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REFRIGERANT RETROFIT IN SWEDEN -- FIELD AND LABORATORY STUDIES

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Introduction

Field retrofits from CFC to HFC refrigerants have now been going on for a couple of years. The refrigeration industry have thus faced some new technical problems. One of them is, of course, the difference in thermodynamic, and transport properties, another one is the difference in chemical properties. This paper will deal with the latter but not less important subject -- the difference in chemical behaviour between CFC's and HCFC's from the users point of view.

Background

Especially in conversion the stability of the refrigerant and the oil is of greatest interest. When the CFC refrigerant and the mineral oil is substituted to an HFC refrigerant with ester oil there will be a mixture of a number of components. A high stability of the consistuents is thus very important.
To examine what happens in a refrigeration or heat pump system after a conversion, a database has been set-up in cooperation with two chemical laboratories. The database now consists of approximately 800 analysis results from oils samples from converted refrigeration and heat pump units in field operation. The samples originates from all kinds of units. Small reciprocating units in grocery stores to large screw compressor units in district heating systems.
Some questions that hopefully could be answered with the collected data are:

- How high levels of different contaminants are commonly found in plants in field operation?
- How high levels of contaminants are accepted?
- Which are the most important parameters and what are the correlations between them?

In the search of answers to these questions the work has been concentrated to three main areas: database study, interviews and sealed tube tests.

The situation in Sweden

The Swedish EPA (Statens Naturvårdsverk) has decided that Sweden should be one of the leading countries in the settlement of clorinated refrigerants. The shedule for the settlement is:

ASHRAE Number	Type of refrigerant	Stop for impor and installation	Stop for refill	Stop for use	Share of total refrigera charge[1] in Sweden
R12	CFC	1995	1998	2000	32%
R500	CFC	1995	1998	2000	6%
R502	CFC	1995	1998	2000	12%
R22	HCFC	1998	2002	xxxxx	50%

The retrofit activities have been going on for at least four years now, thanks to this plan. As much as 50% of the units working with R12 are believed to have been converted to R134a. Experiences from this work are good among the refrigeration companies. The last two years R404A has appeared as the main substitute for R502 in conversion. When it comes to R22 the choice is not that obvious. Some companies have started converting to R407C, also here with good results. A small number of chillers with tube and shell heat exchangers have also been retrofitted to R407C. The performance, for the pure refrigerants, are in most cases unchanged and in some cases even better, probably dependent of the service of the system during a conversion.

The use of hydrocarbons has also started on a small scale. There are, however, no reports of retrofits to hydrocarbons. The reason for this is mainly the safety requirements. Propane has been installed in new small- and

[1] Natural refrigerants are not included.

medium sized systems (< 5MW refrigerating capacity) in liquid chillers. Isobutane is used by Electrolux in 16% of their refrigerators and freezers for domestic appliances.

Two major retrofit methods have been worked out. The *oil changing method* and the *flushing method*. The methods have different advantages. The oil changing method is used when a longer stop is unacceptable. It is also used in DX-systems where it is often difficult to clean the heat exchangers with the flushing method. On the other hand, the oil changing method is more expensive in large systems with large quantities of oil. The method requires 3-8 oil changes depending on the system design. This leads to repeated service-visits, since the system has to run for some time between the oil changes. The conclusion is that the flushing method is preferable when possible. Special caution need to be taken at the start up of the system after the flushing. The sliding parts in the compressor may be completely free from oil. The compressor should therefore be run only for a few seconds at a time until full lubrication is achieved.

Gathering of data

As mentioned above the retrofit activities have been going on for some years now in Sacandinavia. One way of collecting experiences form these conversions, is to study oil samples taken after a conversion. Oil samples are taken to insure that the recommended levels of residual mineral oil and water not are exceeded (included in the standard retrofit procedure). Oil samples collected by the Swedish refrigeration industry are evaluated by two laboratories, Invicta in Norway and Mobil Oil in Sweden. The analysis results has been put together in a database and evaluated at the Royal Institute of Technology in Stockholm. The results form this database study are presented below.

Describing statistics

The database is a kind of register where each test result shows the levels of residual mineral oil, moisture, TAN, Fe, Al and Cu etc. There area total of 20 different substances for each sample. Type of compressor, type of oil and operating time is also registered for each sample. In fig.1 the substances measured in a standard oil analysis are shown. Each horizontal line in the diagram represents a converted unit. The crosses represent the mean values.

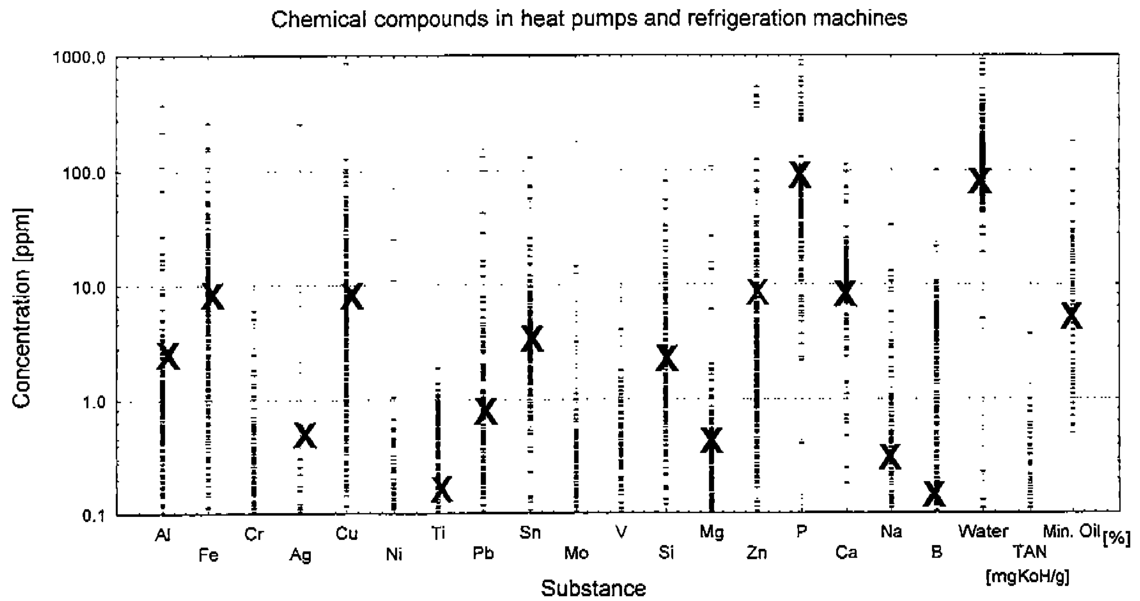

Fig 1. Environment in heat pumps and refrigeration machines.

Substances indicating a high compressor wear are aluminium, copper and iron. Other materials that should be mentioned are: aluminium, nickel, copper and tin from valves, valve seats and fittings made of brass and bronze alloys and, finally, silicon which is released from the filter-drier. High levels of Cu, Fe and Al is probably the result of a high total acid number which in its turn is the outcome of hydrolyzation of the ester oil caused by a high water content. The acids affect the copper which may migrate to the hot parts of the compressor, so called copper plating. This accelerates compressor wear. Phosphorus is used as an oxidation inhibitor (clearly seen in figure 1).

A high water content and/or high residual mineral oil level is the result of an unsatisfactory performed retrofit. The scandinavian refrigeration industry, for example, recommends evacuation down to an absolute pressure level below 150 Pa at temperatures above 15°C during at least 12h. Laboratory tests at the Royal Institute of Technology has shown that the *evacuation time* is of the utmost importance. The lab tests also showed, that even if these recommendations were followed, it was difficult to lower the moisture content to recommended levels. It is therefore important to change the filter-drier during the conversion. A better way to show commonly found levels in units in field operation is in histograms. Some of the substances that most likely affects the life time of a unit are shown in fig. 2 - 7.

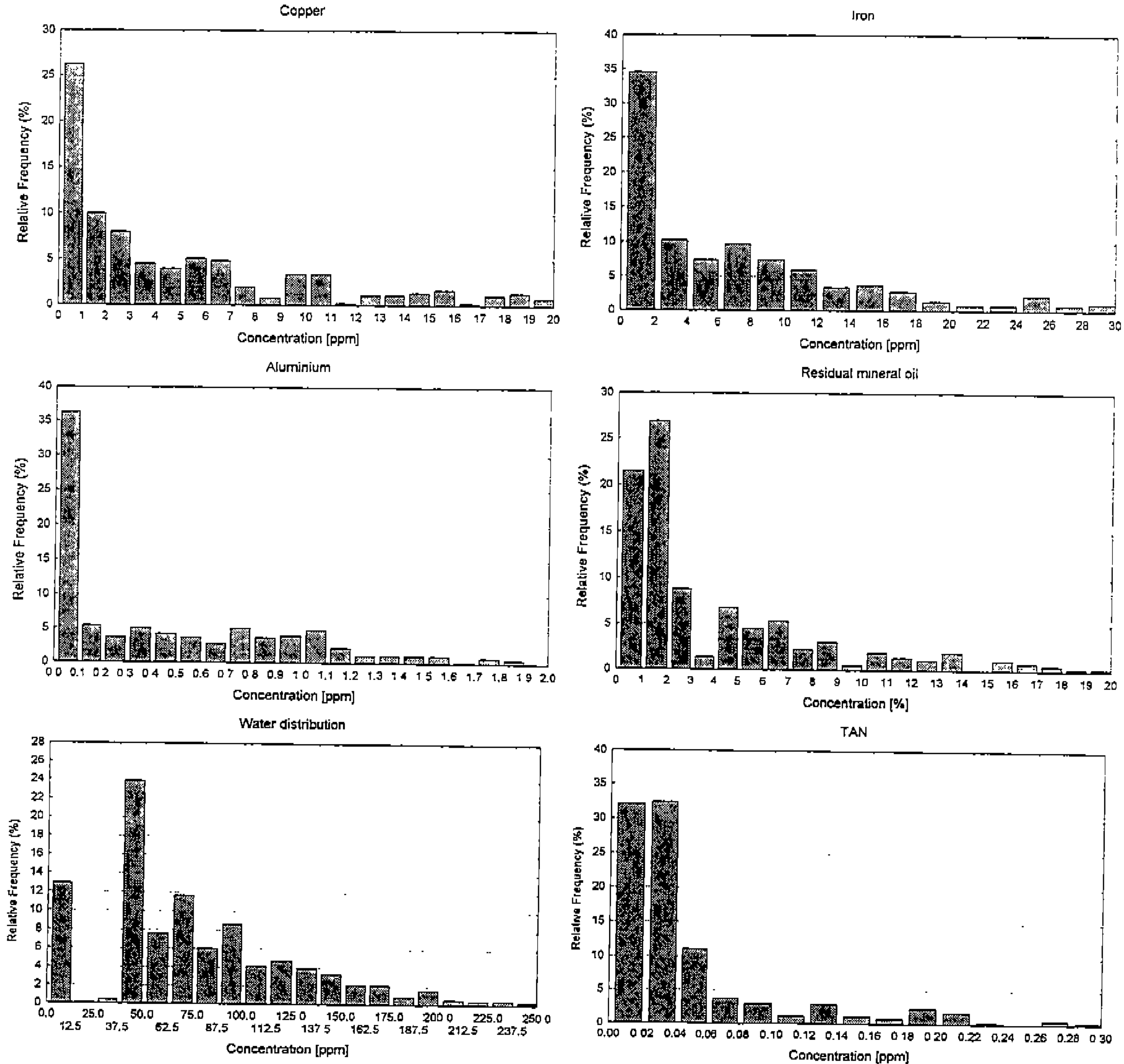

Fig 2-7. Distribution of Cu, Fe, Al, residual mineral oil, water and TAN in oil samples from converted refrigeration and heat pump units.

By adding the bars in each histogram one can see that 75 % of the samples contains less than: 14ppm Cu, 11ppm Fe, 1ppm Al, 7% min.oil, 110ppm moisture and 0,05 as TAN. These values should be compared with target levels chosen by the Swedish refrigeration industry: 10ppm Cu, 25ppm Fe, 2-5 % mineral oil and 50-100 ppm water. In a telephone inquiry accomplished in 1994 and 1996, refrigeration companies in Sweden were questioned about their conversion activities. The experiences concerning operation reliability were generally good if the above recommendations were followed.

Categorisation

By grouping the material into different "wear levels" it is possible to obtain an indication of when to expect increased compressor wear. One approach is to classify the data after moisture content or TAN, and then study the distribution of iron, copper and aluminium separately for these groups. In fig. 9-10 below, the samples have been divided into three groups after the moisture content. The distribution of copper is represented for each of these groups. The groups are: Samples with < 50ppm water, 50 - 200 ppm water and >200 ppm water.

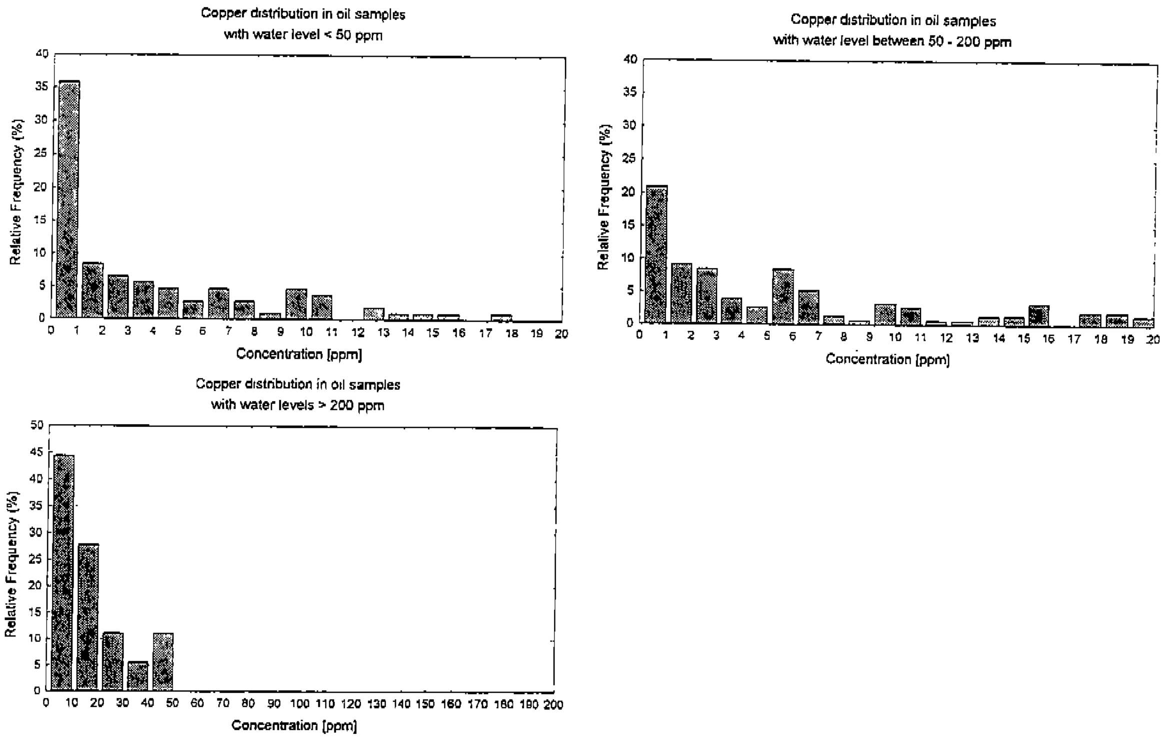

Fig 8-10. Cu distribution in oil samples for the moisture level groups: < 50 ppm, 50 - 200 ppm and >200ppm.

The histograms in fig. 8-10 shows that, in the group with less than 50 ppm moisture, 75% of the samples contained less than 9,6 ppm Cu. In the group with 50 -200 ppm moisture, 75% of the samples contained less than 18,6 ppm copper and in the last group, with moisture levels higher than 200ppm, 75 % of the samples contained less than 23,2 ppm copper. This shows two things: 1) The amount of copper in refrigeration- and heat pump units *is* dependent of the moisture level. 2) Moisture levels lower than 50 ppm results, in most cases (75% of the cases), in copper levels lower than 9,6 ppm, which is slightly lower than the target levels believed not to cause any problems or increased wear.

Principal Component Analysis (PCA)

Multivariate analysis has been utilised to find patterns how the contaminants influence each other. With this method it is also possible to get a picture of how the variables correlates. A short description of the methods is: The samples are plotted in an n-dimensional room, where n is the number of variables, in this case n=21. A new axis is adapted to the points, so that it describes the maximum variance among them. This axis is called PC1 (Principal Component nr.1). Another axis, PC2, is adjusted perpendicular to PC1, so that it describes the maximum variance around PC1. The third axis, PC3, is perpendicular to PC1 and PC2, and so on. The number of necessary PC's are dependent of the data. The stronger the correlations are between the variables, the fewer PC's are needed to completely describe the data. Two main results are obtained with the PCA analysis: 1) a two-dimensional representation of the data, so that relationships among points may be observed, 2) the magnitude of so called *loadings*, which is the coefficients that describes the variables in the PC's. The loadings gives an indication of the significance of each variable. The scores-plot is the points (the samples) plotted in a diagram with the PC1 as abscissa and PC2 as ordinate.

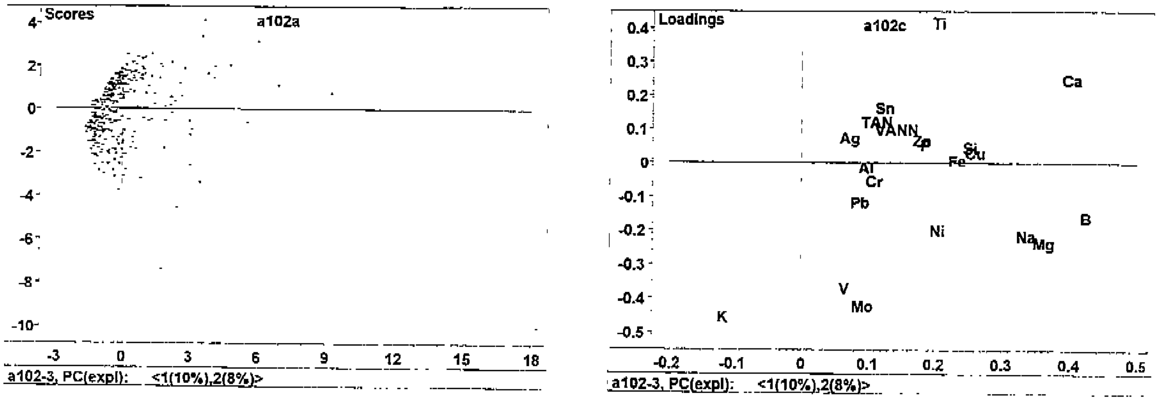

Fig 11-12. Scores and lodings for all samples and variables in the database.

The results from some initial work with a program called "Unscrambler" are presented in fig. 12-13. The scores-plot show that more than two PC's are needed to correlate the variables. The same goes for the loadings-plot. It is however possible to see is that copper correlates with iron and silicon (they are near each other in the diagram). They also have a great effect on the direction of PC1. They possess high PC1 values and are situated on the axis. This means that all the variance in copper and iron is completely explained by PC1. Another strong correlation is TAN Vs water (as expected). Further work will include so called "Partial Least Square" (PLS). By a PLS model based on the samples in the database, levels of, for example, Cu Fe and Al could be predicted by knowing only the levels of TAN or moisture. The model is potentially interesting and eventual results will be presented in the future.

Sealed tube tests

To confirm the results from the database study, sealed tube tests have been accomplished according to ANSI/ASHARE standard 97-1989 "Sealed glass tube method to test the chemical stability of material for use within refrigerant systems". A short description of the method is: Glass tubes are prepared with the components that are to be tested. The glass tubes are then fused and aged in an oven to accelerate possible reactions.
Two types of ester oils were tested (Castrol Icematic SW32 and SW220). The tubes were prepared with metal strips of copper and aluminium, ester oil, aged mineral oil (composition, see below) and refrigerant R134a, see tab.1.

All 24 tubes contains (CDA110 = SS5010, electrolytic copper),
Flapper valve steel (20C = SIS 1770-04, i.e. 0.1% C and 0.25% Si) and R134a.
Moisture- and residual mineral oil combinations:

SW220	50 ppm moist.	25% min oil	1000 ppm moist	25% min oil
SW32	50 ppm moist	25% min oil	1000 ppm moist	25% min oil
SW220	50 ppm moist	2% min oil	1000 ppm moist	2% min oil
SW32	50 ppm moist	2% min oil	1000 ppm moist	2% min oil

The moisture content is based on the weight of the ester oil and the residual mineral oil on the total oil weight.

Moisture content, based on total oil mass (ester + mineral oil), when the two oils were mixed.

SW220	195 ppm moist.	25% min oil	873 ppm moist.	25% min oil
SW32	195 ppm moist.	25% min oil	873 ppm moist.	25% min oil
SW220	181 ppm moist.	2% min oil	1112 ppm moist.	2% min oil
SW32	181ppm moist.	2% min oil	1112 ppm moist.	2% min oil

Composition of unmixed aged mineral oil (contaminants in ppm): Al 0, Fe 10, Cr 0, Ag 0, Cu 8, Ni 0, Ti 0, Pb 0.4, Sn 0, Mo 0, V 0, Si 5, Mg 0, Zn 3, P 5, Ca 0, Na 0, B 0, K 4, H2O 232, TAN 0.01mgKOH/g.

Fig 13. Composition of sealed tube tests.

The tests were visually evaluated after one week and after four weeks and the results are:

Visual evaluation after:		**One week** Fluid: Transparent. Copper: Bright.		**Four weeks**	
25% residual min. oil	SW220	Partly slightly yellowish brown	Partly plated with a yellowish brown cover	Cu: Bright Fe: Light bronze coloured cover	Cu: Bright Fe: Dark bronze coloured cover
25% residual min. oil	SW32	Bright	Bright	Cu: Slightly corroded Fe: Bright	Cu: Slightly corroded Fe: Bright
2% residual min. oil	SW220	Slightly yellowish brown at the edges	Partly plated with a yellowish brown cover	Cu: Bright Fe: Light bronze coloured cover	Cu: Bright Fe: Dark bronze coloured cover
2% residual min. oil	SW32	Bright	Bright	Cu: Bright Fe: Bright	Cu: Slightly corroded Fe: Bright
		50 ppm moisture	1000 ppm moisture	50 ppm moisture	1000 ppm moisture
The moisture content is based on the weight of the ester oil and the residual mineral oil content is based on the total weight of the oils (ester and mineral oil).					

Fig 14. Visual evaluation of sealed tube tests after one and four weeks of aging.

The tests, so far, indicates that Castrol Icematic SW220 is more easily affected by moisture than Castrol Icematic SW32. High moisture levels (1000ppm) also seem to have a greater effect than high residual mineral oil levels (25%). The results are strongly associated with these specific oils and should not be taken as generally applicable. However a low moisture level is desirable since moisture is always required for the acid formation process. A low moisture level is thus more important than a low residual mineral oil level. (Excess residual mineral oil may cause other negative effects such as decreased heat transfer coefficients in the evaporator).

Conclusion

Moisture and residual mineral oil plays an important role in the decomposition of the HFC refrigerant - ester oil mixture. Exactly which levels of contaminants that are acceptable are dependent of many parameters, such as: present alloys, type of oil and refrigerant and type and size of the unit and the compressor. Operational parameters, such as temperature levels and operating time, also affects the system. This means that the tolerable level of contaminants varies from case to case.

The experiences and the material available from the past four years of intensive conversion work on the field, indicates that the levels accepted today, in the refrigeration industry, prevents increased wear and other problems.

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