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Lecture - 04 Refrigerants

Today we are going to focus on refrigerants. Refrigerant is related to a refrigeration system just like the breath is to the human body. It permeates the entire system and the whole system's performance depends on the refrigerant. If we look at choosing the right refrigerant from a pure thermodynamic perspective then we would focus on COP and how much of cooling we can get per kg of refrigerant at the target conditions.

Now, wish life was that simple, and it was that simple when air conditioning was just invented. When people were beginning to look at substances for air conditioning systems. At that point of time this was the case, and in fact even coefficient of performance wasn't so dominant. It was just the ability to produce cooling. And that is what we will learn as we go forward to review the history of refrigerants.

But before that there are certain relatively new developments that are dominating the choice of refrigerants and a lot of developments in air conditioning and refrigeration today are governed by either legislation or international agreements or guidelines for what is likely to happen in the future.

We will now look at the drivers for refrigerant choice that have changed over the last 30 years or so. Today we have a scenario where there is a growing world population and by 2050 we expect 70 percent of the population would live in urban areas. They would have aspirations for energy for air conditioning, for heating in countries where heating is needed and for different appliances.

And then apart from air conditioning, there will be a need for energy in agriculture, in transportation and all other sectors. That puts a huge demand on the eco-system. By 2035, it is expected that energy consumption will grow by 50 percent.

Now, what does this mean for the climate? Let us look at a scenario that we have a growing population and we have increasing needs for welfare of the human population. If the growth happens unchecked and this is not so much as an economic limitation; if we use all the resources we have, and we allow the current level of technology to lead to growth for air conditioning, refrigeration and all other human needs. Then we will go much above the sustainable limit that mother earth can cope with. If you look at a sustainability limit, there is a cycle of reverting to the balanced state in the environment that must be ensured.

There is a certain amount of energy, there is a certain amount of heating that happens and then there is a compensated cooling that happens. There is also the balance between $CO₂$ and oxygen that happens between plants and human beings and in all living things, so all that exists in a certain symbiosis. But today there is a concern that the climate will change because of the huge energy consumption that is happening across the world and that has drastic consequences for mankind.

It is not just the ability to produce cooling and heating, but also doing it in a responsible way that is important and therefore, we need some levers for bringing about a change. What can those levers be? By levers, I mean things like energy efficient technology and some standards which are mandatory, and we will talk about that and how they are influencing change and then international agreements. It doesn't help if one country continues to deplete the ozone layer through its activities and other countries are doing all that they can because the ozone layer depletion impacts the earth as a whole. There is a need for collaboration between nations and at the same time, there is an argument that developing countries will make: the developed countries have already taken their share of damage to the environment and therefore need to compensate the countries that haven't yet done any significant damage. So, there is negotiated settlement that needs to lead to an agreement.

What is possible if we use all these levers, is that, we can keep the climate and energy imbalance to limits which are sustainable, and that can be impacted both by taking care of substances which damage the environment and when we will talk about refrigeration and air conditioning, then it is refrigerants. And next is energy and energy is widespread, but within air conditioning it is the impact that an air conditioning system has on the overall CO² footprint. To get an appreciation of that, today you do not have air conditioning in the IIT Delhi hostels or it is at the initial stage of having air conditioning in some parts of the hostels.

What is air conditioning in hostels going to lead to is? That air-conditioning load is going to be rejected in some multiple of the cooling load to the environment around the hostels or to the air and that will have an impact on the air temperature when you are taking a walk or going on a bike because all that heat is being rejected to the environment outside the hostels. How much of that is going to be acceptable? These are some of the things that we need to start thinking about. When we accumulate the entire heat that is rejected through air conditioning, it forms a very substantial part of the overall global warming impact and for that reason energy efficiency is becoming increasingly important for RAC (Refrigeration and Air Conditioning) systems.

We will look at what is happening in refrigerant development right now. But before that let us also look at how this relates to refrigerants and what has happened to refrigerants over the last maybe 100 years or so.

There have been some global agreements for climate protection and in March 1984 there was a Vienna convention where some of the countries got together and began to look at means to protect the ozone layer.

The chlorofluorocarbons which were the miracle refrigerants for the period 1930 to 1990 roughly, and that is a period in which there was a lot of use without any concern for ozone depletion because no one knew that those refrigerants when released into the atmosphere finally, find their way up and then when they decompose, they cause the ozone layer to deplete. Following this there was an international agreement, the Montreal protocol was signed which was effective first of Jan 1989 limiting the use of chlorofluorocarbons throughout the world and there were some member countries which signed it and agreed to implement it from first of Jan 1989.

What that meant was that there will be a limit on each country as to how much it would consume. Think about a scenario that you are about to design the air conditioning system and then the very core of it like you know I earlier suggested it is like comparing the human breath to refrigerant in the system and that gets controlled. Instead of looking at coefficient of performance or how much cooling you will get, you also have to be concerned about whether it is legally permissible to use that refrigerant and what is going to happen long term in 15 years, 20 years to available needs of servicing. If gasleaks, we need a refrigerant to service.

Essentially in this slide what I want to really communicate to you people is that, refrigerants like CFC11 which was introduced in 1932 as a replacement for flammable and toxic refrigerants used at that time became very popular and it was used widely in centrifugal chillers. It is classified as an A1 refrigerant and we will talk about it in the classification of safety for refrigerants. It is a substance which has an ODP (Ozone Depleting Potential) which is the reference number of 1, which means it is among the highest ozone depleting substances.

And the next in line is R 12 which is a chlorofluorocarbon and that was introduced in 1931 as a replacement again to flammable and toxic refrigerants. From 1930 to 1990 the whole focus was on having refrigerants that are reliable and safe and they do not have any flammability hazards. HCFC22 was originally used for low temperature refrigeration and later air conditioning, and today it is the most popular refrigerant for air conditioning and certain categories of refrigeration. Again it is an A1 refrigerant and you will understand these terminologies as we go forward. And then the trend today is to look for refrigerants which not only have a zero ozone depletion potential, but also a low global warming potential.

Now, if we talk about CFCs they are already phased out. No new production is happening, it is phased out and all refrigerators that are produced in the world today do not use R12 and the alternative refrigerant choices have been environment friendly. It was R134a in the beginning and then with the global warming concerns we moved to hydrocarbons. And where the charge quantities are small, hydrocarbon is not an issue at all. This chart here now, talks about the new, currently active phase out schedule of hydrochlorofluorocarbons. Among them the most critical one is R 22 that is used in air conditioners that we see, which is residential air conditioners, light commercial air conditioners and all that.

If you look at this chart there is a mandate to phase out R22 by 2030 for developed countries and by 2040 for article 5 countries which means developing countries which are funded in some cases for technology and the cost of changeover and that funding is essentially through the Montreal protocol multilateral fund and it compensates those nations for having given up on some of the growth and welfare advantages they would have had in case technology was what it was. Which means it was unconstrained growth.

You have R 22 which is available in the country. We in India have our own manufacturing of R22 and if we were to just address the aspirations of people at cost effective or cost led price effective price points for air conditioners, then we would go in a particular direction. This addresses depletion of ozone layer.

And then there is another concern which is global warming, and to address the global warming there is now an increasing trend towards labeling appliances for energy efficiency and in India we have bureau of energy efficiency which drives the standards and we can look at this slide, it shows a typical label on a residential air conditioner up to 3 tons.

If you go to buy an air conditioner you do not have to do complicated calculations, you even need not be an engineer. If you have a basic sense about power and cooling, you could look at this label and decide whether you want to go for a slightly higher price and low operating cost or you just want the air conditioner for a few hours in a day and you would be happy with just the minimum energy efficiency ratio. Now, this label may not be clearly visible to you, but I invite you all to look at the BEE website where you can look at the parameters. The key parameter here is energy efficiency ratio, it is the ratio of cooling at standard conditions to the power input. All the air conditioners carrying this label would need to go through a balanced ambient calorimeter test to define EER at a particular standard which is outdoor temperature of 35° C and indoor conditions of 27° C dry bulb temperature and 19° C wet bulb temperature. This air conditioner would have been tested to demonstrate that it complies with what is on the label within 5%.

When you are making a choice using the label, there is a backbone of properly testing and proving that what is on the label is through a robust test mechanism and it can even be challenged. When you look at the energy efficiency ratio and cooling you can compare and then you can choose what is it that you want to do, means buy the least price product or buy a product which will have the least overall cost, which is a lifecycle cost over a 10 year period.

Indian Energy Labeling Program

The star rating parameters EER shall be obtained from TABLE 2.1 / 2.2 / 2.3/2.4, depending on the year of manufacturing/import/assembling

Source: https://www.beestarlabel.com/Content/Files/Schedule3A-RAC1.pdf

This is an example of using legislation as a lever for reducing the global warming impact.

If you look at these 4 different phases of energy labeling they have gone from EER starting from 2.3 to an EER of 2.7 as the minimum required energy efficiency ratio.

Star Rating	EER (W/W)	
	Min	Max
1 Star * 2011	2.30	2.49
2 Star **	2.50	2.69
3 Star ***	2.70	2.89
4 Star ****	2.90	3.09
$5 \,$ Star *****	3.10	
	EER (W/W)	
Star Rating	Min	Max
1 Star $*$	2.70	2.89
2 Star **	2.90	3.09
3 Star ***	3.10	3.29
4 Star ****	3.30	3.49
Star *****	3.50	

"Source: https://www.beestarlabel.com/Content/Files/Schedule3A-RAC1.pdf

This is all available at the BEE website. You can refer to and look at more details of the products that are covered and the companies that have got approvals to use the label and the numbers, specific numbers of energy efficiency ratio and cooling capacity.

If you look at the period from 2011 to 2017, the minimum EER has gone up from 2.3 to 2.7. The minimum EER that is allowed for any product is also the minimum EER for one star level. A product which does not meet the one star level cannot be sold in India anymore. That is the power of legislation. Before the labeling program was made mandatory, products were as low as 1.9 and 2.1 on EER. It was an unregulated environment where the customer did not know the real product performance and EER.

Similarly for a 5 star product earlier 3.1 was adequate. Do you understand this number 3.1? It is a ratio. It is a dimensionless ratio between cooling capacity in watts and the power consumed by the appliance in watts. For reference, a 1.5 ton AC would be in the region of 5.2 KW. Now, if you do the calculations around the power that was required at 2.3 and 2.7 you will see how much of an impact has been made over the total volume of air conditioners sold in the market. If you are estimating 2 million air conditioner sold in a year, how much of an impact that will have on the required infrastructure to produce power to meet those new appliances addition.

This is how the lever of legislation is impacting global warming and that has obviously an impact on the environment.

Then there are other legislative drivers used by different countries. We looked at India we have ratified the Montreal Protocol and the amendments to it and therefore, we are bound to take care of the ozone layer by phasing out the fluorocarbons and the hydro chlorofluorocarbons. Then there are other means of looking at global warming potential refrigerants and what different countries are doing to limit their use.

There is a tax on F- gases in Denmark, Norway. It is not just the price of the refrigerant, there is a severe tax penalty on using gases that contribute to global warming. There are scientists who look at comparing one refrigerant to another and there is there is some debate on whether to look at the 20 year life of the refrigerant or to look at 100 year life of the refrigerant. But then there is a comparative index, whatever index you use you can make out how significantly a refrigerant impacts global warming because of its presence in the environment. A refrigerant makes an impact on the environment when it leaks. It could leak because of some problem during installation, it could leak because of its service life and in supermarkets leakage is a big issue because of the way they are maintained. There are too many joints there is too frequent use. Some part of the refrigerant that is there in the new system will obviously go into the environment and it goes into the environment it forms a reflective layer in the stratosphere that will prevent the heat getting radiated by the earth to outer space.

And then that contributes to global warming. Said differently if we are doing all that we can, can we limit the temperature rise of earth to below $2^{O}C$ by 2100. By the next century can we limit the temperature rise to less than $2^{O}C$? That is the big concern when it comes to global warming. And there are two ways an air conditioner contributes to global warming, one is direct which is due to leakage of refrigerants. The second is energy that is consumed by the air conditioner. The energy consumed by the air conditioner is leading to greenhouse gas emissions from the place of electric power generation, and it would be different for different sources of power generation. If it is coal based its going to be very high, if it is nuclear it perhaps will be negligible. Every country will have its own footprint of electricity and that is related to global warming.

We have talked about legislative lever of F-gas that is a tax in Australia and Europe. Then there is also a weight limit on charge quantity by appliance type and by size of the equipment, and then there is an element of subsidy that is being used in Japan, Germany and some parts of America. And there is funding available from the multilateral fund, so that also is a means for some countries to incentivize high efficiency systems and subsystems that use low global warming potential refrigerants. Two of the developments in China are use of R 32 on an experimental basis in some chillers which was never considered before has happened out of this funding, and then use of propane in a small residential air conditioners.

Use of propane in residential air conditioners started in china and then through another project in India. One of the manufacturers has used propane in residential air conditioners. Propane has a negligible global warming potential. These are the two major developments. The whole intention on loading all of you at this stage with this information is when you get down to designing an air conditioner, you will need to look at choosing a refrigerant and you will need to look at what agreements or legislation governs use of refrigerants. When I got into air conditioning (1993) I didn't have these constraints. I could just look at R 22 properties which were well documented, it was a safe refrigerant, I could build a system, test it, no concerns. By the time concerns came, they were limited to CFCs. While the refrigerator guys were struggling with the different refrigerants, for air conditioners it was still was fine to use HCFCs.

Most of the legislation today around the world is forcing companies to look at natural refrigerants a different way. When I use the word natural refrigerants some people have an affinity to something natural, like $CO₂$ is in the air, propane is available as a natural substance and all that. But if you look at the refrigerant that will go into a product, it will be a refined product. We have to be cautious. In terms of cost there will be higher costs even for refined propane, refined CO2. The distinction is that what we are looking at is a parameter, a parameter which is global warming and if you are taking steps to minimize that it is fine, whether it is natural or synthetic should not make so much of a difference. The other argument in favor of natural refrigerants is that they have been there so long.

We know ammonia. Ammonia is a natural refrigerant. It has been available so long we know how toxic it is, how to handle it. There is no new risk likely to be discovered. With the newer synthetic molecules, they go through an accelerated approval process by different companies, but we can never be sure they have taken care of all potential impacts on life; like long term toxicity, like long term impact on the environment. There always is an element of question mark that 10 years later we will discover something else. And it's driven by experience. When there was focus on saving the ozone layer there was a move towards refrigerants that were having a high global warming potential and inadvertently the refrigerants like R 407C that became popular choices because of their pressure comparison to the refrigerant in use like R22. We ended up solving one problem, but magnifying another problem in one category which is air conditioners.

In refrigerators fortunately there was a dual benefit. While the ozone layer was protected the alternative refrigerants also had a lower relative global warming potential to what refrigerants were replaced, but still they are not in the acceptable category of GWP. The key message is that looking at substances which are natural is one of the trends, and that is shown by use of $CO₂$, ammonia and hydrocarbons as all of them have no ozone depleting potential and low, very low global warming potential. Having done all that let us start looking at the refrigerant classifications and nomenclature so that you familiar with it.

There are two categories into which we can split refrigerants. Primary refrigerants which are a part of the vapor compression cycle. Those are the primary refrigerants. The secondary refrigerants are the refrigerants used as a means of heat transfer. When we want to transfer heat from one place to another like in a chiller, water is used as a secondary refrigerant. We cool water in the chiller evaporator and then this cool water goes into different terminal units where it cools the air that comes in contact with another heat exchanger. They are also called antifreeze and brines.

When you talk about a number like R11, R12, R22, what does that mean? For halocarbon compounds, the nomenclature is that the first digit on the right hand side represents the number of fluorine atoms. The second digit is number of hydrogen atoms plus 1, and then the number of carbon atoms minus one is the first digit from the left or third from the right. So that 0 means that there is one carbon atom and it is often omitted. When we say R12 or R11 means there is one carbon atom.

If you apply this nomenclature, then these are some of the commonly used refrigerants and their chemical formulations. As you can see, R11 one fluorine, R12 two fluorine atoms, and R13 three fluorine atoms. Are you following? This is kind of pretty straightforward. Methyl Chloride means zero fluorine. We first take care of the number of fluorine item then we take care of number of hydrogen and then carbon, and remaining is chlorine, and that is assuming the molecular structure is that of a saturated compound.

Now, what happens if it is not saturated or if there is another element like bromine?

If there is bromine then we will add the letter B and after the letter B will follow the number of bromine atoms that have displaced the chlorine atoms. Then there could be scenarios where there are two different molecular structures although the formulation is the same. So, same chemical formula, different molecular structure then we use subscripts a, b, etc. That will differentiate one from another. And then unsaturated, so we talked about saturated, if we have unsaturated halocarbons which means a double bond between two carbon atoms then we will add another digit before the number.

If it is 150 then we will add another 1 to make it 1150, that means it is an unsaturated compound. Now, all of this you will find in any refrigeration and air conditioning textbook. The key thing to remember is that these are compounds derived out of molecules which have a particular structure, and you could look at deriving some things out of methane, then out of ethane, and the way the chemists would formulate refrigerant molecules is to look for which refrigerant will best be suited for a particular application. And there is a lot of money invested in doing research to find out the ideal refrigerant and no ideal refrigerant has been found so far.

We will end up as engineers choosing the best fit for the application that we have in mind.

We also have inorganic substances, the ones I was referring to as natural substances, so water, ammonia, carbon dioxide and here it is simple. You take a number 700 add the molecular weight to 700 and that is the designation of those substances.

Then we also have mixtures. Nothing limits us from mixing refrigerants together and then trying to see what happens in the system. When we mix refrigerants we could have two scenarios, one case they evaporate at different temperatures and they condense at different temperatures and then we would have a glide.

Instead of looking at an evaporator temperature which is $5^{O}C$ we will have evaporation starting at 7° C going up to 9° C, starting at 5° C going up to 7° C, those kind of scenarios. We look at glide between $3\text{-}7\text{ }^{\text{o}}$ C. And in the condenser again depending on the application we would have it. If it is water cooled we could have something between 44° C to 49° C, in case of air-cooled it could be anywhere from 51 $\rm{^{0}C}$ to 55 $\rm{^{0}C}$. All those scenarios exist. In case of azeotropes we have two substances which are mixed together, but they behave as if it is a pure substance. R410A which is a replacement for R22, which is zero ODP and a high global warming potential refrigerant behaves like a pure substance. Azeotropes do not have any well defined nomenclature that I am aware of and so we will need to live by remembering the numbers assigned and the formulations that exist.

We have briefly looked at it, but look at what happened until 1930. 1830 to 1930 was a period I did not discuss before, it was a period when whatever could be used as a refrigerant was used. Whether it is carbon tetrachloride or it is ammonia or $CO₂$ or sulfur dioxide or calcium chloride. They were freely used and the end objective was just to produce cooling, that's it. There was no awareness about minimizing energy use or impact on environment. Even toxicity was not so well documented for those substances and people only later discovered the toxic nature of some of the refrigerants.

In the period 1931 to 1990, safety was key. Du-Pont got some big business by identifying the chlorofluorocarbons and they formulated refrigerants and those refrigerants were safe, i.e. they had no toxicity and they were not flammable. They became the ideal refrigerant for that period, and it was not known what impact they will have on the ozone layer. This period from 1931 to 1990 was primarily driven by CFCs and HCFCs and some systems like large industrial systems continued to use ammonia, which a natural substance.

Once the Montreal Protocol was signed, there was concern about CFCs, there was a shift. HFCs became popular. New molecules were looked at and the molecules were HFCs and those are the ones that replaced R12 in refrigerators and R11 in chillers and we are going to look at a refrigerant by refrigerant summary of each of the refrigerants as we go forward. Then let us look at the some of the criteria for refrigerant selection and how will we go about selecting a refrigerant.

The first and foremost thing is what temperature difference are we talking about? Where are we going to reject the heat? It will be different when it is a water cooled chiller or a water cooled condenser. It will be different if it is air cooled. And then depending on country and to appreciate how country makes a difference, in Europe where temperatures are low, CO² systems, single stage CO² systems are used forsome of the retail refrigeration applications. You go to a super-mart in Europe, you might see a $CO₂$ system which is considered environment friendly both from ODP and global warming perspective. If you try and use the same system in India where the climate is warm or even goes towards hot there is no chance of using that system. If you insisted you would need to look at newer technology like using a cascade system. In a cascade system, you have one system which is making use of $CO₂$ and another system which is making use of ammonia with an intermediate heat exchanger. In Middle East again the same challenges are there even bigger than India because the duration of high temperatures is very high.

First criteria is selection of refrigerants is condensing and evaporating temperature, the next is pressures, and you might ask why pressures? As mechanical engineers you would understand why pressures, right? Pipelines would burst if you are not designing for those pressures and costs would go up, high pressures, thick pipes, difficult to handle manufacturing, all that. Then the critical temperature and pressure. If you recall the pressure enthalpy diagram there is a point beyond which there is no two phase region for a particular refrigerant. The higher the critical point the larger is the net refrigeration effect that we can get and the closer is the approach to an ideal reverse Carnot cycle for performances like COP calculation.

If you really want to get to efficient systems with a high net refrigeration effect per kg of refrigerant then looking at a refrigerant with a high critical point is going to be important, and this is always in reference to the ambient. Here again another example and we will have some data to prove that as well, is R 410A. When you are looking at cold climates the critical point which is 68° C it is not so critical, the critical point is not so critical. Whereas, when we come to situations in middle-east the temperatures are high, it becomes difficult and in fact, there is a penalty on energy efficiency when we use R410A as a replacement to R22.

Then the freezing point is important because we cannot make the refrigerant flow if it is touching temperatures close to its freezing point, very simple. Volume of suction vapor will determine how big a compressor we need and so the volumetric efficiency of the compressor is driven by the specific volume at suction conditions. Then also the COP. One of the easy ways to compare refrigerants is look at the ideal cycle which means we include wet compression and we include isentropic expansion and we compare it to the ideal cycle. That is one straight cut comparison for the conditions that we are interested in and what is the COP with reference to an ideal reverse Carnot cycle.

Then we look for specific heat and oil miscibility. Dielectric strength you might wonder why oil miscibility why dielectric strength? Oil miscibility is to allow for oil to circulate with the refrigerant. A compressor requires oil for lubrication, and that oil will flow with the refrigerant. If it is miscible it will return back easily and the compressor will continue to work reliably. Then, dielectric strength is important because of hermetically sealed compressors. Since we have electrical windings that are directly exposed to the refrigerant, a high dielectric strength means there is low probability of short circuiting.

Thermal conductivity leads to better heat transfer. There is a thin refrigerant film which is the boundary layer inside the refrigerant tubes of a heat exchanger, a higher thermal conductivity would mean higher heat transfer. Viscosity, the lower the viscosity the better it is because the pressure drop is influenced by viscosity and then also the tendency to leak, so some molecules which are very very small like hydrogen would tend to leak very easily and it would be a concern. And then along with the leak tendency is also how easily can we detect the leak? Do we have equipment that can help us pinpoint the original leak and repair it both during manufacturing as well as in service? Then continuing on with the refrigerant selection parameters the newer ones is zero ODP.

Today if you are designing equipment we will not look for anything which has an ozone depleting potential. R22 is something not to be considered any more, R12 not to be considered any more, though they are ideal refrigerant from a thermodynamic perspective.

And then we will look at climate change impact. There is no agreement globally yet, but then there is concern, and there are guidelines to look for lower global warming potential refrigerants. If we have everything equal for two different refrigerants we will go for a refrigerant which has a lower global warming potential. Performance, capacity and efficiency, we addressed it when we said COP, but that was just at the ideal refrigerant level. Now we look at real mass flow rates of refrigerants at the conditions of interest. Safety, we are going to touch in the next few slides, but both flammability and toxicity are important considerations along with some of the pressure considerations that are there today.

Impact on product cost, availability and cost of the refrigerant, skills and technology required to use the refrigerants. People who are used to the earlier HCFCs and CFCs in manufacturing and service never really were concerned about a short exposure to air. Air as you know contains some moisture, and some of the newer lubricants that are used in HFCs are having a high affinity for moisture. Short exposure to the ambient air like leaving the compressor connections open or the system open to air leads to the hygroscopic oil taking a lot of moisture and changing its viscosity and that leads to performance impact as well as the reliability impact. There is a compromise on the life of the air conditioner as well as the performance.

There is a lot of emphasis today on educating people. Similarly when we use hydrocarbons we are going to look at hydrocarbons as a flammable refrigerant during service, during installation. It requires a different skill set at the installer level, and not just at the manufacturing level. Of course, at the manufacturing level we need to be prepared for leaks, major leaks, potential for spark leading to an explosion and all that. This is what we mean by skills and technology required to use. Recyclability, can we recover and recycle the refrigerant is one of the considerations. If you cannot recycle is there a way to safely destroy the refrigerant and then stability over the life of the equipment.