

**EFFECTS OF WATER IN SYNTHETIC LUBRICANT SYSTEMS AND
CLATHRATE FORMATION: A LITERATURE SEARCH AND REVIEW**

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EXECUTIVE SUMMARY

Moisture is a universal contaminant of refrigeration systems, and a scientific understanding of the effects of water in these systems is needed for their proper design, efficient operation, and reliable service. The effects of water on chlorofluorocarbons and mineral oil have been extensively studied. In these non-polar systems with low solubility for water, moisture levels are usually controlled to twenty five parts per million or less to avoid free water and the associated corrosion of metals, compatibility problems with polymeric materials, and possible ice formation in expansion valves, capillary tubes, or evaporators. The phase-out of chlorofluorocarbon/mineral oil systems and the introduction of alternative hydrofluorocarbon (HFC) refrigerants and their compatible synthetic lubricants have once more raised concerns about the effects of water on the stability of refrigeration systems. The HFC/synthetic lubricant systems are polar and have good solubility for moisture, thus present reduced risk of free water with its associated problems. The current common practice of equipment manufacturers is to allow moisture levels of 50-100 parts per million (ppm) or less in new equipment with HFC and synthetic lubricants. However, service practices are not well controlled and may lead to high levels of water in the refrigeration system. Because of the different types of synthetic lubricants and system designs encountered in the refrigeration and air-conditioning industry, initial investigations into the effects of excess water with the HFC/synthetic lubricant working fluids are limited, proprietary, or of a screening nature. There has not been a reported in-depth study of the effects of moisture on the long-term stability of the HFC/synthetic lubricant systems. Such a study would assist the equipment manufacturers in defining allowable maximum limits of water concentration for

satisfactory long-term operation of the HFC/synthetic lubricant systems, and evaluating potential difficulties associated with the presence of excessive water.

Under ARTI 21-CR Project 610-50035-01, Spauschus Associates, Inc. has compiled and critically evaluated the current state of knowledge of the effects of water on the stability of HFC/synthetic lubricant systems to identify key areas requiring further investigation. An extensive literature search was conducted and a confidential survey was prepared and sent to compressor, lubricant, desiccant and filter-drier manufacturers to determine the industry specifications on the amount of water allowable in the HFC/synthetic lubricant systems. Following are highlights from the extensive literature review and analysis of the survey:

- Clathrate hydrates, first discovered in 1810, are solid solutions formed when water molecules are linked through hydrogen bonding creating cavities that can enclose various guest molecules also known as hydrate formers. The formation, nucleation, growth, decomposition, structures, properties, and thermodynamic phase equilibria have been reported for a number of hydrate formers, including HFC refrigerants such as R-32, R-125, R-134a, R-407C and R-410A. Four methods for preventing the formation of clathrate hydrates were cited, including drying the gas, heating it to a temperature above the equilibrium formation temperature at a given pressure, reducing the gas pressure to below the hydrate formation pressure at a given temperature, or injecting inhibiting substances.

- Polyolester (POE) lubricants hydrolyzed in the presence of water while polyvinylethers (PVE) do not. Hydrolysis activity of POE was more frequently acid-catalyzed than base-catalyzed and tended to increase with high water content and high residual carboxylic acids. The hydrolysis reaction rate constants typically showed temperature dependence consistent with an activated process following the Arrhenius equation. Hydrolytic stability of POE was shown to improve with hindered POE, and with the presence of acid catcher additives and molecular sieve desiccant. In general, under lubricated conditions, water vapor can modify the adsorption of long-chain fatty acids that act as boundary lubricants, thus influencing friction and wear. Water can also affect the chemistry of protective film formation by oxygen. However, depending on the lubricants tested and the conditions of the tests, the effects can be either positive or negative. A positive effect corresponds to a decrease in wear with increasing water content while a negative effect corresponds to an increase in wear with increasing water content.
- In the study of the distribution of moisture between R-134a, polyalkylene glycol (PAG) and desiccant, it was concluded that at equilibrium, some moisture from the PAG redistributed between the refrigerant and the desiccant with the larger fraction going to the desiccant. In addition, the study of moisture dynamics showed that under steady state operation, moisture is distributed between the refrigerant and the lubricant after twenty-four hours. The amount of moisture varies according to the total system moisture and, if desiccant is present, on the degree of desiccant saturation. It was also determined that approximately fifty to sixty percent of the moisture injected into an air-conditioning system remains in the refrigerant and the

rest mixes with the compressor oil. In an automotive air-conditioning system using R-134a, it was discovered that ice would form in the refrigerating cycle at 0 °C evaporating temperature when the water content in the vapor refrigerant on the low-pressure side is more than 350 ppm.

- The presence of moisture was observed to cause the embrittlement of polyethylene terephthalate and the hydrolysis of polyester materials. On the positive side, water was shown to reduce the effect of amine additives on fluoroelastomer rubbers. The reactions of water with refrigerants or the hydrolysis of organic solvents and lubricants have been shown to cause formicary and large-pit corrosion in copper tubes, as well as copper plating and sludge formation in refrigeration systems. Moreover, studies of blockage of capillary tubes showed that blockage is low in dry systems, but increases rapidly in the presence of water or when the system is doped with carboxylic acid.
- The responses from the twenty-four companies that participated in the survey suggested that the water concentrations specified and expected for different refrigerant/lubricant systems vary depending on the products, their capacities and applications, and also on the companies. Among the problems that would most likely result from the presence of high moisture level in the refrigeration systems, lubricant breakdown is of greatest concern, followed by acid formation, compressor failure and expansion valve sticking. Elastomeric seal failure and sticking of suction valve cause fewer concerns.

The following research topics are suggested for future investigation, in the order of their importance, practicality and ease of implementation:

1. The air-conditioning and refrigeration industry needs to measure and record the water content and total acid number of the lubricant of newly installed systems as well as operating systems that are shutdown for service or repair. The reason for the shutdown and repair needs to be documented. A database can then be established to correlate water content in systems with type of breakdown or problems encountered. This research project is easy to implement and has practical application, because the database, combined with detailed studies on the distribution of water in refrigeration and air-conditioning systems, would help the industry in setting meaningful limits on the allowable water content in newly installed equipment, either field-erected or factory-sealed.
2. Along with the database, detailed studies on the distribution of water in refrigeration and air-conditioning systems should be conducted to pinpoint problem areas associated with free water, and to help in the formulation and implementation of effective solutions to these problems.
3. Although formicary corrosion is a real phenomenon leading to copper tube failures, it is less well known than other forms of corrosion. Formicary corrosion has been successfully replicated in the laboratory, but research is still needed to validate the current theories and mechanisms for this type of corrosion. Studies are needed to determine the rate of pit formation and propagation, the conditions of temperature,

water content, acid content, and oxygen content needed to initiate the corrosion process. Corrosion inhibitors need to be developed and evaluated.

4. Although studies have been conducted on a number of hydrate formers including hydrofluorocarbon refrigerants, the conditions for formation and decomposition of clathrate hydrates of other alternative refrigerants under consideration for use in refrigeration and air-conditioning systems and water should be determined to avoid possible problems associated with tube plugging. These alternative refrigerants may include R-23, R-41, R-116, R-125, R-143a, and refrigerant blends such as R-404A and R-507C.
5. The mechanism by which water facilitates or hinders lubrication is not known and needs to be studied and characterized in order to formulate more effective lubricants and lubricant additives.

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EFFECTS OF WATER IN SYNTHETIC LUBRICANT SYSTEMS AND CLATHRATE FORMATION: A LITERATURE SEARCH AND REVIEW

I. INTRODUCTION

Moisture is a universal contaminant of refrigeration systems and a scientific understanding of the effects of water in these systems is needed for their proper design, efficient operation, and reliable service. The effects of water on chlorofluorocarbons (CFC) and mineral oil have been extensively studied (Walker 1962; Borah 1955; Nippon Reito Kyokai 1981). In these non-polar systems with low solubility for water, moisture levels are usually controlled to twenty five parts per million or less to avoid free water and the associated corrosion of metals, compatibility problems with polymeric materials, and possible ice formation in expansion valves, capillary tubes, or evaporators. The phase-out of CFC/mineral oil systems and the introduction of alternative hydrofluorocarbon (HFC) refrigerants and their compatible synthetic lubricants have once more raised concerns about the effects of water on the stability of refrigeration systems. The HFC/synthetic lubricant systems are polar and have good solubility for moisture, thus present reduced risk of free water with its associated problems. The current common practice of equipment manufacturers is to allow moisture levels of 50-100 parts per million (ppm) or less in new equipment with HFC and synthetic lubricants. However, service practices are not well controlled and may lead to high levels of water in the refrigeration system. Because of the different types of synthetic lubricants and system designs encountered in the refrigeration and air-conditioning industry, initial investigations into the effects of excess water with the HFC/synthetic lubricant working

fluids are limited, proprietary, or of a screening nature. There has not been a reported in-depth study of the effects of moisture on the long-term stability of the HFC/synthetic lubricant systems. Such a study would assist the equipment manufacturers in defining allowable maximum limits of water concentration for satisfactory long-term operation of the HFC/synthetic lubricant systems, and evaluating potential difficulties associated with the presence of excessive water.

Under ARTI 21-CR Project 610-50035-01, Spauschus Associates, Inc. has compiled and critically evaluated the current state of knowledge of the effects of water on the stability of HFC/synthetic lubricant systems to identify key areas requiring further investigation. An extensive literature search was conducted. Databases such as Engineering Index (ENGI), Science Abstracts (INSPEC), National Technical Information Service (NTIS), Applied Science and Technology Abstracts Citation, Academic Press Journals, IBM Patent server, Science citation index, Current Contents and Ferret (ARTI Refrigerant Database) were accessed. A confidential survey was prepared and sent to compressor, lubricant, desiccant and filter-drier manufacturers to determine the industry specifications on the amount of water allowable in the HFC/synthetic lubricant systems. From the extensive literature review and the data collected from the survey, critical research needs were identified, which would fill any existing gap in the scientific understanding of the effects of water in HFC/synthetic lubricant systems.

II. CLATHRATE FORMATION AND DECOMPOSITION IN HFC-WATER SYSTEMS

2.1. STATE OF KNOWLEDGE

Clathrate hydrates, first discovered in 1810, are solid solutions formed when water molecules, linked through hydrogen bonding, create cavities that can be occupied by various guest molecules also known as hydrate formers. Englezos (1993) reviewed the formation, structures and properties of clathrate hydrates, described their phase equilibria and thermodynamic models, and discussed their nucleation, growth and decomposition. If the hydrate former is only sparingly soluble in liquid water, the hydrate preferentially forms at the water/hydrate-former-interface, replacing the interface with a polycrystalline hydrate film. Sugaya and Mori (1996) visually estimated the film thickness of R-134a clathrate hydrate to be around 10 microns (μm) or less, while Ohmura, Kashiwazaki and Mori (2000) measured the thickness of clathrate-hydrate of liquid R-134a and water with a laser interferometer. Ohmura, Shigetomi and Mori (1999) studied the thick hydrate films growing along the surface of R-141b drops immersed in liquid water at a relatively small subcooling, and estimated the film thickness to be 0.1-0.2 millimeters. Similarly, two discrete hydrate crusts grow along the liquid-liquid interface when a drop of HCFC-141b is formed from a single nozzle into a water stream in favorable thermodynamic conditions (Kato, Iida and Mori 2000). Using high-speed videography, Mori (1996) observed a solid clathrate hydrate phase form at the fluorocarbon/water interface and

encapsulate a drop of R-134a in a water pool. On the microscopic level, Sloan et al. (1998) described the first Raman spectra for the formation of both uninhibited and inhibited methane hydrates with time. This method has the potential to provide a microscopic-based kinetics model.

Clathrate compounds have been found under the evaporating pressure condition of a refrigeration unit using R-407C and R-410A (Matsuo, Tagashira and Yoshida 1996). The critical decomposition temperature of the clathrate between HFC-32 and water was reported as 17.6 °C (Davidson 1973), and that of the clathrate between HFC-134a and water was 10 °C (Oowa et al. 1990). The critical decomposition temperature is the maximum temperature for the existence of the clathrate. Tanii et al. (1997) recorded the critical decomposition temperature of HCFC-141b clathrate as 8.5 °C and showed that the addition of 0.05% by weight of surfactant increased the clathrate formation rate while the addition of ethylene glycol lowered the clathrate formation/decomposition temperature. Akiya et al. (1997, 1999) studied the formation conditions of clathrates between HFC refrigerants and water. Mixtures of refrigerant and deionized water were first cooled until clathrate formation was observed. The temperature of the mixtures was then raised until the clathrate disappeared. Equilibrium pressures were recorded at selected temperatures during the cooling and heating cycles. Pressure (P) versus temperature (T) curves before the formation of the clathrate were condensation curves. P versus T curves between clathrate formation and clathrate decomposition were called clathrate formation curves.

Condensation and clathrate formation curves, which were linear with a logarithmic pressure scale and linear temperature scale, were obtained for each of the following refrigerants and water: HFC-32, HFC-125, HFC-134a, and refrigerant blends R-407C and R-410A. The critical decomposition temperature T_c and the critical decomposition pressure P_c were obtained from the intersection of the condensation line and clathrate formation line. From their studies, the authors concluded that R-407C and R-410A form clathrate compounds with water under the evaporating temperature condition in the refrigeration cycle of air-conditioners and heat pumps, operating below 14 °C. Ethirajan and Najafi (1993) described a cool energy storage system that operated in a “direct-charge” mode to form solid refrigerant R-134a clathrate as its storage medium. A mathematical model was formulated to predict the temperature field within the storage tank during the charging operation. Another cool storage system using R-141b was described by Akiya et al. (1991). The formation of hydrate layers in pipes was observed by Dorstewitz and Mewes (1994). They noted that a plug started forming on the pipe wall where the interface between water and R-134a was located, then a hydrate layer covered the whole perimeter of the wall and grew radially towards the center of the pipe. The thickness of the hydrate layer can be related to the measured heat transfer resistances and measured pressure losses.

2.2. PREVENTION OF CLATHRATE FORMATION

Englezos (1993) cited four methods for preventing the formation of clathrates, including drying the gas, heating it to a temperature above the equilibrium hydrate

formation temperature at a given pressure, reducing the gas pressure to below the hydrate formation pressure at a given temperature, or injecting inhibiting substances. Known clathrate inhibitors include methanol, ethanol, ethylene glycol, diethylene glycol, butanone, acetone, or electrolytes such as NaCl, KCl, CaCl_2 , and NH_3 (Holder, Zetts and Pradhan 1988; Gubbins 1993; Koga, Tanaka and Nakamishi 1994). Becke, Kessel and Rahimian (1994) determined that liquid hydrocarbons add to the effects of inhibitors in lowering the critical decomposition temperatures of gas hydrates. In addition to alcohols, glycols, and electrolytes, which are known as thermodynamic inhibitors, water-soluble polymers are found to have inhibiting potential (Englezos 1992; Lederhos et al. 1996). These inhibitors, also called kinetic inhibitors, generally are effective at less than one weight percent in the aqueous phase whereas methanol is used between 10 and 60%. They work by increasing the time delay in the formation of clathrate hydrates. Because of the high degree order required to arrange the water molecules around the guest molecules, the formation of hydrates requires some time even under thermodynamically favorable conditions (Notz et al. 1996). King et al. (2000) and Hutter, King and Lin (2000) used small-angle neutron scattering to characterize the mechanism for kinetic hydrate inhibition of nonionic water soluble polymers such as poly(ethylene oxide), poly(N-vinyl-2-pyrrolidone), poly(N-vinyl-2-caprolactam) and N-methyl, N-vinylacetamide/N-vinyl-2-caprolactam copolymer. They discovered that a principle mechanism of hydrate kinetic suppression involves surface adsorption onto the growing crystals accompanied by slowing of the growth. Another mechanism of inhibition

involves an association between the hydrate-forming components and the polymer, which might act to alter the nucleation behavior, as suggested by Lederhos et al. (1996).

2.3. RESEARCH NEEDS REGARDING CLATHRATES

- The study of the formation conditions of clathrates between single component HFC refrigerants, such as R-23 (trifluoromethane), R-41 (fluoromethane), R-116 (hexafluoroethane), R-125 (pentafluoroethane), R-143a (1,1,1-trifluoroethane), and water should be continued.
- Based on the research of Akiya et al. (1997, 1999), when T_c is plotted on linear scale versus P_c on logarithmic scale, the point representing R-410A is located on the straight line connecting those representing R-32 and R-125. Similarly, the critical clathrate decomposition point of R-407C is close to the straight line connecting those of R-410A and R-134a. These results would suggest that it is possible to determine the clathrate decomposition conditions of a blend of HFC refrigerants from the data of its individual components. This phenomenon should be investigated for various refrigerant blends, such as R-404 A (which is 44% R-125, 52% R-143a, and 4% R-134a) and R-507 C (which is 50% R-125 and 50% R-143a).
- There is a need to research and develop new inhibitors to prevent clathrate formation, agglomeration or deposition, because the currently used thermodynamic inhibitors have to be used in large quantities and thus tend to be costly (Pakulski 1998; Rabeony et al. 1998; Colle et al. 2000), while the current kinetic inhibitors are either not very

effective or can only be applied under limited conditions (Klug and Holtrup 2001; Namba et al. 2001).

- In situ measurement techniques, such as the laser interferometer, axial flow viewing and photography, or Raman Spectra should be developed and applied in the measurement of clathrate film thickness at various locations in the refrigeration system where the thermodynamic conditions are conducive to the formation of clathrate hydrates.

III. WATER IN REFRIGERANT AND LUBRICANT SYSTEMS

3.1. WATER AND LUBRICANT

3.1.1 Hygroscopicity

In describing the water absorption of synthetic lubricants, Echin, Novosartov and Popova (1981) stated that hygroscopicity of oils based on esters increased with increasing relative humidity of the air (according to Henry's law) and with increasing temperature. For the diesters and pentaerythritol esters, the water solubility is directly proportional to temperature. In addition, pentaerythritol esters that have higher hydroxyl number were seen to absorb more water. Kussi (1985) studied the water absorption of various synthetic polyether lubricants (also known as polyalkylene glycol or PAG). He reported that water absorption is dependent on the content of ethylene oxide in the polyether molecule, the degree of polymerization, and the temperature. Pure, higher-molecular weight propylene oxide polyethers absorb little water (less than 5% water based on lubricant weight), while polyethers with a small proportion of ethylene oxide content absorb more water (35% or more). The capacity of these polymers to absorb water decreases with increasing molecular weight. Polyethers with an ethylene oxide content greater than 40% by weight are miscible with water in every ratio at room temperature. However, upon heating, they may show a phase separation temperature, which depends on structure and concentration, and, as a rule, lies between 45 and 100 °C. In similar studies, the water solubility of PAG was reduced by end-capping the hydroxyl group on the PAG molecular structure with an

alkyl group (Idoux, McCurry and Amimabhavi 1994). Sheiretov, Glabbeek and Cusano (1996) reported that the approximate saturation limit of polyalkylene glycol is 18,000 ppm and that of polyolester is between 2000 and 4500 ppm. Fukui, Sanechika and Ikeda (2000) remarked that, compared with polyalkylene glycol and polyol ester, moisture absorption of fluorinated alkyl aryl ethers is much slower and reaches a lower equilibrium water content of around 200 ppm.

3.1.2. Hydrolysis

Tazaki, Konishi and Nagamatsu (1998) noted that moisture enters into the refrigeration and air-conditioning systems during installation or repair and is quite difficult to eliminate by vacuuming. Both polyvinylether and polyolester lubricants are hygroscopic, but polyolesters hydrolyze in the presence of water, while polyvinylethers do not. Sealed tube tests of R-134a/polyolester in the presence of iron, copper, and aluminum and controlled amounts of water indicated that hydrolysis activity tends to increase with high water content or residual carboxylic acid (Jolley 1991). Boyde (1999) looked in detail at the effect of synthetic ester lubricant structure on rate of hydrolysis. He stated that in lubricant service applications, acid-catalysed hydrolysis occurred more frequently than base-catalysed hydrolysis. The hydrolysis reaction rate constants typically showed temperature dependence consistent with an activated process following the Arrhenius equation. The activation energy for hydrolysis of aromatic esters is higher than that for simple polyolesters and diesters, and polyolesters generally had lower rates of

hydrolysis than analogous diesters. In polyolesters, branching at the 2 or 3 position relative to the ester carbon drastically reduces the rate of hydrolysis compared with analogous linear esters. High acid value and high hydroxyl value in the esters also resulted in faster hydrolysis reactions. The use of acid catcher additives, such as epoxides, could significantly improve the hydrolytic stability of ester lubricants. Similarly, Dick et al. (1996) showed that hindered polyolester is more resistant to hydrolysis than the conventional polyolester and both molecular sieve desiccant and hydrolysis inhibiting chemicals markedly enhance the stability of unadditized and additized lubricants. Epoxy-type acid catchers were shown to be good hydrolysis inhibitors (Iizuka et al. 1996).

3.1.3. Effect of Water on Tribological Properties of Lubricants

Lancaster (1990) reviewed the effect of humidity on the friction and wear of metals. In general, under lubricated conditions, water vapor can modify the adsorption of long-chain fatty acids that act as boundary lubricants, thus influencing friction and wear. Water can also affect the chemistry of protective film formation by oxygen. However, depending on the lubricants tested and the conditions of the tests, the effects can be either positive or negative. Drauglis and Snediker (1980) investigated the effects of oxygen and water vapor on the compressive film strength of boundary films on iron substrates and concluded that water is detrimental while oxygen is necessary for the formation of good boundary films from the diester di-2-ethylhexyl sebacate. This conclusion is in agreement with the results of Echin, Novosartov and Kondrat'eva (1983) who stated that the

hydrolysis of ester-based synthetic oils result in a considerable drop in the level of antiwear and extreme-pressure properties. On the other hand, Helmick and Sherma (1996) studied a commercially available linear perfluoropolyalkylene ether fluid with M-50 steel under boundary lubrication, and reported that both friction and wear decrease sharply as humidity increases from 5 to 20 percent, then remain constant as humidity increases to 100 percent. A detailed study by Sheiretov, Glabbeek and Cusano (1996) on the effect of dissolved water on the tribological properties of polyalkylene glycol and polyolester lubricants showed that the lubricant, the contact metals (steel pin on aluminum plate or steel pin on cast iron plate), the atmosphere (whether refrigerant R-134a or air), and the moisture content, all have an effect on friction and wear, as shown in Table 3.1. A positive effect corresponds to a decrease in wear with increasing water content and a negative effect corresponds to an increase in wear with increasing water content.

3.2. WATER AND DESICCANT

The gas adsorption properties of zeolites are related to the distinctive interaction of the adsorbed molecules with the zeolitic cations in the sterically restricted environment of the tetrahedral framework (Coe 1984; Ruthven 1984). The presence of adsorbed water has a large impact on the arrangement of the cations in the zeolites and on the interactions between the adsorbent and the adsorbed gas (Smith et al. 1967; Dempsey 1969; Breck 1974; Dendooven et al. 1984; Van Dun and Mortier 1988). Kirschhock et al. (2000) studied the arrangements of residual water and alkali-metal cations in Zeolites Y and X

using Rietveld refinement in combination with Fourier analysis of X-ray powder patterns. They discovered that only the cation sodium participates in the interaction with the water molecules, causing the formation of four types of water-sodium structures at low water contents. Heavier alkali-metal ions that are also present affect the formation of these structures by blocking the cation positions for sodium.

TABLE 3.1: SUMMARY OF EXPERIMENTAL RESULTS FROM SHEIRETOV , GLABBEEK AND CUSANO (1996)			
Lubricant	Contact metals	Atmosphere	Water Effect on Wear
PAG	Steel/Aluminum	R-134a	Positive from 200 ppm up to 5000 ppm moisture. After that, no effect
PAG	Steel/Cast Iron	R-134a	Negative
PAG	Steel/Aluminum	Air	Positive
PAG	Steel/Cast Iron	Air	Slightly positive
POE1	Steel/Aluminum	R-134a	No effect
POE1	Steel/Cast Iron	R-134a	No effect
POE1	Steel/Aluminum	Air	Positive
POE1	Steel/Cast Iron	Air	Positive
POE2 (higher viscosity)	Steel/Aluminum	R-134a	No effect
POE2	Steel/Cast Iron	R-134a	No effect
POE2	Steel/Aluminum	Air	Positive
POE2	Steel/Cast Iron	Air	Slightly positive (wear is small at either high or low water content)

3.3. WATER AND REFRIGERANT

The water solubility of hydrochlorofluorocarbons (HCFC) and HFC refrigerants, including R-22, R-123, R-124, R-125, R-134a, R-141b, R-142b, R-152a has been

reported by McLinden (1989), while Thrasher et al. (1994) studied the moisture solubility in R-123 and R-134a. According to Gehring (1995), water is the single most deleterious contaminant in air-conditioning and refrigeration systems. He discussed sampling and analysis sensitivity to the phase of the sample and showed that higher accuracy can be obtained by using liquid phase samples.

3.4. PARTITIONING OF WATER BETWEEN REFRIGERANT, LUBRICANT AND DESICCANT

Cohen and Tucker (1998) stated that, for molecular sieve desiccants, the maximum water capacity is achieved when the refrigerant is excluded from the molecular sieve micropores, because the refrigerant and water molecules compete for the available adsorption sites. They showed that molecular sieve type 3A can be modified to exclude refrigerant R-32, and reported the partitioning of water between refrigerants R-410A and R-407C and molecular sieves at 52 °C. When the equilibrium water concentration in the refrigerant is 10 ppm, the water capacity of unmodified molecular sieve 3A-6 is 2.0 g of water/100 g of desiccant with R-410A, and 2.9 with R-407C. When the water concentration in the refrigerants is 50 ppm, the water capacity of 3A-6 is 8.7 with R-410A and 11.8 with R-407C. In modified molecular sieve 3A-11, the corresponding water capacity at 10 ppm is 8.8 with both R-410A and R-407C, and at 50 ppm, the water capacity is 13.9 with both refrigerants. Cohen and Tucker also measured the drydown rate of the molecular sieves in R-407C and R-410A and concluded that both 3A-6 or 3A-11 would dry the refrigerants very fast in about two hours, and almost completely in

about six hours. Cavestri and Schafer (1999) studied the equilibrium water capacity of desiccants in mixtures of R-134a and polyolester lubricant. For R-134a containing 2% by weight mixed acid polyolester lubricant, water loading of 15.5 to 16.5% on 3A molecular sieves provides a 50 ppm equilibrium water, at both 24 °C and 52 °C. The moisture content of the lubricant is generally below 5 ppm. For alumina, under similar concentration of water in the refrigerant and lubricant, water loading of 5.25% was measured at 24 °C and 2.5% at 52 °C. For alumina cores, the water loading was 3% at 24 °C, and 2.5% at 52 °C. Similar studies were conducted to examine water adsorption by driers in refrigeration systems using R-407C and R-410A with polyolester lubricants (Matsuo, Tagashira and Yoshida 1996).

Rohatgi et al. (2000) studied the distribution of moisture between R-134a, polyalkylene glycol, and desiccant, and concluded that at equilibrium, some moisture from the PAG is redistributed between the refrigerant and the desiccant with the larger fraction going to the desiccant. In addition, the study of moisture dynamics showed that under steady operation, moisture is distributed between R-134a and the PAG lubricant after twenty four hours. The amount of moisture varies according to the total system moisture and, if desiccant is present, on the degree of desiccant saturation. In typical “dry” systems, moisture content of the R-134a is about 25 to 50 ppm. In “wet” systems, the moisture level rises to 300 to 400 ppm, and with moisture above the saturation level of the desiccant, water content in the R-134a will go to 1500 ppm and above. Goswami et al. (1996) investigated the effect of moisture on the performance of an air-conditioning

system and determined that approximately 50 to 60% of the moisture injected into the system remains in the refrigerant and the rest mixes with the compressor oil. Kitamura et al. (1993) conducted a detailed study of the water distribution in an automotive air-conditioning system using R-134a. They determined that the saturated water content in the saturated vapor refrigerant at 0 °C is 350 ppm. They concluded that ice will form in the refrigerating cycle at 0 °C evaporating temperature when the water content in the vapor refrigerant on the low-pressure side is more than 350 ppm. In addition, they found that the ratio (β) of water content in the vapor over liquid refrigerant in the evaporator is always 0.41, which is between the β in the equilibrium state ($\beta = 0.18$, following Henry's law) and the β in the state of instantaneous evaporation by the expansion valve ($\beta = 0.51$). The β value varies depending on the evaporation rate. Moreover, the water content in the liquid refrigerant before the expansion valve is distributed in a fixed ratio to the water content in the vapor refrigerant as well as to the water content in the liquid refrigerant after the expansion valve. With an increase in water content in the refrigerating cycle, the water content in the vapor refrigerant after the expansion valve exceeds the saturated water content, resulting in free water in the refrigerant.

3.5. RESEARCH NEEDS REGARDING WATER IN REFRIGERANT/LUBRICANT SYSTEMS

- The mechanism by which water facilitates or hinders lubrication is not known and needs to be studied and characterized. It will be different depending on the chemistry

of the lubricant, the chemistry and surface of the contact metals, the atmosphere and the temperature around the point of metal to metal contact.

- Detailed studies on the distribution of water in refrigeration and air-conditioning systems, such as the study by Kitamura et al. (1993), would be useful in pinpointing problem areas associated with free water and would help in the formulation and implementation of effective solutions.

IV. EFFECT OF WATER ON MATERIALS OF CONSTRUCTION IN REFRIGERATION SYSTEMS

4.1. EFFECTS ON DESICCANTS

Cavestri and Schooley (1998) noted that the ability of molecular sieve and alumina desiccants to adsorb hydrochloric acid from R-12 and R-22 refrigerant depends on temperature and water content of the refrigerant. With 3A molecular sieves, at less than 10 ppm moisture content, the rate of HCl adsorption is very slow. The HCl loading capacity at saturation is at 10.5 to 11% by weight, both at 24 °C and 52 °C. When the moisture content is around 60 ppm, the rate is about a third faster and the capacity at saturation is 11% at 24 °C and 20% at 52 °C.

4.2. EFFECTS ON POLYMERS

The presence of moisture was observed to cause the embrittlement of the polyethylene terephthalate (PET) found in Mylar and Melinex sheet and sleeving insulations (Korleski 1991; Sundaresan and Finkenstadt 1991; Doerr and Waite 1996a; 1996b). Polyester material (used as screen for orifice tube in automotive air-conditioners) is hydrolyzed by humidity, and Hunter et al. (2000) have developed a model to express the rate of polyester hydrolysis in terms of the relative humidity and to connect the degree of hydrolysis to hardness. Kumagai and Yoshimura (2000) reported that absorbed water in cycloaliphatic epoxies (used as electrical insulating material for motors) caused

hydrolysis of ester linkages leading to decreased tracking resistance or surface resistivity. On the positive side, the presence of water was shown to reduce the effect on fluoroelastomer (FKM) rubbers of amine additives, which can cross-link with the rubbers thus changing their properties (Smith 1960; Dinzborg 1995).

4.3. EFFECTS ON METALS

Campbell (1972) described the forms of corrosion encountered in heat exchangers for air conditioning and heating and indicated that corrosion can be avoided by correct choice of alloys, design of components, and equipment operation. The hydrolysis of organic solvents and lubricants or the reactions of refrigerants with water have been shown to cause formicary and large-pit corrosion in copper tubes (Nagata and Kawano 1994; Lenox and Hough 1995), as well as copper plating and sludge formation in refrigeration systems (McGovern 1942). Elliott and Corbett (2001) described formicary or ant-nest corrosion as a particular form of localized corrosion of a submicroscopic nature. The morphology of the corrosion damage within the metal includes a series of minute interconnecting tunnels, starting from the tube surface and propagating rapidly into the tube wall. The corrosion product (copper oxide Cu_2O) is usually found in the micro channels. The mechanism of formicary corrosion generally involves the presence of moisture, oxygen and a corrosive agent such as an organic acid. Corrosions of cold-rolled steel 1020, copper, aluminum 2S, zinc, and magnesium alloy FS-1 were observed after exposure in R-123 with water for one hundred days (Dupont de Nemours and Company, undated). Sealed tube tests of aluminum, copper and steel specimens in

R-134a/POE with 50, 250 and 500 ppm water showed that copper plating increases with moisture, but can be partially or fully inhibited with additives depending on the moisture level (Greig, Smith and Swallow 1993). Copper plating was observed with both high moisture level and an additive-free lubricant, but not with the fully formulated polyolester at 300-ppm moisture (Smith, Beggs and Greig 1993).

Herbe and Lundqvist (1997) reviewed the experiences of companies with refrigerant and heat pump equipment that have converted from R-12/mineral oil to R-134a/polyolester. They concluded that all the companies surveyed believed that the problems with copper plating and formation of acid could be avoided if residual mineral oil was kept at less than one percent and moisture at less than fifty parts per million. In addition, 75% of the samples drawn from different converted equipment contained 130 ppm moisture or less.

4.4. EFFECTS ON SYSTEM PERFORMANCE

The presence of water in refrigeration systems leads to loss of performance (ICI Americas Incorporated 1994), ice deposition, corrosion of metals, blockage of expansion devices, copper plating, and poor lubrication. Goswami et al. (1996) investigated the effect of moisture on the performance of an air-conditioning system using R-22. They reported that cooling capacity of the system is not affected until about 100 ppm of injected moisture. Beyond that point, the capacity and COP of the system begin to drop with increasing moisture, decreasing by 10-15% at 1000 ppm injected moisture (around

700 ppm moisture in the refrigerant). Moreover, studies of blockage of capillary tubes showed that blockage is low in dry systems, but increases rapidly in the presence of water or when the system is doped with carboxylic acid (Herbe and Lundqvist 1997).

4.5. RESEARCH NEEDS REGARDING THE EFFECT OF WATER ON MATERIALS OF CONSTRUCTION

- Although formicary corrosion is a real phenomenon leading to copper tube failures, it is less well known than other forms of corrosion. Elliott and Corbett (2001) have successfully replicated formicary corrosion in the laboratory, but research is still needed to validate the current theories and mechanisms of formicary corrosion. Studies are needed to determine the rate of pit formation and propagation, the conditions of temperature, water content, acid content, and oxygen content needed to initiate the corrosion process. Corrosion inhibitors need to be developed and evaluated.
- The effect of moisture content in the refrigerant/lubricant system on the degradation of polymeric materials such as O-rings and shaft seals needs to be investigated.

V. SUMMARY OF INDUSTRY SURVEY

A survey was developed, with the ARTI 21CR Project Monitoring Subgroup, to determine the refrigeration and air-conditioning industry's concerns about the presence of water in the refrigerant/lubricant systems, as well as the industry's specifications regarding the amount of water allowable in HFC and synthetic lubricants. A sample of the survey is shown in Table 5.1. Twenty-four companies responded to the survey, including four companies producing or servicing equipment in commercial refrigeration, two in residential air-conditioning, and three in commercial air-conditioning. Two companies manufacture flow controls, and two manufacture commercial icemakers. Of the remaining eleven companies, two have products in commercial refrigeration and residential air-conditioning, four in residential and commercial air-conditioning, and five in commercial refrigeration as well as residential and commercial air-conditioning. Table 5.2 shows the type of products covered in the survey and their corresponding capacities, and Table 5.3 shows the different refrigerants and lubricants reported in use in the survey. In Figure 5.1 and Table 5.4, the refrigerant/lubricant systems used in the different product lines are compared. R-22/mineral oil is still the refrigerant/lubricant system most in used. In the survey, a larger number of companies reported the use of R-22/mineral oil in residential or commercial air-conditioning than in commercial refrigeration, where more companies reported the use of R-134a/POE or R-404A/POE. Fewer companies with products in commercial refrigeration indicated the use of R-410A/POE than in residential or commercial air-conditioning. While more commercial air-conditioners than residential air-conditioners or commercial refrigerators reportedly use R-407C/POE,

R-22/alkylbenzene is found in all the three types of equipment. A few products also use R-134a/PAG, R-410A/POE, R-507A/polyolester, R-507C/PVE, and R-401A/POE. Two commercial refrigeration companies reported using R-22/POE with scroll and screw compressors. The water concentrations specified and expected for different refrigerant/lubricant systems vary depending on the products, their capacities and applications, and also on the companies. In flow controls, the specified values for new field-erected or factory-sealed equipment are less than 50 ppm for HCFC as well as HFC. The expected values after service and re-assembly are also less than 50 ppm, but the actual measured values in the field can be as high as 300 ppm. In residential air-conditioning, for HCFC refrigerants, the specified water contents ranged from 10 ppm to 1.5 weight percent (reported by one company that did not specify whether the percentage was based on refrigerant, lubricant or refrigerant plus lubricant weight), while the expected water contents are from 10 to 150 ppm. For HFC refrigerants, the specified values are from 10 to 50 ppm, while the expected values are between 50 and 150 ppm. The measured moisture for both HCFC and HFC is between 13 and 700 ppm. In commercial refrigeration and commercial air-conditioning, the specified values for HCFC and HFC are 100 ppm on the low side or 1.5 weight percent on the high side. The expected values are between 20 and 100 ppm, while the measure numbers are as high as 700 ppm. Among the problems that would most likely result from the presence of high moisture level in the refrigeration systems, lubricant breakdown is of greatest concern, as shown in Table 5.5. Next in importance is acid formation, followed by compressor failure and expansion valve sticking. Elastomeric seal failure and sticking of suction valve cause fewer concerns. One of

the respondent engineers noted that, in his opinion, contamination of the POE lubricant with traces of mineral oil is a much larger problem than moisture in the system. Of the twenty-four companies that responded to the survey, seventeen (71%) use filter driers and six (25%) employ acid catchers.

5.1. RESEARCH NEEDS FROM INDUSTRY SURVEY

- The industry needs to measure and record the water content and total acid number of the lubricant of newly installed systems, as well as operating systems that are shut down for service or repair. The reason for the shutdown and repair needs to be documented. A database can then be established, similar to the one reported by Herbe and Lundqvist (1997), to correlate water content in systems with type of breakdown or problems encountered. Combined with the detailed studies on the distribution of water in refrigeration and air-conditioning systems, such as the study by Kitamura et al. (1993), the database would allow the air-conditioning and refrigeration industry to set meaningful limits on the allowable water content in newly installed equipment, either field-erected or factory-sealed.

TABLE 5.1. CONFIDENTIAL SURVEY: EFFECTS OF WATER IN HVAC SYSTEMS

1. Please fill in the following table where appropriate:

	Residential A/C		Commercial A/C		Commercial refrigeration		Other (specify)	
Company's products (Check where appropriate)								
Product Size Range (in HP, ton, or BTU)								
	HCFC	HFC	HCFC	HFC	HCFC	HFC	HCFC	HFC
Refrigerants used or intended for use in your products: R-22, R-134a, R-410A, R-407C, other (specify)								
Lubricants used/specified in products: POE, PAG, mineral oil, alkylbenzene, other (specify)								
Moisture level specified for new equipment in field- erected equipment (in ppm or percent)								
Moisture level specified for new equipment in factory- sealed equipment (in ppm or percent)								
Moisture level that you expect would exist in equipment after service and re-assembly (in ppm or percent)								

2. In your opinion, high water content in the system would most likely cause (please check all that apply):

☐ compressor failure

☐ elastomeric seal failure

☐ sticking of expansion valve

☐ lubricant breakdown

☐ degradation of motor insulation material

☐ ice formation in the evaporator

☐ refrigerant breakdown

☐ deterioration of wire coating

☐ plugging of suction filter or heat-exchanger (clathrate

formation)

☐ acid formation

☐ copper plating

☐ metal corrosion

☐ suction/discharge valve sticking

☐ other _____

3. Are you using/specifying filter-dryers?: _____ ☐ yes ☐ no

4. Do you use chemicals to catch acids in the lubricant?: _____ ☐ yes ☐ no

5. Have you measured moisture level in the field?: _____ ☐ yes ☐ no

6. If yes, what range of moisture level have you observed/recorded? _____

7. What fraction of your warranty cost has been attributed to moisture in the system? _____%

Comments: _____

Company's name: _____

Name of person completing this form (optional): _____

Title/Position: ☐ engineer, ☐ chemist/scientist, ☐ materials, ☐ manufacturing, ☐ research, ☐ field service, ☐ reliability/quality control

TABLE 5.2. PRODUCTS COVERED IN INDUSTRY SURVEY		
Company Number	Products Manufactured	Capacity Range
1	Flow controls	¼ to 400 tons
2	Flow controls	All system capacities
3	Commercial refrigeration	¼ to 4 HP
4	Commercial refrigeration	4,000 to 24,000 BTUH
5	Residential air-conditioning	Less than 7 ½ tons
	Commercial air-conditioning	Less than 350 tons
	Commercial refrigeration	Less than 40 tons
6	Commercial ice-maker	1,500 to 28,000 BTUH
7	Residential air-conditioning	1.5 to 5 tons
8	Residential air-conditioning	1 ½ , 2 and 2 ½ tons
9	Commercial refrigeration (display case)	1/3 to 1 ½ tons
10	Residential air-conditioning	1 to 5 tons
	Commercial air-conditioning	Not specified
	Commercial refrigeration	Not specified
11	Residential air-conditioning, including room air-conditioning	Not specified
	Commercial air-conditioning	Not specified
12	Commercial air-conditioning	12.5 to 2,100 tons
13	Commercial air-conditioning	10 to 2, 5000 tons
14	Residential air-conditioning	1 ½ to 7 ½ tons
	Commercial air-conditioning	1 ½ to 40 tons
15	Commercial refrigeration	½ to 35 tons
16	Residential air-conditioning	Not specified
	Commercial air-conditioning	Not specified
	Commercial refrigeration	Not specified
17	Residential air-conditioning	3 to 7 tons
	Commercial air-conditioning	3 to 48 tons
	Commercial refrigeration	2 ton 30 tons
18	Commercial ice machines	Not specified
19	Commercial air-conditioning	20 to 900 tons
20	Commercial air-conditioning	Not specified
	Commercial refrigeration	Not specified
21	Residential air-conditioning	1 to 6 tons
	Commercial air-conditioning	1 ½ to 120 tons
22	Commercial air-conditioning	200 to 1,500 tons
	Commercial refrigeration	200 to 1, 500 tons
23	Residential air-conditioning	12,000 to 65,000 BTUH
	Commercial air-conditioning	65,000 to 300,000 BTUH
24	Residential air-conditioning	Larger than 5,000 BTUH
	Commercial air-conditioning	Less than 150,000 BTUH
	Commercial refrigeration	200 to 35,000 BTUH

TABLE 5.3. REFRIGERANTS AND LUBRICANTS REPORTED IN USE IN SURVEY	
Refrigerants	
R-22	Chlorodifluoromethane (CHClF_2)
R-32	Difluoromethane or methylene chloride (CH_2F_2)
R-124	2-chloro-1,1,1,2-tetrafluoroethane (CHClFCF_3), a component of R-401A
R-125	Pentafluoroethane (CHF_2CF_3)
R-134a	1,1,1,2-tetrafluoroethane (CH_2FCF_3)
R-143a	1,1,1-trifluoroethane (CH_3CF_3)
R-152a	1,1-difluoroethane (CH_3CHF_2), a component of R-401A
R-401A	Refrigerant blend containing 53% R-22, 13% R-152a and 34% R-124 by weight
R-404A	Refrigerant blend containing 44% R-125, 52% R-143a and 4% R-134a by weight
R-410A	Refrigerant blend containing 50% R-32 and 50% R-125 by weight
R-407C	Refrigerant blend containing 23% R-32, 25% R-125, and 52% R-134a by weight
R-507	Refrigerant blend containing 50% R-125 and 50% R-143a by weight
Lubricants	
MO	Mineral oil
AB	Alkyl Benzene
PAG	Polyalkylene glycol
POE	Polyolester
PVE	Polyvinyl ether

TABLE 5.4. REFRIGERANT/LUBRICANT USAGE			
Refrigerant/ Lubricant	Number of companies reporting usage of refrigerant/lubricant system		
	In commercial refrigeration	In residential air-conditioning	In commercial air-conditioning
R-22/MO	5	11	12
R-22/AB	4	5	5
R-22/POE	2	0	1
R-134a/POE	10	1	8
R-134a/PAG	2	1	2
R-410A/POE	2	8	8
R-410A/PVE	0	1	1
R-401A/POE	1	0	0
R-404A/POE	9	1	2
R-407C/POE	2	4	10
R-407C/PVE	0	1	1
R-507A/POE	2	0	1

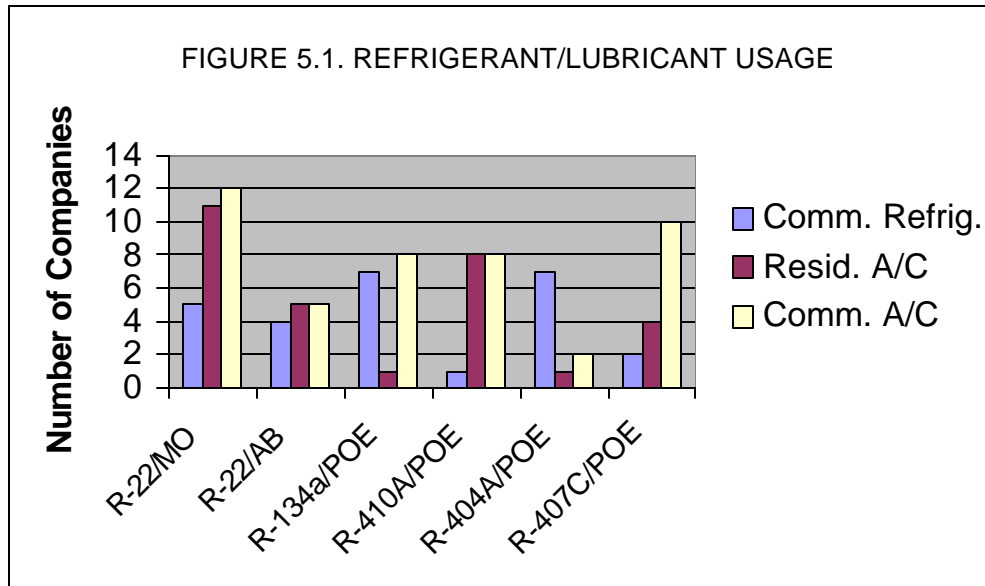


TABLE 5.5. SPECIFIED, EXPECTED AND MEASURED WATER CONTENTS								
Water Content, ppm * Note: different values are reported by different companies	Products							
	Flow controls		Commercial refrigeration		Residential air-conditioning		Commercial air-conditioning	
	HCFC	HFC	HCFC	HFC	HCFC	HFC	HCFC	HFC
Limits specified for new field-erected equipment	< 50	< 50	100	No spec.	50	10 50	50 100	< 10 30 50 100
Limits specified for new factory-sealed equipment*	< 50	< 50	100 1.5%	10 20 100 1.5%	10 50 1.5%	10 50	10 30 < 35 50 100 200 1.5%	10 30 50 100 1.5%
Limits expected after service and re-assembly *	< 30 < 50	< 45 < 50	20-25 < 30 100	20-30 < 30 50 100	10 25 100 150	50 100 150	25 < 30 60 < 100 150 < 500	< 20 < 30 50 60 < 100 150
Measured, recorded in the field	10-300		20-155 13-711		250-500 13-711		< 50 250-500 200-800 13-711	

TABLE 5.6. POSSIBLE PROBLEMS CAUSED BY HIGH WATER CONTENTS	
Types of problems	Number of responses
Lubricant breakdown	22
Acid formation	21
Compressor failure	19
Copper plating	16
Expansion valve sticking	16
Refrigerant breakdown	13
Degradation of motor insulation material	13
Metal Corrosion	12
Ice formation in the evaporator	11
Deterioration of wire coating	9
Plugging of suction filter or heat-exchanger (clathrate formation)	7
Elastomeric seal failure	6
Suction/discharge valve sticking	4
Plugging of liquid line filter-drier	1

VI. CONCLUSIONS

Since the introduction and use of HFC/synthetic lubricant systems in air-conditioning and refrigeration, there has been active research in the area of water content in the new operating fluids and its effect on system components and performance, as evidenced by the number of references cited in this review. However, much remains to be investigated. Based on the literature reviewed, the following research topics are suggested for future investigation, in the order of their importance, practicality and ease of implementation:

1. The air-conditioning and refrigeration industry needs to measure and record the water content and total acid number of the lubricant in newly installed systems as well as operating systems that are shutdown for service or repair. The reason for the shutdown and repair needs to be documented. A database can then be established to correlate water content in systems with type of breakdown or problems encountered. This research project is easy to implement and has practical application, because the database, combined with detailed studies on the distribution of water in refrigeration and air-conditioning systems, would help the industry in setting meaningful limits on the allowable water content in newly installed equipment, either field-erected or factory-sealed. Such a study can be conducted according to the following tasks:

Task 1: Request participating companies to measure and record the water content and total acid number of the lubricant in newly installed systems. The type of equipment, type of compressor, refrigerant/lubricant systems used need to be documented.

Task 2: Request participating companies to measure and record the water content and total acid number of the lubricant in operating systems that are shutdown for service or repair. The time in operation before shutdown and the reason for the shutdown and repair, as well as the type of equipment, type of compressor, refrigerant/lubricant systems used need to be documented.

Task 3: Establish a database from which different correlations can be drawn. Such correlations include: water content versus total acid number, water content versus type of breakdown, total acid number versus type of breakdown, change in water content with time, depending on the type of equipment, type of compressor and refrigerant/lubricant system.

2. Along with the database, detailed studies on the distribution of water in refrigeration and air-conditioning systems should be conducted to pinpoint problem areas associated with free water, and to help in the formulation and implementation of effective solutions to these problems. Following the research of Kitamura et al. (1993) for an automotive air-conditioning system using R-134a/PAG, the following tasks can be conducted in a detailed study of the distribution of water in a refrigeration or air-conditioning system. The equipment for the various measurements can be of similar design to those described by Kitamura et al.

Task 1: Measure the saturated water content in the gas phase of the refrigerant of interest, if not already available in the literature.

- Task 2: As the amount of water added to the refrigerant circuit is changed, measure the water content in the liquid refrigerant before the expansion valve, and in both the liquid and gas refrigerant after the expansion valve.
- Task 3: Compare the water content in the gas refrigerant with the saturated water content of task 1 to assess possible formation of free water during expansion.
- Task 4: Measure the water content in the gas refrigerant after the evaporator.
- Task 5: Simulate a differential section of the evaporator as described by Kitamura et al., and measure the water content in the liquid and gas refrigerant during evaporation of the liquid refrigerant in a pressure vessel at a constant temperature.
- Task 6: Measure the saturated water content in the oil at a temperature corresponding to the low-pressure side of the system.
- Task 7: Simulate the water behavior in the evaporator, with the presence of the lubricant, to determine whether free water will separate in the evaporator.
3. Although formicary corrosion is a real phenomenon leading to copper tube failures, it is less well known than other forms of corrosion. Formicary corrosion has been successfully replicated in the laboratory, but research is still needed to validate the current theories and mechanisms for this type of corrosion. Studies are needed to determine the rate of pit formation and propagation, the conditions of temperature, water content, acid content, and oxygen content needed to initiate the corrosion process. Corrosion inhibitors need to be developed and evaluated.

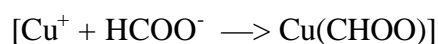
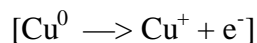
Elliott and Corbett (2001) were able to successfully replicate formicary corrosion of copper tubes in the presence of a corrosive agent such as formic acid, acetic acid, trichloroethane, and water-based drawing and fitting lubricants. The test copper tubes were placed inside glass test tubes (to avoid direct contact between the copper and the corrosive agent) and the glass tubes were placed in spring clamped Mason jars containing the corrosive agent. Following similar experimental procedures, the following tasks can be conducted to define the rate of formicary pit formation and propagation as functions of acid content, water content, oxygen content and temperature:

Task 1: Develop a test matrix to test the effect of each parameter (water, acid, oxygen concentrations, temperature and exposure time) on the extent of corrosion, separately and in combination with one another.

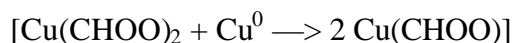
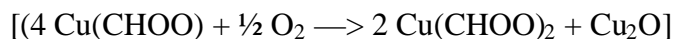
Task 2: Measure the rate of corrosion, using different analytical techniques such as metal weight loss, x-ray radiography, ultrasonic velocity measurements and sound attenuation measurements, as functions of water, acid, oxygen concentrations and temperature.

Task 3: Determine the minimum value of each parameter for corrosion initiation.

Task 4: Verify that the mechanism for formicary corrosion of copper, as supported by current consensus, involves first an oxidation step, followed by a reaction with a carboxylic acid:



In the next step, the copper complex is oxidized. The cupric formate reacts with fresh copper, yielding the unstable cuprous complex. The last two reactions will repeat over and over, resulting in formicary corrosion tunnels.



4. Although studies have been conducted on a number of hydrate formers including hydrofluorocarbon refrigerants, the conditions for formation and decomposition of clathrate hydrates of other alternative refrigerants under consideration for use in refrigeration and air-conditioning systems and water should be determined to avoid possible problems associated with tube plugging. These alternative refrigerants may include R-23, R-41, R-116, R-125, R-143a, and refrigerant blends such as 404A and 507C. A research project, built on the work of Akiya et al. (1999), can be conducted to study the formation and decomposition of clathrate hydrates of R-125, R-143a, and their blends R-404A (44% R-125, 52% R-143a, and 4% R-134a) and R-507C (50% R-125 and 50% R-143a). Such a research, in addition to providing additional thermodynamic data, would verify the theory that it is possible to determine the clathrate decomposition conditions of a blend of HFC refrigerants from the data of its individual components. The following tasks would be included in the research program:

Task 1: Obtain the condensation and clathrate formation lines of R-143a. From the intersection of these lines, obtain the critical clathrate formation conditions T_c and P_c .

Task 2: Use the thermodynamic data available from Akiya et al. for R-125 or perform additional measurements as desired.

Task 3: Obtain the condensation line, clathrate formation line, T_c and P_c for R-404A and R-507C.

Task 4: Plot T_c on linear scale versus P_c on logarithmic scale for R-125 , R-143a, R-404A and R-507C.

Task 5: Develop correlations between the T_c and P_c of the refrigerant blends and those of their individual components.

5. The mechanism by which water facilitates or hinders lubrication is not known and needs to be studied and characterized in order to formulate more effective lubricants and lubricant additives. Sheiretov, Glabbeek and Cusano (1996) indicated that water can oxidize the metal surfaces or it can react with an already existing oxide layer (such as (Al_2O_3)) to form hydroxide (such as aluminum trihydroxide). The oxides or hydroxides provide protective layers against wear of the metal surfaces. Based on the results of Sheiretov, Glabbeek and Cusano, a study to determine the effects of water on lubricity can be developed, involving the following tasks:

Task 1: Expose metal surfaces to different concentrations of water in the presence of lubricant and refrigerant, but in the absence of air, at various exposure time and temperature.

Task 2: Measure the thickness of the oxide layer using Auger Electron Spectroscopy.

Task 3: Relate the rate of oxide formation to water concentration and temperature.

Task 4: Expose metal surfaces to different concentrations of air in the presence of lubricant and refrigerant, at various exposure time and temperature.

Task 5: Measure the thickness of the oxide layer formed and relate the rate of oxide formation to the concentration of air and temperature.

Task 6: Expose the oxide layer obtained in task 4 to different concentrations of water and determine the rate of hydroxide formed as functions of water concentration and temperature.

Task 7: Conduct tribology tests in systems similar to the High-Pressure Tribometer (HPT) described by Sheiretov, Glabbeek and Cusano on the metal surfaces protected by oxide or hydroxide layers obtained in tasks 1 and 6 and determine the rate of wear of the oxide or hydroxide layers.

Task 8: Compare the rates of oxide or hydroxide formation and wear. If the rate of formation were faster than the rate of wear, the presence of water would have a positive effect, resulting in lower wear of the metal surfaces with increasing water concentrations. On the other hand, if the rate of formation were slower than the rate of wear, the presence of water would have a negative effect on lubricity. It should be noted, however, that the type of lubricant and refrigerant used would have the greatest impact on the total lubricity of the system.

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