

A Discussion of Acid in Refrigeration Systems

By Lawrence R. Grzyll, M.S., ChE., and Robert P. Scaringe, Ph.D., P.E.

Mainstream Engineering Corporation
Rockledge, Florida 32955

The development of acids in the refrigerant of vapor compression refrigerators, heat pumps, and air conditioners can severely shorten the life of the compressor and the refrigerant. These acids can be formed by chemical reactions with components and/or materials of construction, lubricating oils, and/or impurities. The instability of the refrigerant, and thus the formation of acids, is accelerated by elevated temperatures which could be the result of improper operation, such as a failed condenser fan or clogged air flow path. Checking the system for acid is a common maintenance recommendation since acidic conditions can be cleaned up before a compressor motor burns out.

You can check the oil for acid (with any one of oil test kits on the market), or you can check the refrigerant for the acid using the Carrier TotalTest™ or Mainstream QwikCheck®. We recommend the Mainstream QwikCheck 5-second acid test of the refrigerant because it is accurate, fast and inexpensive. It will detect acid levels well before they get to a harmful concentration. Prevention of acid build-up is the best preventative maintenance. QwikCheck works with all refrigerants and all oils, and will not give a false reading when used with POE (ester-based) oils. QwikCheck's ability to provide an accurate reading with any oil is critical because you may not know the type of oil in a system! Many oil acid test kits give a false acid reading with ester-based POE oils because the oil behaves like an acid to the test kit (that is, the ester oil displays amphoteric properties). This is the reason some oil acid test kit manufacturers have one kit for mineral oils and a different test kit for POE oils. If a small concentration of acid is detected, this acid should be removed, not neutralized, before the system is damaged. This is discussed later in this article.

If a compressor does burn out, the oil becomes extremely acidic. If all this acid is not removed when the compressor is replaced, the elevated acid levels will attack the new compressor and cause another compressor motor burn-out. Acid cleanup normally involves changing the compressor oil and the refrigerant to reduce the acid level (and changing the hermetic or semi-hermetic compressor if it did burn out). Unfortunately, removal of the oil contained in the compressor does not remove all the acid in the system since acid is carried throughout the vapor-compression loop by the flowing refrigerant, and therefore, acidic oil or its residue is throughout the system. This residual acid has been shown to shorten the life of the system since it will lead to accelerated acid formation in the system. This has been supported by experimental evidence that after a burn-out the frequency of subsequent burn-outs increases.

A discussion of the types of acids present in the system is necessary to fully understand the acid removal process. Depending on the refrigerant and oil being used a refrigeration system can contain two types of acids, organic acids (such as oleic acid) and inorganic (mineral) acids, such as hydrochloric acid. Organic acids are soluble in the oil (and do not vaporize) and therefore stay predominately in the liquid oil in the compressor oil sump. Inorganic acids are only slightly soluble in the oil. The organic acids are significantly less corrosive and only found in ester based oil or in systems where a strong oxidizer and high temperatures are present. Therefore organic acids are rarely if ever found in today's air conditioning systems in any appreciable concentration.

Both inorganic and organic acids are corrosive. However, inorganic acids have a higher dissociation constant making them strong and very reactive acids, while organic acids react much slower. In the case of mineral oils, elevated temperature causes the oil to ultimately break down and the ultimate products are carbon and hydrogen gas. Only in the presence of an oxidizer, such as oxygen or air, can organic acids be formed. In the case of synthetic POE oils, organic acid may be initially present (up to 8 PPM) as a residual from the esterification manufacturing process used to make the ester oil. It is therefore clear that the real acid problem in refrigeration/air conditioning systems is an inorganic acid problem not an organic acid.

During a compressor-motor burn-out, inorganic acids are formed as a result of the refrigerant decomposition at elevated temperatures. These inorganic acids which are formed are only slightly soluble in the oil. A significant portion of the inorganic acids generated during a motor burn-out remain in the vapor phase and react quickly with the materials of construction or are adsorbed in the filter/drier. Experiments have shown that the amount of inorganic acid vapor decreases by 85% in a matter of hours. However, experiments have also shown that an appreciable quantity of inorganic acid (more than enough to destroy another compressor) is also contained in the oil. The concentration of acid trapped in the oil is higher than the quantity which would be simply dissolved in the oil (remember the solubility for inorganic acid is low). This increased acid concentration is a combination of acid dissolved in the oil, acid trapped in the oil due to the oil's foaming and agitation, acid dissolved in any trapped moisture, and acid adsorbed onto the hard particles present in the oil. This inorganic acid has been shown to remain in the oil for an extremely long time and is in contact with the compressor components, including the motor windings. The inorganic acid in the oil will etch the lacquer insulation from the wire causing the motor winding to short-out electrically and resulting in a subsequent motor burn-out. An acid concentration of 50 PPM has been found to cause compressor motor burn-out in a matter of days!

One way to remove the acidic residue throughout the system is by performing several flushes of the vapor-compression system with refrigerant, since refrigerant will dissolve the oil and reduce the oil and acid concentrations by dilution. Because of EPA-mandated refrigerant recovery requirements, this is a costly and time consuming task and the cost of the refrigerant used in the flushing operation is not trivial.

An unacceptable alternative approach is to neutralize the acid by reacting the acid with a basic solution (a solid base dissolved in a liquid carrier), which results in the formation of undesirable salts as byproducts of the neutralization. Typical neutralization approaches are to neutralize the acid with a base, such as potassium hydroxide (KOH). These bases are solid and are dissolved in a non-water solvent. In such a reaction, the acid and base combine to form a metallic caustic salt and water. While the water can be removed by the filter/drier in the system, the salt remains trapped in the system and could cause problems. Since the salt is a solid it will not vaporize, but instead will remain in the system and cause corrosion!

A further problem with any acid neutralization is the addition of the proper amount of base. Too little base and the refrigerant is still acidic, too much base and the refrigerant is basic. An acidic or basic environment will cause corrosion and premature compressor life (burn-out).

Yet another problem with a neutralization reaction is that the neutralizing materials are solids and must be dissolved into a liquid solvent carrier or physically held in the vapor compression system's flow. The base can not vaporize and therefore the transport of the base throughout the system, even if dissolved in a liquid solvent, is severely limited. Some acid neutralization manufacturers have proposed that the neutralization solution be introduced in the compressor discharge, so that it will be forced through the condenser, filter/drier, TXV, and evaporator, before getting trapped in the compressor's oil supply. They explain that the liquid neutralization solution is thereby forced to travel throughout the system before becoming trapped in the compressor oil. However, the flashing at the TXV could also cause the solvent

to vaporize leaving a deposit of the solid base material, such as KOH, to clog the TXV. Even if the basic solution passes through the TXV, the solvent will likely evaporate in the evaporator leaving the solid basic material in the evaporator.

Every acid neutralization reaction will result in the formation of a salt residue, it is basic chemistry and cannot be changed. Some have proposed the use of sodium bicarbonate as the base but this acid-base reaction will produce a salt and also carbon dioxide gas (an undesirable non-condensable gas).

Finally, these acid neutralization techniques can ONLY be applied to mineral oils or alkylbenzene oils. This is because the ester-based POE oil possess amphoteric properties which make the oil behave as a base in the presence of an acid and vice versa. Consequently, the added base will react with the ester oil.

An acceptable way of removing the acid is to liberate or free it from the liquid and hard surfaces that contain the acid, and let the filter-drier in the system remove the acid. A filter-drier does an excellent job of removing acid by adsorption not by neutralization. The problem with relying on the filter-drier to remove the acid is that the significant portion of acid that is trapped on the hard surfaces and in the oil never gets to the filter-drier to be removed.

After a compressor burn-out change-out, we have measured very high concentrations of inorganic acids (significantly greater than 200 PPM) in the new compressor's oil. Theoretically this inorganic acid is not very soluble in the oil, however, this inorganic acid is being trapped in the oil and/or adsorbed on the surface of the solid particles which are present in the system (as a result of the motor burn out). In some cases this acid is also dissolved in water which is trapped in the oil. POE oil typically has much higher levels of water than other refrigeration oils. Agitation of the oil has not been found to release this trapped acid. In order to demonstrate this, an oil sample with an initial acidity value of 133 PPM (inorganic acid) was vigorously stirred for 32 hours using a magnetic stirrer. The acidity dropped 45 percent to 73 PPM. While this may seem like a significant drop, it should be pointed out that the compressor would have burned out in less than 33 hours of operation at this acid level. Therefore, the compressor would fail (burnout) before sufficient acid could be naturally removed from the oil, even if the compressor agitated the oil as much as in this experiment. However, if the trapped inorganic acid could be liberated from the oil (as well as from the acidic surfaces) in a reasonable time (and vaporized), the existing filter/drier in the system would remove this acid. QwikShot works by liberating the trapped acid from the oil and acid contaminated surfaces. QwikShot also vaporizes so that it travels throughout the system. The agitation of the acidic-oil experiment was repeated except QwikShot was added to the oil prior to stirring. After 20 minutes the acid was completely (100 %) stripped from the oil by QwikShot! The ordinary filter/drier in the vapor-compression system will adsorb the liberated acid and the QwikShot.

Ideally, the QwikShot should be introduced into the compressor's oil sump so that it can thoroughly mix with the oil during compressor lubrication. The QwikShot oil concentrations are less than 1% and will not affect the lubrication properties of the oil. As the QwikShot mixes with the oil it serves to dissolve and liberate the acid from the oil and acidic surfaces. The QwikShot and acid are vaporized (thereby leaving the oil) and travel through the system where they become adsorbed on the filter/drier (molecular sieve, carbon, or activated alumina filterdriers all work). The net result is that the acid is removed and no residue is left in the system, since both the acid and the QwikShot are adsorbed by the filter/drier. The QwikShot dosage charts are formulated so that the QwikShot will not use up the total capacity of the filter-drier, but will leave about half the filter-drier's capacity for future clean up of water or acid.

By using QwikShot a system can be thoroughly cleaned of acid without leaving any residue. This has been demonstrated by experiment. In the first experiment discussed, QwikShot was introduced into the acidic oil of an R-22 system. These tests were repeated both with and without a filter/drier in the system. Remember the performance of QwikShot depends on the use of the filter-drier to remove the liberated acid and the QwikShot from the system. The results of the tests are presented in Figures 1 through 3.

By referring to Figure 1, which shows the QwikShot in the vapor of the R-22 system, it is clear that the QwikShot is going into the vapor phase as it releases the acid from the compressor oil. However, if the filter drier is not present the QwikShot will remain in the system and eventually reach equilibrium which means no more QwikShot can vaporize and acid liberation will stop. This is also supported by Figure 2, which shows the drop in QwikShot in the oil. Note that by using the filter-drier, more than 60 percent of the QwikShot is removed from the oil in less than 6 minutes (0.1 hour).

However, the key issue is acid removal, and these results are shown in Figure 3. By referring to Figure 3 it can be seen that when a filter-drier is used about 7% of the acid is removed in less than 6 minutes (0.1 hour) and about 18% is removed after 1.5 hours. What is not shown in the Figure is that it takes about 12 to 16 hours to remove all the acid from the system. Also note that without the filter-drier the acid removal is much slower. The filter-drier should always be changed when QwikShot is added to the system. As shown in Figure 3, a failure to change the filter-drier when the QwikShot is added could result in a 3-times slower reduction in acid removal and complete acid removal may not be achieved!

The experiment described above was repeated for a R-134a system. This data is presented in Figures 4-6. The results are similar to the R-22 results, but the QwikShot removed the even more acid in 1.5 hours in the R-134a system (Figure 6).

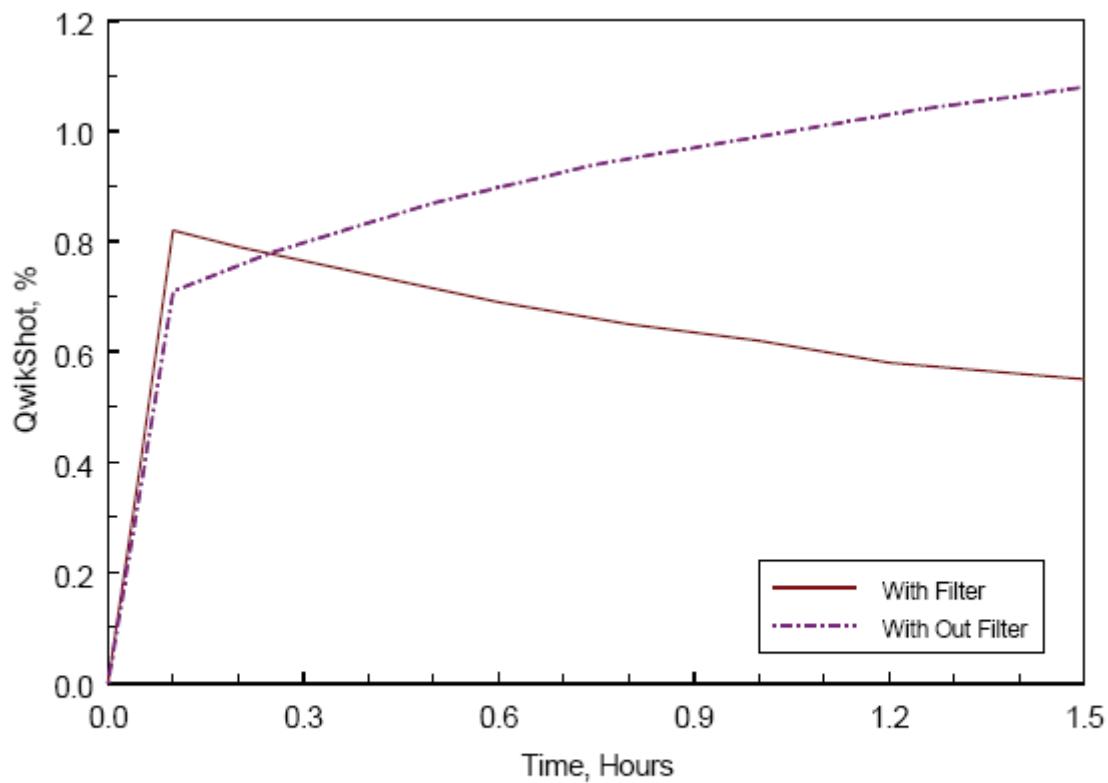


Figure 1. QwikShot in the Vapor of an Operating R-22 System

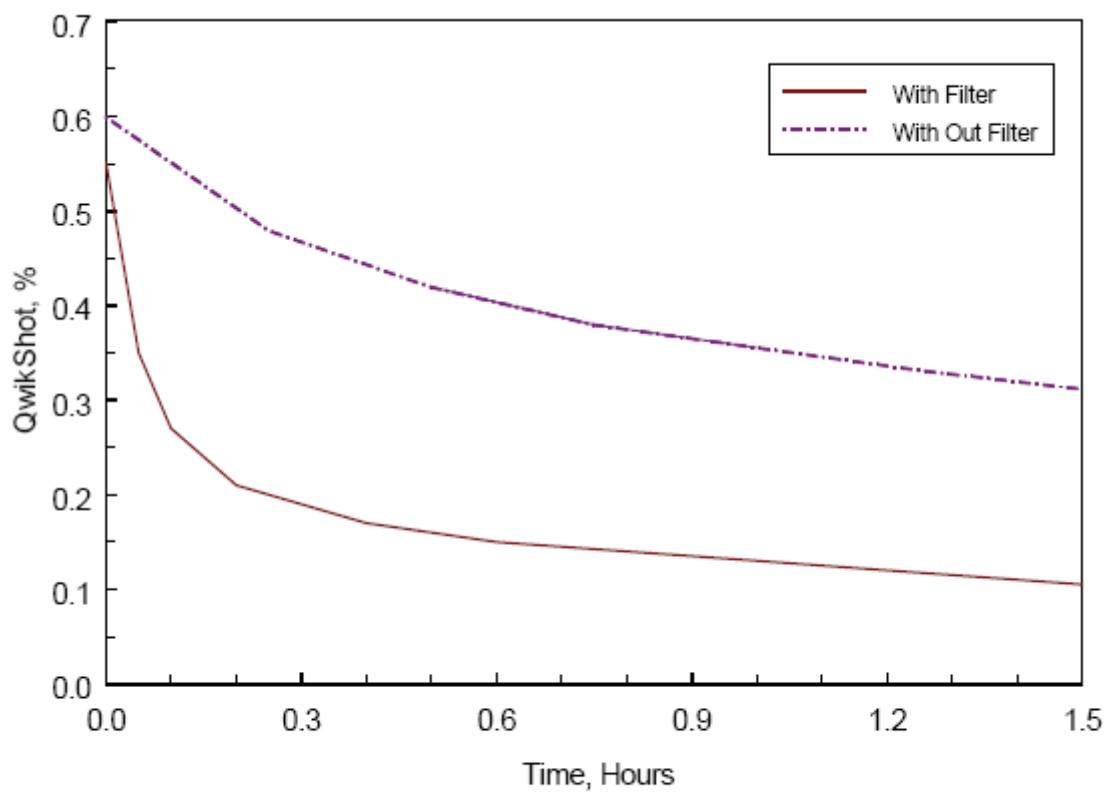


Figure 2. QwikShot in the the Compressor Oil of an Operating R-22 System

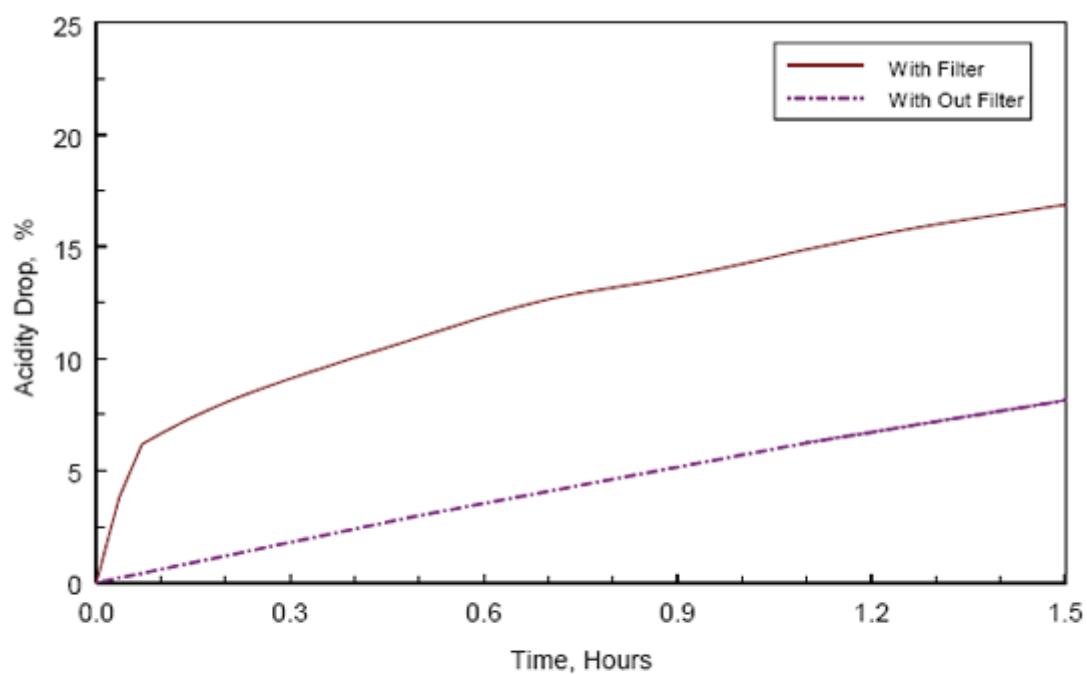


Figure 3. QwikShot Effect on the Acidity of an Operating R-22 System

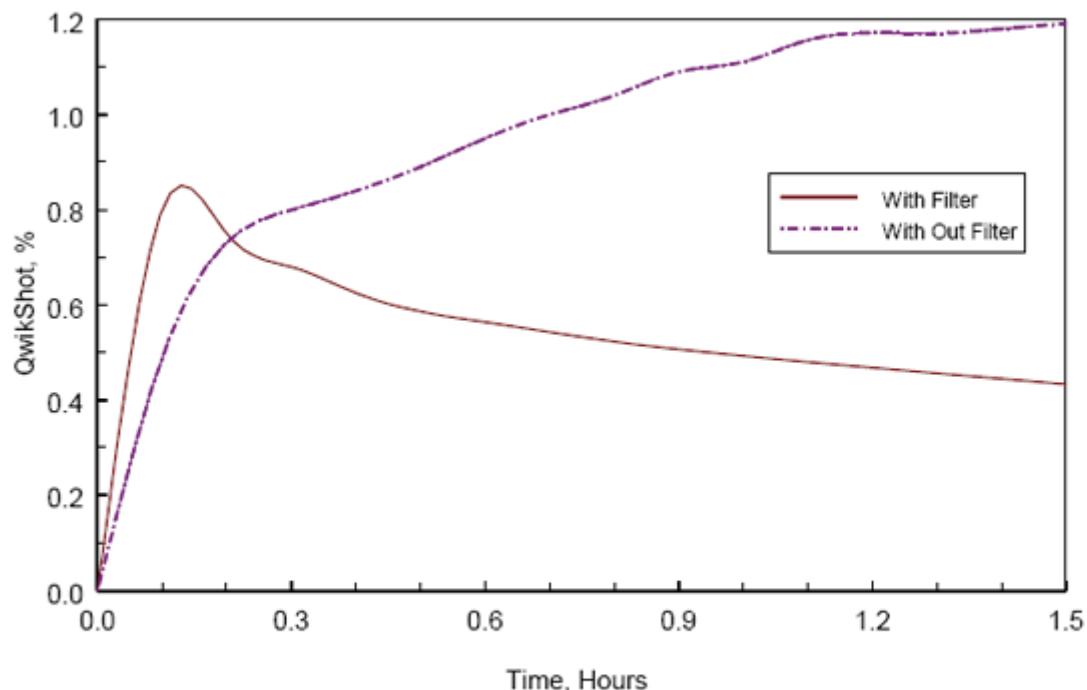


Figure 4. QwikShot In the Vapor of an Operating R-134a System

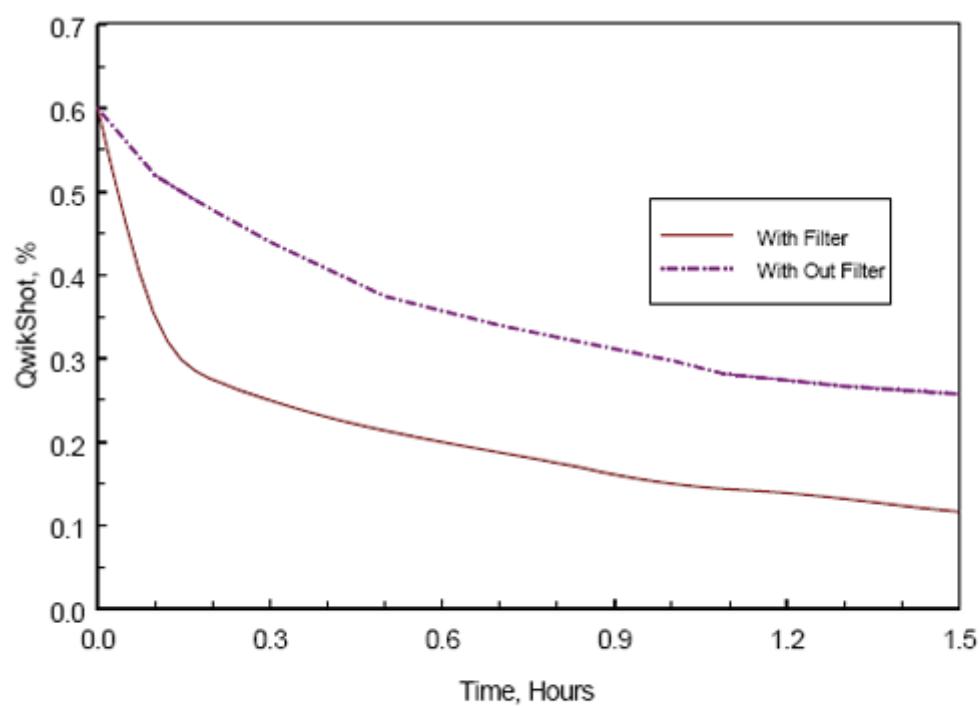


Figure 5. QwikShot In the Compressor Oil of an Operating R-134a System

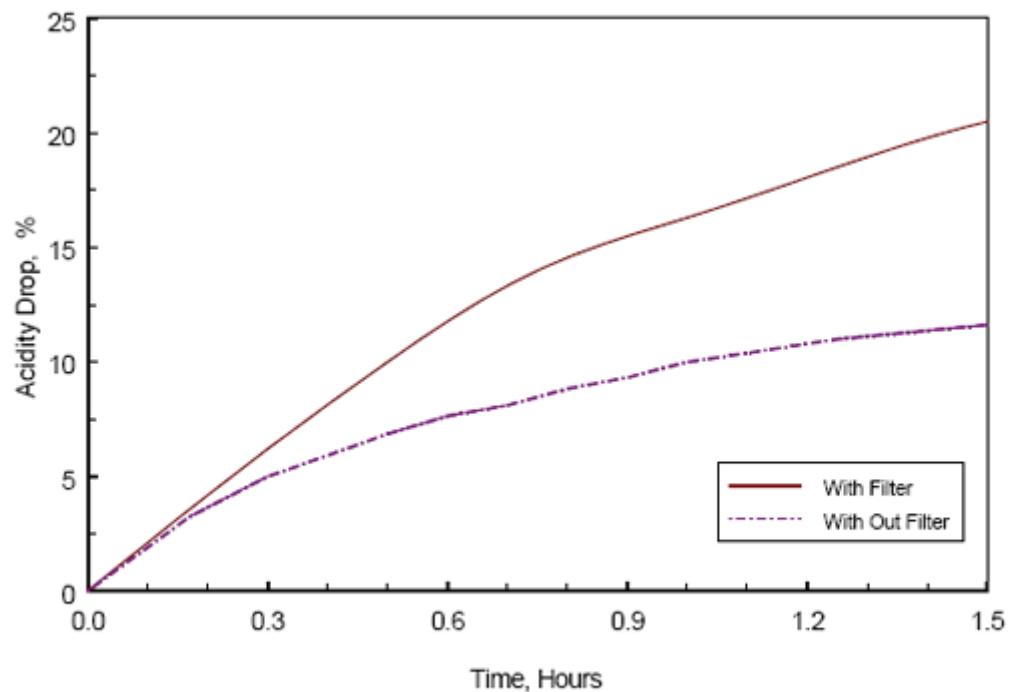


Figure 6. QwikShot Effect on the Acidity of an Operating R-134a System

The advantage of this patented QwikShot approach of liberating the acid is that there is no acid neutralization reaction and therefore no formation of a caustic corrosive solid salt residue. This innovative technology to provide this acid liberation is only available with QwikShot manufactured by Mainstream Engineering Corporation. Remember that when using QwikShot, not only is the acid removed from the system by the filter-drier, the QwikShot is also removed by the filter-drier. QwikShot acid treatment leaves no residue in the system.