# Water in industrial R717 refrigeration systems.

Pump-circulated ammonia refrigeration systems are affected by water contamination, which affects both the evaporation temperature and the capacity, but it is very difficult to measure. On a heat pump, the output is easy to measure, and that has brought several contractors into trouble because the heat pumps lack capacity. Water in the ammonia is one of the important challenges they face because 1% water can reduce the capacity by 8%.

#### 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 the 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 maximum 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 leaves 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. If the new pure ammonia has a water concentration of 0,3% and half of the ammonia is on the HP side, we will soon have 0,6% water on the LP side.





## 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.

Calculations on the effect of water in the refrigeration systems must be based on these physical factors and demand knowledge of the impact on the compressors and system performance to be determined.

## **Calculation program**

Cool Partners has developed a program that 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. If the price of water separators and air purgers, electricity, and the running hours of the system are known and inserted, it will calculate the payback time for the investment as well.

The Cool Partners calculation program is a free download from the Cool Partners website: <a href="https://www.coolpartners.dk">www.coolpartners.dk</a>





#### 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 chemically 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 H2O 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 that immediately will attack the acid and, in the end, create amides (nitro compounds). Some of the long oil molecules will become an amide as the amide structure will be attacked by the oil molecule. Amides are a group of polar substances where most of which dissolve 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 have been carried out in cooperation with Cool Partners. These tests have shown a distinct difference in the time it takes for 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, was shown to drain much slower off 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 extend the heat pumps cannot meet the capacity demand and COP value they were supposed to.

Industrial ammonia heat pumps are especially vulnerable to this phenomenon for several reasons. These types of heat pumps are mostly built as high-pressure float valve-controlled systems (no HP receiver). 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) gathering 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 passed on to the LP side and continue to pass through the compressor from the HP side to the LP side. This gives the oxygen in the air the possibility and time to react with the oil in the compressor.

As the temperatures and pressures in heat pumps are higher than normally seen in 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 industrial ammonia refrigeration systems, just much slower. So, over time, the oil will suffer from degradation and decomposition and create amides (nitro-compounds).





## Measuring the water content in the ammonia and the CPAW 12 system

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 by 0,66 to get the volume of water into percentages by the weight of the sample.

This method has been 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.

In the pictures below, a CPAW 12 system (combined air purger and water separation system) can be seen during test runs where the CPAW 12 part is running normally on the picture to the left. In the picture to the right, the water concentration is high in the lower part of the CPW 12.





CPA 12 is a very powerful and efficient air purger, and CPW 12 is a very efficient water separator/purger, both with 12 kW nominal capacity. CPAW 12 is a combined air purger and water separator /purger system. The two products work together in a CPAW 12 where the fouled gas from the purge points to the CPA 12 and is also used as a heat source for the CPW 12. For more information on the CPAW 12, see the Cool Partner website:

www.coolpartners.dk





## The water percentage measuring function on the CPW 12 (water separator)

The controller for the CPAW 12 is monitoring the evaporating temperature in the CPW 12 and comparing it with the suction pressure in the vessel. When the evaporating temperature shows an offset compared to the pressure/temperature relation of 100% clean NH3, the controller calculates this offset into a water concentration in the ammonia in the CPW 12. The formulas used in the controller are only reliable up to approx. 40% to 50% water concentration in the ammonia. When the calculated water percentage reaches 40%, the controller gives an alarm to inform the service personnel that it is time to make a pump-down prior to draining the water out of the CPW 12. When the temperature reaches +10 °C (adjustable) independent of the pressure, the controller gives an alarm signal to inform service personnel to drain the CPW 12 for water. In the below picture to the left, the controller is measuring an evaporating temperature of +6.2 °C and a pressure corresponding to -31,6 °C on 100% NH3. In the picture to the right, the drained water with some broken-down oil components (nitro compounds) can be seen.





The CPAW 12 controller will not show any higher water concentrations than 50% as the formulas used for the calculations from the temperature/pressure offset are not sufficiently accurate or reliable at higher concentrations.

The observations done on the CPAW 12 system indicate that water will concentrate at the bottom of the vessels, at least at high water concentrations in the NH3. If this is correct and the water will not be distributed equally in the NH3 on the LP side of the system, it raises questions about where and how to measure the correct percentage of H2O in the NH3. I don't think anyone will have a clear answer to these questions. But practical experiences show we can get very different measurements with the same measuring method depending on where on the LP side and when we take the measuring samples.





#### **Alternative measurement method**

Another way of measuring the H2O content in the NH3 is to try and measure the evaporation temperature at the given pressure as we do in the CPW 12. This measurement will give a very good idea about the penalty in temperature the H2O in the NH3 is giving. Such measurements can be carried out, but they need to be done very accurately. We can take a sample of the NH3 with its content of H2O 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 an atmospheric pressure of 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 NH3. 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 NH3 surface will be the sum of partial pressures where the partial pressure from NH3 is the only one affecting the boiling point of the NH3 in our test sample glass. This makes it very important to ensure that there is no air in the test sample glass over the NH3 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 NH3 vapor to go out through a smaller hole, and air will not go into the glass in counter flow. The hole also has to be large enough for the pressure drop to be negligible so as not to affect the measurement.

In the pictures below from Cool Partners Training seminars, two different measurements can be seen on the same NH3 sample from a pump separator with very different results. The color of the NH3 in the sample also indicates there is severe pollution of the NH3, but this could not be confirmed by the "normal" measuring method. By measuring the evaporating temperature, we got a very different water percentage.



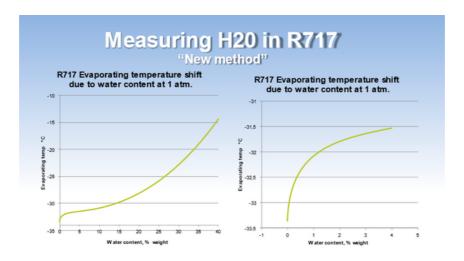




Evaporating temperature indicates approx. 15% H2O

H2O meassurement indicates less than 1% H2O after evaporation of NH3

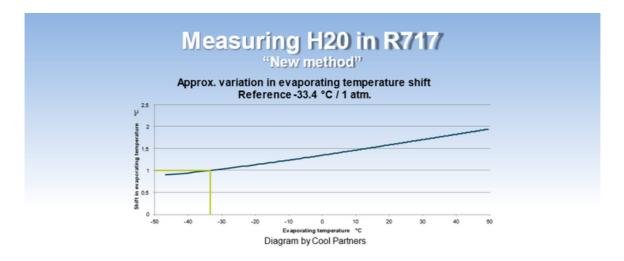
Curves below from Cool Partners training seminars can be used to determine the water percentage in a system from an evaporating temperature measurement of an ammonia sample taken from the evaporator.



The curve above gives the water percentage of the ammonia sample from the measured evaporating temperature at 1 bar pressure.







The above curve gives the correction factor for converting the measured evaporating temperature at 1 bar into the temperature off set of the given evaporator pressure where the sample was taken from.

The conclusion is that reliable measurements of the water percentage are very difficult to perform. Some of the variations in the measuring results can be explained by 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 NH3 refrigeration system

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 of the NH3 in the system can be accurately calculated.

To do these calculations, we need to know the exact evaporating temperature of the NH3 at different water percentage levels at the suction pressure in question. These can be found in different special handbooks where some calculation formulas are also given. Some of the calculation formulas will only be valid within some water concentration areas, which must be noted when using them.

The Cool Partners calculation program can do these calculations very accurately. (Free download from Cool Partner website: <a href="https://www.coolpartners.dk">www.coolpartners.dk</a>

Using the Cool Partners calculation program, we will try to calculate the effect on the performance and efficiency of a refrigeration system and a heat pump with different levels of water and air in the systems.





It must be noted that such calculations are only valid for making a business case for investing in effective water separators and air purgers if they can and will clean the system completely. Unfortunately, many industrial refrigeration systems are operated with water separators and/or air purgers which seems to work, as they find both water and air, but the systems are not cleaned completely. Experience and practice show many systems working with inefficient water separators and air purgers can have high amounts of water and air anyway when tested correctly for air and water. The water separators and air purgers need to rely on highly efficient separation systems with sufficient capacities for the job

The pictures below are prints from the Cool Partners calculation program shown with a -30 °C / +30 °C and 1000 kW capacity system running 5000 hours/year with varying amounts of water and air. As an example, an electricity price of 0.08 Euro/kWh and an investment of 33,333 Euro in an air purger and water separator are used for calculating savings and payback time on the equipment.

0% H2O in NH3 on the LP side and 0 °C higher CP because of air in the system. System efficiency is: 100%

1% H2O in NH3 on the LP side, and 1 °C higher CP because of air in the system. System efficiency is: 93,19%

Savings by removing H2O and air: 15,264.40 Euro/year, payback time: 2.2 years.

3% H2O in NH3 on the LP side, and 3 °C higher CP because of air in the system. System efficiency is: 86,36%

Savings by removing H2O and air: 30,503.40 Euro/year, payback time: 1.1 years.

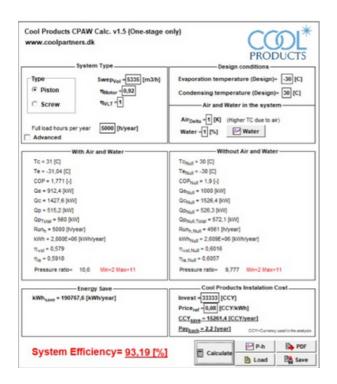
10% H2O in NH3 on the LP side, and 5 °C higher CP because of air in the system. System efficiency is: 76,76%

Savings by removing H2O and air: 49.641,60 Euro/year, payback time: 0.7 years.

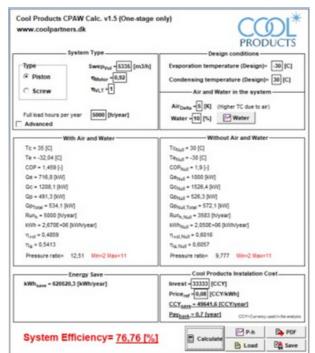




These calculations give a good picture of both the capacity and economic consequences of water and air pollution in the systems. As the calculations are done on a 1000 kW system, they can be multiplied by 2 or 3 for 2,000 kW or 3,000 kW systems (Note: payback times must be divided instead).











## Calculations of water and airs influence on heat pumps efficiency

As heat pumps nearly always are sold because of their COP values, water and air in the system can be very damaging for the economy in the investment. When the heat pump supplier has guaranteed the performance (COP) of the heat pump based on 100% pure ammonia, like the compressor calculations are based on, he can easily get in trouble when doing a performance test on the unit prior to delivery. If the new anhydrous ammonia charged to the system contains approx. 0,3% water and approx. 1/3 of the NH3 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 the initial startup of the system, we will have min. 0,5% water in the ammonia on the LP side from the beginning.

We also ensure everything has been done to pull the 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, aluminium, 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 built in a proper way and according to the best possible praxis being started up with appropriate 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 efficiencies with varying amounts of water and air in the system. (See calculations below)

0,5% H2O in NH3 on the LP side, and 0.5 °C higher CP because of air in the heat pump. System efficiency is: 94,7%

1% H2O in NH3 on the LP side, and 1 °C higher CP because of air in the heat pump. System efficiency is: 92,28%

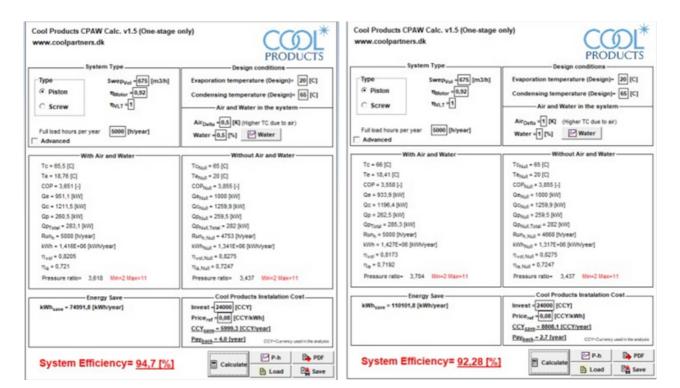
3% H2O in NH3 on the LP side, and 3 °C higher CP because of air in the heat pump. System efficiency is: 85,7%

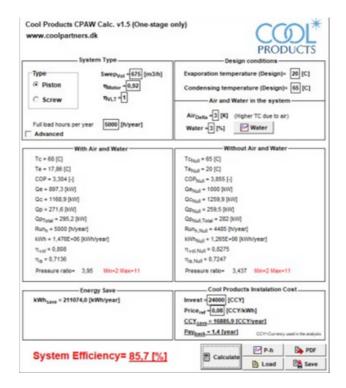




As it can be seen from the calculations, even the very small amounts of water and air that must be expected to be in a brand-new heat pump will have a damaging consequence on the efficiency. In this case, we lose 5,3% efficiency even with brand-new ammonia, state-of-the-art design, and best praxis craftsmanship during erection and start-up.

As can be seen from the calculations, when the amount of water and air slowly increases in the heat pump during service, etc., the penalty on the efficiency rises quickly.









#### **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.

Links to Cool Products videos on YouTube:

- Video CPA10-3 test veile:
- Video CPA10-3 start up on the Philippines:
- Video CPA10-3 Unilever Jakarta:
- <u>Video CPAWM testing at small to medium seized plant:</u>
- Video CPWM being drained during test of CPAWM system:
- Video of Cool Partners purging air and training refrigeration engineers in Mexico:
- <u>Video of emptying CPW15 in Asia:</u>
- <u>Video of draining water from a R717 chiller in Denmark equipped with a CPAWM system:</u>
- <u>A CPAWM system installed on a R717 chiller system with approx 200 kg R717 charge is</u> drained for separated water in Denmark
- <u>Draining water from CPAW12 system during test at large Danish coldstore. It was not</u>
   believed there was water in the ammonia, but the new CPAW12 system found and
   drained approx. 100 liters of water out of the ammonia system in approx on month after
   start up.



