



# Water in Industrial R717 refrigeration systems

In earlier day's Wijbenga has used some CPW15, also known as "system cleaner" an effective unit to remove water from  $\text{NH}_3$  systems. In 2019 when Wijbenga received an request for another CPW 15 we got in contact again which ended up in an cooperation between Cool-Partner and Wijbenga. For both company's there is a focus on industrial refrigeration and heat pumps with Natural refrigerants. What we share is that Wijbenga and Cool-Partners are convinced the problems occurred due to air and water in refrigeration systems are underestimated.

Per Skærbæk Nielsen, owning an consulting company in the industrial refrigeration Cool-Partners, saw the need for better air and water purgers and started developing a complete product range for different applications. Text below is an summary of an article from Cool-Partners.



## Water and ammonia

The affinity between water and ammonia is very high, so ammonia will mix with water when it gets a chance to do so. Opening an ammonia refrigeration system to the free air will allow for some water to get into the system and systems operating on vacuum will get water in the systems with the air being sucked in through small leaks in shaft seals, valve stems etc.

Pure anhydrous ammonia will normally have a max. water content of 0,3 % when delivered from the factory. So small amounts of water will also come with the new ammonia from the factory.

An ammonia refrigeration system with liquid separators behaves like a distillery where the water will concentrate on the low-pressure side in the evaporators and separators. Ammonia liquid with water enters the evaporators and separators and ammonia vapor with nearly no water vapor leave to the compressors. So, in a very short time all the water is concentrated on the LP side of the system and there is nearly no water at all left on the HP side of the system. This effect means that the water concentration on the LP side of the system can and will easily rise to quite high values.

## Thermodynamic effect of the water in the ammonia

The water in the ammonia on the LP side will affect the evaporating temperature in the evaporators as the ammonia and water mixture will evaporate at a higher temperature at the same pressure than "clean" water free ammonia. This change in the pressure / temperature relationship means the compressors on the system will have to create a lower pressure to keep the desired temperature in the refrigeration system.

The necessary lower pressure means the compressors must work more and harder to keep the desired temperature resulting in more energy consumption and less capacity (loss of COP value) on the system.





Test of CPAW12 system on large coldstore scaled.



## Chemical effects on the oil

Water contamination of the ammonia refrigeration system will not only affect the COP of the system but also turn it into a very chemical reactive place, where all kinds of chemical reactions will happen. The presence of both water and air (oxygen) in the system will allow for chemical reactions with the oil. The oil will react with oxygen from either air in the system or from any water present in the system as the H<sub>2</sub>O also delivers oxygen to the oil.

Oxidation of all kinds of industrial refrigeration oils will create organic acids. Ammonia with just a little bit of water is a very strong base which immediately will attack the acid and, in the end, create amides (nitrocompounds). Some of the long oil molecules will become an amide as the amide structure will be attached to the oil molecule. Amides are a group of polar substances where most of them dissolves in ammonia but not in oil. The rule is that polar substances dissolve well in polar substances but not in non-polar substances. Ammonia is polar and refrigeration oils are non-polar.

As any dissolved amides and the oil can travel with the ammonia they will end up in the evaporator. If the evaporator is not hot gas defrosted it can contain high amounts of oil. And if the oil contains amides which are polar substances, it will stick to the metal surface in the evaporators. A polar substance will stick much more to a metal surface than a non-polar substance due to the electric potential difference.

So, a polar oil can possibly stick much more to steel surfaces like the stainless steel plates in a plate heat exchanger. This is a known phenomenon as polar substances like phenol and amines are used by oil companies as additives to make motor and gear oils stick much more to metal surfaces to ensure proper lubrication.

Tests on this oil "sticking" phenomenon in evaporators has been carried out in cooperation with Cool Partners. These tests have shown a distinct dif-

ference in the time it takes for a used oil from an evaporator and new oil of the same type to drain off a plate from a plate heat exchanger. The used oil which will properly contain polar amides showed to drain much slower of the plate than new unused oil.

The only thing we can do to avoid these chemical reactions from happening in the oil is to efficiently remove any air and water continuously from the systems and do it right from the starting up of the system.

## The effect on ammonia heat pumps

This phenomenon is properly what is often seen on industrial ammonia heat pumps where the evaporators are not performing as expected and / or calculated. The oil seems to stick to the heat exchanger plates or pipes and reduces the heat transfer to such an extent the heat pumps cannot meet the capacity demand and COP value they were supposed to.

Industrial ammonia heat pumps are especially vulnerable for this phenomenon for several reasons. These types of heat pumps are mostly built as high-pressure float valve-controlled systems (no HP receiver). And these types of systems must have a little hot gas bypass to ensure they will not stop working due to small amounts of non-condensable (air) gathers in the HP float valve preventing it from opening. (Note: when saying HP float valve-controlled system it refers to the type of system. This type of system can also be equipped with a liquid level sensor and a motor valve controlling it instead of a mechanical HP float valve). Because of this bypass any air in the system will be passing on to the LP side and continue to pass through the compressor from HP side to LP side. This gives the oxygen in the air possibility and time to react with the oil in the compressor.

As the temperatures and pressures in heat pumps are higher than normally seen on industrial ammonia refrigeration systems it increases the amount of chemical reactions and speeds up the reaction time. The "rule of thumb" is for every 10 °C higher temperature the chemical reactions double.

Most of the chemical reactions seen with the oil on ammonia heat pumps will also take place on in-



Figure 1A



Figure 1B

dustrial ammonia refrigeration systems, just much slower. So over time the oil will suffer from degradation, decomposition and create amides (nitro-compounds).

### Measuring the water content in the ammonia

The most common way for Industrial refrigeration service supervisors to measure the water content in the ammonia is to take a 100 ml ammonia sample from the LP side of the system in a special measuring glass and leave it in dry surroundings for the ammonia to evaporate. When the ammonia is completely evaporated, we assume only water is left and we divide the measured amount of water with 0,66 to get the volume of water into percentage by weight of the sample.

This method has shown to be rather inaccurate for some reason, but it is not clearly understood why. Using different measuring methods or measuring in different places on the same system will often give very different results.

One reason can be water is not equally distributed in the system with a tendency to concentrate in the bottom of vessels due to the difference in density between water and ammonia. If this is correct it

might explain why a series of measurements on the same system can show very different results.

On figure 1A and 1B a CPAW 12 system (combined air purger and water separation system) can be seen during test runs. On figure 1A the CPW 12 is running normally. On figure 1B the water concentration is high in the lower part of the CPW 12.

On figure 1B the bottom part of the CPW 12 is filled with water and in the upper part the ammonia coming from the LP receiver is boiling off and cooling the vessel of the CPW 12. If the  $H_2O$  and  $NH_3$  would mix completely at these concentrations, we would expect the vessel to be iced up equally in the area where the  $NH_3$  and  $H_2O$  is mixed.

The observations done on the CPAW 12 system indicates that water will concentrate at the bottom of the vessels at least at high water concentrations in the  $NH_3$ .

If this is correct and the water will not be distributed equally in the  $NH_3$  on the LP side of the system, it raises questions about where and how to measure the correct percentage of  $H_2O$  in the  $NH_3$ . I don't think anyone will have a clear answer for these questions. But practical experiences shows we can get very different measurements with the same measuring method dependent on where on the LP side and when we take the measuring samples.



Figure 2: Water drained out of the CPAW-12

### Alternative measurement method

Another way of measuring the  $H_2O$  content in the  $NH_3$  is to try and measure the evaporation temperature at the given pressure, like we do in the CPW 12. This measurement will give a very good idea about the penalty in temperature the  $H_2O$  in the  $NH_3$  is giving. Such measurements can be carried out, but they need to be done very accurately. We can take a sample of the  $NH_3$  with its content of  $H_2O$  out in a measuring glass and place a very accurate thermometer in it to measure the evaporation temperature. But we need to be very careful with the pressure, as we cannot rely on atmospheric pressure is 1 bar. We can have high pressure weather and low-pressure weather and we can be at sea level altitude or at maybe 800 m altitude. So, our surrounding pressure will easily vary enough to give a wrong measurement result. We will have to measure the surrounding pressure accurately which is difficult but luckily, we can get some help for this on the smartphones most of us have. An app called "Bar-O-Meter" can be downloaded for free and will make your smartphone able to do a quite accurate measurement of the surrounding

pressure when doing the evaporating temperature measurement. The Danfoss app "Ref tools" is also a free app and can provide us with the precise evaporating temperature at the given surrounding pressure for 100% pure  $NH_3$ . So, the special tools needed for this are all available for free on our smartphones.

However, there is another thing to take special care of and must be taken into consideration as well. The pressure on the boiling  $NH_3$  surface will be the sum of partial pressures where the partial pressure from  $NH_3$  is the only one affecting the boiling point of the  $NH_3$  in our test sample glass. This makes it very important to ensure that there is no air in the test sample glass over the  $NH_3$  liquid surface as this will affect the measurement. In practice this can be done by restricting the opening of the glass with an obstacle of some kind enabling the  $NH_3$  vapor to go out through a smaller hole and air will not go into the glass in counter flow. The hole has also to be large enough for the pressure drop to be negligible not to affect the measurement.

The conclusion is that reliable measurements of the water percentage are very difficult to perform. Some of the variations on the measuring results can be explained with a possible uneven distribution / concentration of the water on the LP side of the system, but not all.

### Calculating the effect of water in a $NH_3$ refrigeration system

#### Calculation program

Cool Partners have developed a program which can make these calculations accurately. The program will also calculate the effect of air pollution in the system by inserting how much higher the condensation pressure is expected to be because of air in the system. The program will calculate the system with water and any air contamination as well as without any contamination and show the difference in capacity and loss of efficiency.



The Cool partners calculation program is a free download from Cool Partners website: [www.cool-partners.dk](http://www.cool-partners.dk)

Calculating the total effect on the efficiency of water in the system is not possible as the effects on heat-exchangers where the oil gets sticky etc. can only be estimated, but the effect on the thermodynamic properties on the  $\text{NH}_3$  in the system can be accurately calculated.

### Calculations of water and air influence on Heat pumps efficiency

If the new anhydrous ammonia charged to the system contains approx. 0.3% water and approx. 1/3 of the  $\text{NH}_3$  is on the HP side of the system during normal running conditions, we will have 0.4 % water on the LP side. If we also assume everything is done according to best practice so only 0,1 % water is added to the LP side ammonia charge during initial startup of the system, we will have min. 0.5 % water in the ammonia on the LP side from the beginning. If we also assure everything has been done to pull proper vacuum prior to start up and care is taken to avoid any air in the system. Then only the non-condensable gases from chemical reactions with Zink, aluminum etc. will be present in the system. We can then estimate the condensing pressure is only 0.5 °C higher than it should be due to air (non-condensable gas) in the condenser.

We will end up with a new industrial heat pump build in a proper way and according to best possible praxis being started up with appropriately 0.5 % water in the ammonia on the LP side and 0.5 °C too high condensing pressure.

A heat pump running +20 °/+65 ° will have the following efficiency with 0.5%  $\text{H}_2\text{O}$  in  $\text{NH}_3$  on LP side, and 0.5°C higher CP because of air in the heat pump.

**System efficiency is: 94.7%**

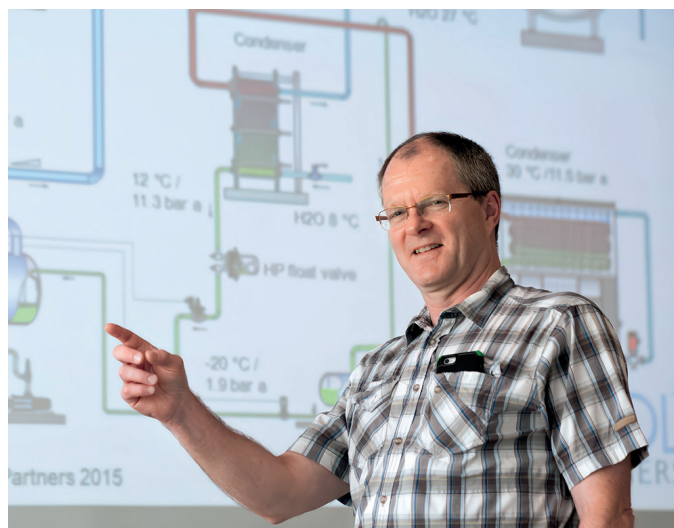
As it can be seen from the calculations even the very small amounts of water and air which must

be expected to be in a brand-new heat pump will have a damaging consequence on the efficiency.

### Conclusions

Water and air in industrial ammonia refrigeration systems and heat pumps have a very damaging effect on COP value and oil decomposition. The effect on the ammonia heat pumps is much worse than we are used in the refrigeration area and the penalty on the COP value is much more important as heat pumps are all about COP value. Most industrial ammonia heat pumps are sold because of their COP value and must often be guaranteed by the supplier. When the drop in COP value due to even very small amounts of water and air is not taken into consideration the supplier can end up in trouble not getting paid for the heat pump delivery as it is not meeting the guaranteed performance. To avoid these problems, it is recommended to mount efficient water separators and air purgers on such units right from the initial start of the system.

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