.

Q. Could you comment on the two existing storage facilities, the one in Norway and the one DuPont has?

SCISSON: In DuPont's case the product being stored is for chemical use, and their moisture requirements are not as stringent as they are for agricultural purposes. The moisture in the form of free running water was very small at that location and it appears that they will have a very good product coming out. The rock was hard and non-porous meaning there will be no problem due to rock dehydration. The principal reason DuPont built their storage cavern was safety. They had need for a large volume of ammonia storage at a location that was within the glide path of the greater Philadelphia airports.

In Norway there was a different condition. Their large cavern was built for the purpose of buying surplus ammonia on the world market and marketing it in the spring—principally in Denmark. They also have a very impermeable and nonporous rock formation. They made no effort to completely grout or seal off all of the inflowing water, and neither did they make any attemp to collect the water and remove it on a regular schedule. They sell their ammonia on the basis of nitrogen content.

Q. How much water is involved?

SCISSON: The water inflow into the Norway cavern was about one gallon per minute; it's considerably less for DuPont at Gibbstown.

ANON: The use of such underground storage in limestone areas would present some interesting problems and possibilities. Where ammonia plants are in certain salt water areas as Aruba, the sea water is actually a saturated solution of calcium bicarbonate and when ammonia hits it, it makes the most beautiful white marble you have ever seen. In a limestone area the water that leaches on could very well either contaminate the ammonia or it might even seal itself off by building its own coral ring in previously existing crevices.

SCISSON: If you have a limestone where there'll be a reaction, it would not be suitable. If you have one where salt water would be coming in, it would not be suitable. Our experience with limestone has been that about 50 to 60% of the location that we have investigated have been satisfactory and maybe as much as 40% of them have been unsatisfactory due to solution cavities, fractures, or other problems. The batting average on shales has been much higher, but with shales, even though they are impermeable, they have some porosity and there is a problem, for some indefinite time, of dehydration of the rock.

Q. Have you investigated the public's viewpoint on this, or any government agency in view of the concern over contaminants in air and water?

SCISSON: Very few states have any regulations that pertain to this type of construction. Pennsylvania is one of the few states that have any regulations at all and they only apply to safety during the mining operation.

Before starting a project of this nature, it's always been our custom, and the custom of our clients, to go to the state fire marshal and explain what we're doing; to go to the state geologist and ask for their assistance. They have been quite helpful in providing information. Once they understand what we're doing. we've had very little resistance.

Q. Could you tell us what kind of investigation you have to make and roughly how much it costs?

SCISSON: To investigate a site for a project would first require going to the state geologist, get all of the information and decide if the site appears to be worth core drilling. If after that investigation it looks like it might have a chance to be feasible, your next step is to institute a core drilling program. The exact number of holes that you might need for location would vary dpending on the size, the complexity of the geology, and the previous information you had.

Generally you would want anywhere from three to seven core holes, circling maybe a 10 acre plot or a 20 acre plot, depending on your size. In each of these core holes you would take selected samples, run laboratory tests for permeability, porosity, reaction with water and reaction with ammonia. You would want to check the rock strength both before and after ammonia had been exposed to it. Also whether or not there's any chemical reaction or dehydration of the rock, and if there is any dehydration you would want to go further and check your structural makeup of the rock before and after.

In the core hole you would want to take straddle packers and run formation pressure tests on the stratas that appeared to be suitable to get some idea of the amount of fracturing in that particular strata. On the basis of all this, why, you can derive the information that is necessary for establishing the design criteria for a cavern.

The cost varies depending upon the complexity and depth, and most of the variance is in the cost of the core drilling. On sites that are suitable, you'd be able to make a complete investigation for somewhere between $25,000 and $40,000. If a site on the first hole appears to be unreasonable, and you find reason to think that there would be problems, you can usually stop an investigation before you spend over more than $5,000 to $8,000.

Q. In a 40,000 ton storage, how much of that is available? By that I mean , how much, how far can you pump out? There must be a sum I'm sure.

SCISSON: Well, for what we would term a 40,000 ton storage unit, we would expect you to take out 40,000 tons. It would be oversized about 3 and 5 per cent so that you would be able to have a working storage of 40,000 tons. When you pump out all of your liquid, it will still be completely filled with vapor at your ground temperature pressure, and that would be considered a dead inventory that would stay there until such time as you were ready to abandon the cavern.