

# **SAFETY IN MINES RESEARCH ADVISORY COMMITTEE**

## **FINAL REPORT**

# **An investigation into the conditions under which HFC134a may become flammable**

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**Project No : GAP 806 (EC 02-0062)**

**Date : January 2002**

## Executive summary

A catastrophic failure of an underground refrigeration plant, retrofitted with HFC134a refrigerant (Tua Tona 1999), highlighted the need to investigate and understand conditions under which HFC134a may become dangerous or explosive.

Since the advent of the Montreal protocol and Kyoto agreement considerable research has been conducted in identifying compatible lubricant/refrigerant packages to replace CFC. Much of this work has been incorporated into refrigeration handbooks and standards. HFC134a has been rated as non-flammable and non-toxic at standard temperatures and pressures by both American (ASHRAE Standards 15 and 34) and European standards (BS 4434: 1995).

Previous research (Schröder et al 1995, Dekleva et al 1993, Reed and Rizzo 1991) investigated the flammability of HFC134a at elevated temperatures and pressures. Schröder et al (1995) concluded that HFC134a can become flammable at temperatures exceeding 280°C at standard pressure or in a 34% oxygen enriched atmosphere (at standard temperature and pressure).

A small quantity of combustible substances (6.5% propane for example) was shown to reduce the lower flammability limit of a propane/HFC134a/air mixture (Schröder 1995). The contribution of the lubricant to the flammability of HFC134a was not well understood.

The literature review and findings of the Tau Tona accident report (Department of Minerals and Energy 1999), identified a single possible scenario whereby a HFC134a/lubricant/air mixture may become explosive. The mechanism involved the escape of HFC134a/lubricant past the over heated bearing surfaces of a failing compressor. Experimentation that realistically replicated the likely scenario was used to explore this possibility.

A simple calorimeter was designed to allow the HFC134a or HFC134a/lubricant mixtures to be heated to typical operating temperatures experienced by the gas in a compressor (60°-80°C). The gas was observed while it passed over a red hot metal surface for any signs of decomposition or flammable behaviour. Despite rigorous efforts for a range of scenarios, no flammability was observed.

Too many variables exist (presence of lubricant, additives and hot metal catalysts) to positively state the exact mechanism for the cause of the Tua Tona explosion. However, similar situations must be avoided in future by stringent monitoring and control.

HFC134a is flammable at elevated temperatures when exposed to an ignition source. Flammable gas such as methane if mixed with a HFC134a/air mixture reduces the mixture's lower flammability limit, and thus requires a smaller ignition source for the gas to become flammable at standard temperatures and pressures. HFC134a can displace air and accumulate in low air velocity areas. It is thus important to consider the following when determining the risk associated with underground refrigeration plants:

- Adequate protective measures against fires are required for the plant and/or any mine sections downstream of the plant.
- Adequate protective measures should be in place for the release of large quantities of refrigerant gas in mine air streams.
- In abnormal high concentrations of HFC134a (above 60 000 ppm) mixed with air, any surface exceeding 180°C (100°C lower than LEL temperature of 280°C as recommended by SABS0147) must be considered as dangerous.

**Based on literature, experimentation and accident reports for the Tua Tona explosion, it is the researchers' opinion that it is highly unlikely that HFC134a/lubricant mixtures combust under normal operating conditions or under conditions where surface temperatures remain below 180°C. Temperatures exceeding or approaching 180°C would be associated with an onset of catastrophic conditions such as plant room fires and total mechanical failure of equipment. It is suggested in that the guidelines listed in Section 5.2, pertaining to abnormal plant conditions, are considered for assessing the risks associated with underground refrigeration systems.**

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# Nomenclature

The **flash point** of a liquid is the lowest temperature at which a liquid gives off vapour at such a rate as to form an air/vapour mixture that will ignite, but will not sustain ignition.

HF or **Hydrogen fluoride** is highly toxic gas that occurs because of the decomposition of HFC134a at temperatures exceeding 900°C. It has an exceedingly irritating smell, even at low concentrations and so provides an automatic and definite warning.

**LEL** Lower explosivity limit describes the percentage of flammable gas that must be in a mixture for the mixture to be flammable.

**PAG** Polyalkylene glycols family of synthetic lubricants.

**SABS 0147** classifies HFC134a according to the European flammability classification as **Group 1**, non-flammable in vapour form (at any concentration in air that is at atmospheric pressure and at 20°C) and that are of low order of toxicity.

# **1 Introduction**

Following the Montreal Protocol all South African mines continue phasing out CFC and HCFC refrigerants. HFC134a refrigerant alternative complied with the five major factors usually considered for the selection of a refrigerant, namely safety, performance, reliability, environmental acceptability and simplicity of application. HFC 134a was developed as a replacement for CFC12 and in many cases, can be substituted directly into existing CFC12 systems by following retrofit guidelines (DuPont 2001).

## **1.1 Problem statement**

A catastrophic failure of an underground refrigeration plant retrofitted with HFC134a has highlighted the need to investigate and understand conditions under which the refrigerant or refrigerant /lubricant mixtures can become explosive. The work must therefore consider both normal and abnormal operating conditions to which HFC134a may be exposed to empower machine operators, mine maintenance personnel and contractors to take preventative and corrective action when appropriate.

## **1.2 Objectives**

The work commissioned by SIMRAC and presented in this report investigated the explosive behaviour of HFC134a under both normal and abnormal operating conditions. This knowledge will be used to promote safety in the operation and maintenance of underground chilling plants using HFC134a refrigerant.

## **1.3 Research design**

### **Literature evaluation**

In Section 2, a summary critical literature review pertaining to the flammability of HFC134a is presented. The complete literature review is attached in Interim report (Kramers, Denys, 2001) as Appendix 1. The work introduces various standards, used worldwide, for the safety classification of refrigerants and the safe use of HFC134a in refrigeration systems. Accident reports for an explosion that occurred at an underground refrigeration plant were studied. Relevant accompanying investigation reports (York and Castrol) were also obtained and technical personnel involved with the investigation were interviewed. An

attempt has been made to identify the behaviour of HFC134a under extreme (abnormal) operating conditions. The lack of literature pertaining to the flammability of HFC134a/lubricant mixtures indicated the need for experimentation to provide these answers.

### **Experimental work**

In Section 3, experimentation to provide qualitative answers for the flammability of HFC134a/lubricant mixtures as opposed to pure HFC134a (with known flammability limits) is described. The work tests the most likely explosion scenario drawn by the various experts involved in the investigation of the accident at Tua Tona underground water chilling plant, namely that HFC134a/lubricant gas mixture escaped from a failing compressor past overheating journal bearings, mixed with air and ignited.

## **1.4 Deployment of study**

- Section 1: Introduction and background.
- Section 2: Literature evaluation on flammability standards.
- Section 3: Research methodology and experimental approach.
- Section 4: Discussions.
- Section 5: Recommended guidelines for the safe use of HFC134a underground.

### **Stakeholder involvement**

Throughout the execution of this investigation, advice has been sought and cognisance taken of the opinions and experience of technical experts representing a spectrum of stakeholders. This aspect was specified as sub-task 3.3 of the project proposal. Experts consulted include:

L.Smit (Environmental Health and Safety Manager)	Tau Tona Gold Mine
C Hegermann (Group Refrigeration Engineer)	AngloGold Ltd.
J Kourellos(Refrigeration consultant)	Gold Fields Ltd.
Dr. J du Plessis(Consultant Occupational Environment)	Gold Fields Ltd.
D. Malcolm (Engineering Service Manager)	York/ MIAC, Inc.
J Kidd	York/ MIAC, Inc.

## **2 Literature evaluation**

This section contains a summary of primary findings from literature reviewed and has been included for completeness. For the full literature review, the reader may refer to the interim report (Kramers, Denys, Sept 2001). The work presented in the interim report completely defines the flammability of pure HFC134a under both normal and abnormal operating conditions. In refrigeration systems, the refrigerant is miscible with the compressor lubricant and so it is important to determine the flammability of the resulting refrigerant/lubricant mixture. For this reason, various lubricants used with HFC134a are also presented. Finally, an attempt is made to understand what contribution the lubricant makes to the flammability of the mixture.

### **2.1 HFC134a**

HFC134a is a refrigerant, the working fluid in refrigeration, air-conditioning and heat pumping systems. Refrigerants absorb heat from one area (such as the air conditioned space) and reject it to another space through evaporation and condensation processes respectively. The selection of a refrigerant often involves compromise between conflicting desirable thermodynamic and chemical properties. Chemical stability is regarded as the most important. Other considerations are safety (flammability and toxicity), cost, availability, efficiency and compatibility with compressor lubricants and construction materials used in the system.

The Montreal Protocol is an international treaty that controls the production of ozone depleting substances, including refrigerants containing chlorine or bromine. Amendments to the protocol called for the complete cessation of production of CFC's (such as R12) by January 1996. In addition production of HCFCs (such as CFC22) is to be phased out by January 2030. The drive to eliminate CFCs has led to widespread retrofitting of refrigeration plants with alternative ozone friendly refrigerants like HFC134a. Retrofitted machines usually need to be modified in order to operate efficiently using the new refrigerants. Which raises questions regarding the chemical stability, tolerance of contamination, etc. of the substitute refrigerants.

### 2.1.1 Flammability of HFC134a

The flammability of HFC134a has been investigated by other researchers. There is general agreement that HFC134a can become flammable and even explosive under elevated temperature (or pressure) conditions. HFC134a at standard temperature and pressure is a non-flammable gas that only exhibits an explosion range in oxygen-enriched atmospheres (34% Oxygen, 66% Nitrogen by volume). When the concentration by volume of HFC134a in air approaches 13% the mixture may become flammable at temperatures exceeding 280°C. The explosion ranges of HFC134a in mixtures with air are also highly dependent on the type of ignition source and the volume of the vessel used.

### 2.1.2 Lubricants used with HFC134a

Lubricants used with refrigerant 134a are mineral oils; alkyl benzenes; dibasic, polybasic and polyol esters; polyalkylene glycols (PAG); polyvinyl ether and fluoro chemical lubricants.

The most important properties to consider when evaluating lubricant suitability for use in a refrigeration application include miscibility, solubility, lubricity, stability, and system compatibility. In the case of retrofitted systems the compatibility of the new refrigerant with the previously used refrigerant and lubricant is important.

**Miscibility** describes when liquid refrigerant and lubricant exist in one phase and are in equilibrium over the working temperature range for the system (-30°C to 80°C). The majority of the liquid present is a solution of refrigerant and lubricant.

**Mutual solubility** of refrigerant and lubricant over the entire range of temperature, pressure and composition is considered essential by most refrigeration engineers. Soluble lubricants ensure that lubricant returns from the refrigeration system and is supplied to compressor bearings.

### 2.1.3 Thermal stability of refrigerant - oil mixtures

All of the listed lubricants and their associated additive packages may oxidize or degrade thermally. Oxidation is usually not a concern in refrigerating systems since no oxygen is available to react with the lubricant. However, if a system is not adequately evacuated or if

air is allowed to leak into the system, organic acids and sludge can be formed. Some researchers have suggested that the oxidative breakdown products of PAG lubricants (Komatsuzaki *et al.*, 1991) and perhaps of esters are volatile as opposed to mineral oils that are more likely to include sludge.

The chemical and thermal stability of the lubricants are evaluated using the ANSI/ASHRAE 97-1989 test method. Equal volumes of the lubricant and refrigerant and metal coupons (aluminium, steel and copper) are sealed in glass tubes and aged at 175°C for a period (between 7 and 56 days). After aging, the tube contents are visually inspected for discoloration and analysed using gas chromatography and infrared analysis. The total acid number (TAN) of the fluid is measured and its change is considered an indication of the extent of molecular breakdown by hydrolysis. The liquid is also analysed for fluorine ion content to estimate refrigerant breakdown. No investigator observed any indication of HFC134a decomposition or reaction, however lubricant breakdown was observed in some cases.

Esters can be degraded by water to the free acid and alcohol (hydrolysis). Thermal decomposition generally yields alkenes, water, CO, and CO<sub>2</sub>. Thermal degradation of ester lubricants yields alkenes, CO, and CO<sub>2</sub> (Schlosberg *et al.*, 1985). In the evaluations (sealed-tube tests at 175°C for 14, 28, and 56 days) performed by Sundaresan and Finkenstadt (1992), no lubricant degradation was detected. Sanvordenker (1991) reported that polyol esters may decompose in the presence of steel to form materials such as organic acids, moisture, and carbon dioxide. It was concluded that decomposition of polyol esters is likely to occur at temperatures above 204°C in the presence of steel. However, Short and Cavestri (1992) report no decomposition at a temperature of 260°C. This disagreement can be due to several factors: the different hydrolytic stability and acid number of the tested lubricants, the presence of air during the test, etc. This shows that the quality, structure, and degree of refining of lubricant-grade esters are of prime importance.

PBE-based fluids perform extremely well in sealed-tube tests, with no sign of chemical change, deposit formation or copper plating.

The polyalkylene glycol lubricants can be degraded by water through a hydrolytic mechanism to the parent glycol and lower oligomers; and by oxygen through an oxidative mechanism to peroxides first and then acids. Polyglycols may also be degraded in the presence of moisture and catalytic quantities of strong acid to undergo acid-catalyzed

hydrolysis and dehydration. At high temperatures, the degradation will eventually yield very low molecular weight compounds such as CO, CO<sub>2</sub>, propene, and propane (Schlosberg *et al.*, 1985). In the evaluations (sealed-tube tests at 175°C for 14, 28, and 56 days) performed by Sundaresan and Finkenstadt (1992), no refrigerant degradation was detected.

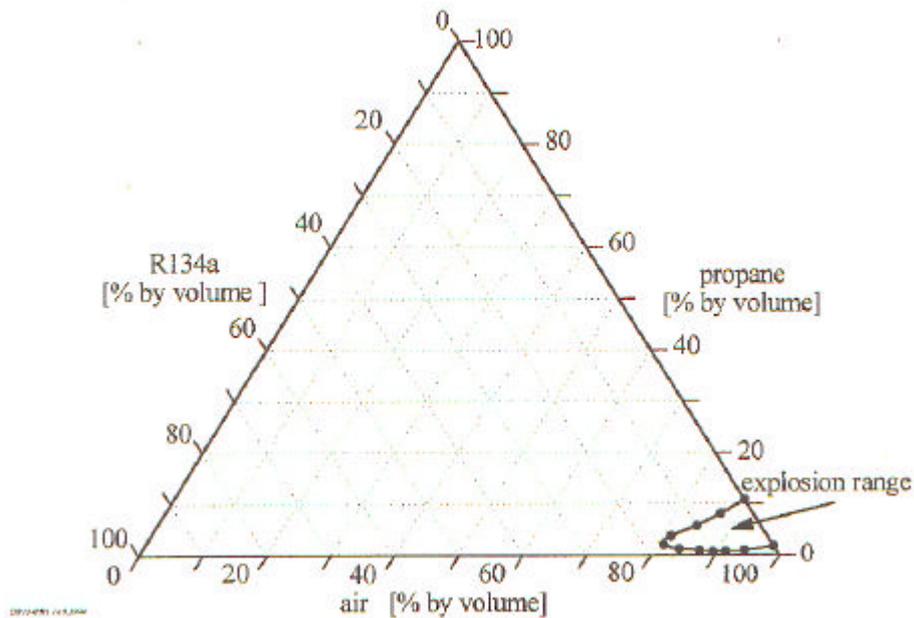
#### **2.1.4 Flammability of refrigerant – oil mixtures**

Very little information about the flammability of lubricants and refrigerant – lubricant mixtures could be found in the literature. The flash point of a lubricant is mentioned in most articles. The flash point of a liquid is the lowest temperature at which a liquid gives off vapour at such a rate as to form an air/vapour mixture that will ignite, but will not sustain ignition. Flash points for mineral oils vary between 143°C and 190°C; for synthetic oils, the flash point varies between 180°C and 290°C.

Flammability limits at atmospheric pressure and room temperature could be found for the compounds resulting from the thermal degradation or cracking of lubricants. However, no flammability data at the working pressure and temperature of a refrigeration compressor could be found.

Schröder *et al.* (1995) investigated some mixtures of flammable gases with HFC134a to determine flammability ranges for combustible HFC134a/air mixtures. The experimental results indicate that very small amounts of combustible substances can cause flammability of such mixtures. According to Schröder the influence of combustible refrigerant oils can be estimated by comparing the amount of gaseous oil or aerosol in the gaseous mixture and propane. The explosion range of propane/HFC134a/air mixtures is as shown in Figure : the lower explosivity limit (LEL) is 1.7% by volume and the upper explosivity limit (UEL) is 10.8% by volume. The LEL decreases by adding HFC134a. Note that the addition of 10% by volume HFC134a (absolutely), results in the LEL of propane to decreased to 0.7% by volume.

The  $T_{ci}$ -value (defined in ISO standard 10156) is the maximum percentage of a flammable gas in an inert gas, for which this mixture of the flammable gas with the inert gas is not flammable in air. For propane in mixture with HFC134a,  $T_{ci}$  is 6.5%. This means that a propane content of little more than 6.5% by volume in HFC134a is sufficient to produce flammable mixtures at room temperature and atmospheric pressure.



**Figure 2.1.4: Explosion range of propane/HFC134a/air mixtures at room temperature and atmospheric pressure (Schroeder 1995)**

The same experiments can be executed for other flammable compounds and for different temperatures and pressures. Adding flammable gases to HFC134a leads to an expansion of the lower explosivity limit (LEL). Therefore, the fire and explosion risks are not generally decreased by adding HFC134a, but rather increased in many cases. Even small fractions of flammable substances in HFC134a can lead to flammability of the mixture.

In all cases, a certain amount of air is necessary to ignite the refrigerant/lubricant/air mixture. In a properly maintained refrigeration system, no air is available to form a refrigerant/lubricant/air mixture that will ignite.

## 2.2 Plant specific considerations

### 2.2.1 Retrofits

HFC134a is regarded as the most appropriate replacement refrigerant for systems previously using CFC12 and mineral oil. The selection of a suitable lubricant for HFC134a is also determined by the effect of residual chlorine (from CFC12) and the effect of residual mineral oil.

The retrofit procedure pioneered by Castrol has been widely adopted by the refrigeration and air-conditioning industry and was. Procedures have been established for systems of all sizes. The procedure entails isolating the CFC refrigerant from the compressor and replacing the original mineral oil with the appropriate viscosity polyol ester. The system is then run normally and the action of the CFC refrigerant passing around the system flushes the remaining oil back to the compressor sump. Through repeated oil changes, the contamination level of the mineral oil within the system is reduced to an acceptable level (usually 3-5%).

### **Pitfalls and problems**

- Maintenance of system cleanliness has assumed greater importance for retrofitted systems. Since, HFC134a-lubricant mixtures are more effective cleansing agents than the CFC-mineral oil mixtures, there is a danger of particles (that accumulated while the system was using the CFC working fluid) becoming dislodged, and contaminating the compressor oil and clogging the expansion devices and other components.
- Care must be taken to minimize lubricant exposure to air moisture or to water directly entering the system through leaks in condenser or evaporator heat exchange tubes. The HFC compatible lubricants are more hygroscopic than the mineral oil and alkyl benzenes. Unacceptable lubricant moisture content can result in the formation of corrosive acids that will attack compressor parts.
- Mixing of CFC12 and HFC134a must be avoided since the presence of the CFC may result in chlorine attack of the synthetic lubricants. In addition the resulting refrigerant azeotrope has a higher vapour pressure than either of the two individual components and may cause frequent high pressure and motor overload shutdowns.

### **2.2.2 Leak detection**

Leak detection is a major problem for manufacturers and service engineers. Several leak detection methods are described below.

#### **Electronic detection**

Electronic detection is widely used in the manufacture and assembly of refrigeration systems. The operation principle relies on the variation of current flow caused by ionisation of decomposed refrigerant between two oppositely charged platinum

electrodes. The instrument can detect any of the halogenated refrigerants except R14. It must not be used in atmospheres that contain explosive or flammable vapours.

### **Bubble method**

A solution of soap is brushed or poured onto joints and other spots where leakage is suspected. Leaking gas forms soap bubbles that can easily be detected. Leaks are also determined by pressurising or evacuating and observing for any change in the pressure or vacuum over a period, however this method does not pinpoint the position of the leak.

### **Halide torch**

The halide torch method is a fast and reliable way of detecting leaks of chlorinated refrigerants. Air is drawn over a copper element heated by a methyl alcohol or hydrocarbon flame. If halogenated vapours are present, they decompose, and the colour of the flame changes to bluish green.

## **2.3 SABS 0147 (1995) Code of Practice**

SABS 0147:1995 code of practice for refrigerating systems including plants associated with air conditioning gives guidance on general safety, construction, erection, operation, inspection and testing of any large industrial refrigeration plants but focuses primarily on refrigeration systems installed in buildings constructed on surface. A refrigeration plant must contain more than 15kg of group 1 refrigerant or have a prime mover greater than 10kW for this standard (SABS 0147) to be relevant.

The document references both national (SABS 1583 and SABS 0108) and international standards (primarily pertinent ASHRAE, BS, DIN, ISO). The provisions of this standard include the following:

- Design and construction of new plants;
- Extension and modification of existing plants;
- Transfer of existing plants to other sites and;
- Conversion of plants (Retrofitting) to a different refrigerant.

In Section 4.3, of the standard, refrigeration systems are classified in accordance with the occupancy classes of areas in which they are situated. Underground refrigeration systems

are classed institutional, and given a category “A” and persons are restricted in their movement.

For surface building locations, distinction is made between high hazard refrigeration systems and low hazard refrigeration systems. A system is high risk if the basic design its location is such that a leak of refrigerant from a failed component, seal or fitting can enter the occupancy-classified area. Indirect closed systems typically used underground can only be considered low risk if all joints and connections are effectively isolated from the occupancy-classified area. For any mining application, all systems should be referred to the Director General, Department of Minerals and Energy Affairs.

The maximum concentration of HFC134a is 60 000 ppm (or 6% by volume) and applies to accidents or incidents that produce a major release of refrigerant and do not refer to day-to-day exposure limits. When the concentrations of the refrigerant, in the event of a leak, can exceed this value, the temperature of any hot surface or flame must be at least 100°C less than the minimum ignition temperature. Schroeder *et al.* (1995) specify this temperature as 280°C. Thus any temperature above 180°C in an accident situation (massive leakage of refrigerant) can be considered dangerous.

Section 6.12 of the standard sets guidelines for machinery areas and plant rooms, and suggests (in point 6.12.1.3) that each plant room must have tight fitting doors that open outwards and should be self closing if they open out into other parts. No openings are permitted that allow passage of escaping refrigerant to other parts of the building. Plant rooms with group 1 refrigerants (HFC134a) must be equipped with vapour alarms to ensure warning against oxygen deficiency.

Section 7.11.1, describing respiratory protection, states that in cases where more than 900 kg of refrigerant is present, at least one self-contained breathing apparatus with an effective life of 25 minutes must be provided. A set of suitable protective clothing must be provided for each set of self-contained breathing apparatus. The protective equipment must be situated immediately outside the refrigeration plant room.

## **2.4 Incident at AngloGold, Tau Tona underground chiller plant**

On Sunday 24<sup>th</sup> October 1999 an explosion took place in the machine room of chiller 1A 100 level refrigeration plant. At the time, 14 people were working in close vicinity of the compressor where the explosion occurred and seven people were hospitalised for smoke inhalation. The information presented in this section was drawn from the Accident report, Department of Minerals and Energy (1999), Castrol's Report on Refrigerator Compressor Failure at Western Deep Levels, (November 1999) and York Miac Inspection, Testing of Plant 1A (100 level) conducted by H.G. Visser and M.A. Keogh 26<sup>th</sup> October 1999. In addition follow up discussions were held with D. Malcolm (York MIAC) and L. Smit (Environmental Health and Safety Manager, Tau Tona).

The refrigeration plant originally operated on CFC12, was purchased in 1967, and would have been commissioned during 1968-1969. The plant is located in the first chamber (1A) of 5 chambers situated on 100 level Tau Tona. Each chamber houses two refrigeration plants. The plant was not retrofitted; however a HFC134a "drop-in" was done by the mine at an unknown date. The compressor and original relay logic was replaced with a programmable logic controller (PLC). The compressor was fitted with a non-original equipment manufacturer (OEM) stainless steel impeller for use with CFC12. It was not possible to determine whether any of the other compressor parts were non-OEM because of the extensive damage to them. The ball valves in the expansion device were also locally manufactured, not OEM York parts.

York Miac (1999) found the following irregularities with respect to the safety devices protecting the underground chiller plant:

### **1. High compressor discharge temperature**

The high discharge temperature protection trip was not present and the control panel wiring was altered to enable the system to operate without this trip.

### **2. Low condenser water flow**

The switch was bridged out and found to be faulty.

### **3. Compressor thrust bearing oil temperature**

The thrust oil temperature trip was not present on the compressor and the tripping device had been removed. The control panel wiring was altered to enable the system to run without the safety device being present.

### **4. Low water temperature**

The switch was bridged out and found to be faulty.

### **5. High motor bearings temperature**

No bearing temperature sensors/trips were found.

### **6. High gearbox bearing temperature**

The gearbox bearing temperature trips were burnt away due to the failure.

### **7. High condenser pressure**

The pressure trip setting was set  $\pm 180$  kPa too high. York was concerned that this condition would allow the compressor to go into surge, thus preventing the trip point from occurring. When a centrifugal compressor surges, there is reversal of airflow through the compressor impeller. Surge is defined as the minimum flow through a centrifugal impeller before reversal occurs. This flow reversal is accompanied by a drop in pressure in the diffuser section of the stage. Surge usually starts in one stage of a multistage compressor and can occur very rapidly moving to other stages. Damage to thrust bearings results from tremendous thrust reversal occurring during surge conditions.

### **8. Gearbox oil temperature**

No protection device found.

York concluded that the initial trip that led to the compressor failure was bridged out. This resulted in a high condenser pressure. The condenser pressure safety trip was set too high and so it was possible for the compressor to operate under surge conditions. The onset of a surge condition would prevent the high-pressure condenser trip from stopping the compressor. In the surge condition, the thrust bearing would have been overloaded and the thrust bearing oil temperature and the condenser temperature would both rise, failing to trip any protection devices as these had been removed or bridged out. These compressor-operating conditions would lead to the destruction of the thrust bearing. With no axial support, the impellers would encounter the compressor housing further increasing

the temperature of the surging compressor. Damage to the remaining journal bearings would result from inadequate lubrication. The failure of the impeller shaft bearings and the heat generated (failing bearing and rubbing impeller with housing) would result in the failure of the main seals. The low oil pressure trip should have stopped the machine under these conditions but it was not activated. York concludes that an explosion occurred before a low oil pressure condition had been reached.

### **2.4.1 Remedial action undertaken at Tau Tona**

- Fire detection sensors were installed in each of five chambers situated on 100 level, Tua Tona, and are monitored and inspected on a daily basis. The sensors are coupled to a control system that opens (self-closing) flaps to divert air to the return air way (RAW) in the event of smoke detection.
- A rescue chamber was constructed around the control room (common room for all 10 refrigeration plants situated on 100 level). Compressed air facemasks are situated in the refuge bay.
- The refrigeration control circuitry and safety devices have been tested and are audited quarterly. At each plant start-up, safety devices are tested as part of the plant start-up sequence.
- Procedures for small and large-scale plant maintenance have been implemented, and restrictions have been placed on how cutting torches and welding equipment is used in refrigeration plants.

### **2.4.2 Investigation conclusions**

Two possible explanations for the explosion were suggested in the accident report (Department of Minerals and Energy, I.R. Patterson 1999):

Air entered the compressor and a high-temperature-high-pressure mist comprising of HFC134a, oil and air ignited resulting in the explosion. A problem with this scenario is that it does not explain how large quantities of air ingresses into the pressurised compressor.

A second possibility is that the pressurised HFC134a and oil mist escaped past the red-hot journal bearing metal of the damaged compressor and mixed with the

surrounding air. Under these conditions, the mixture ignited causing an explosion. Castrol supports this explanation.

### 3 Experimentation

The work to date has identified specific conditions that can cause HFC134a to become flammable. However, no information has been found to describe the contribution of the lubricant on the flammability range of HFC134a/lubricant/air mixtures. The literature indicated that small quantities of flammable gas mixtures can drastically change the flammability of non-flammable gases such as HFC134a. To investigate and provide clarification an experiment was designed to qualitatively evaluate if the presence of the lubricant lowers the LEL of the refrigerant.

#### 3.1 Apparatus

Experimental apparatus was designed and built to realistically model the abnormal circumstances and effects of HFC134a/oil gas mixtures escaping into the atmosphere past overheated journal bearing surfaces and seals. The experimental apparatus is illustrated in Figure 3.1a.

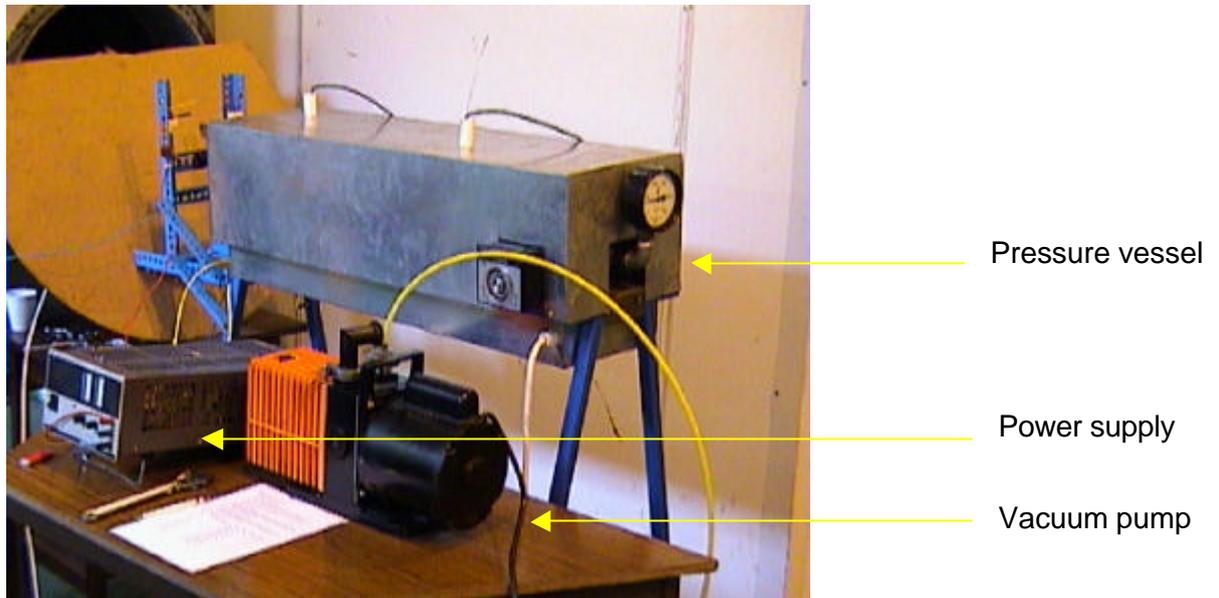


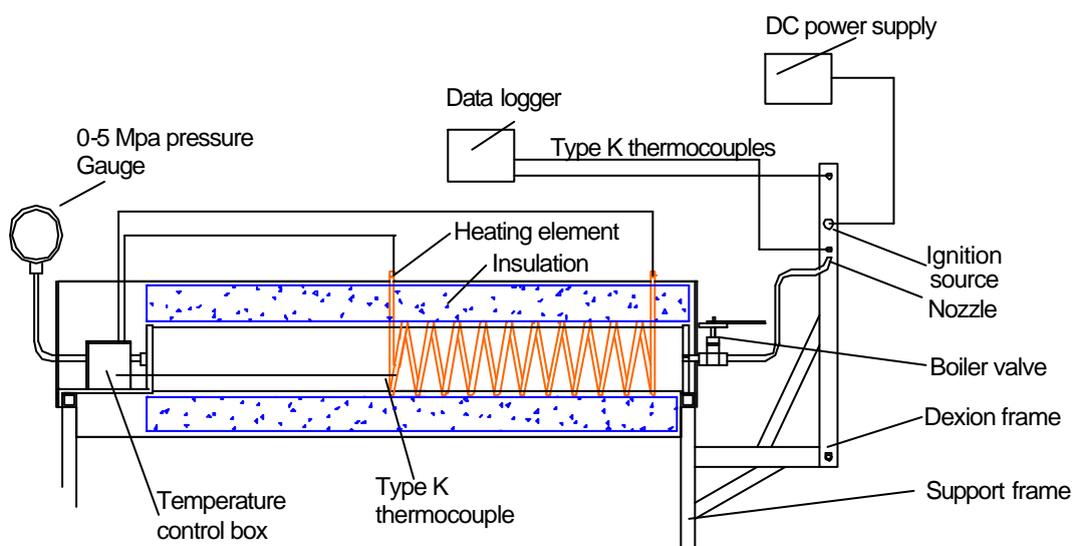
Figure 3.1a: Experimental set-up

A schematic of the proposed experimental apparatus is given in Figure 3.1b. The test rig consisted of a pressure vessel arrangement with a boiler valve to enable the vessel to be filled with HFC134a or HFC134a/lubricant mixtures. A heating element coiled over the outside of the cylinder allowed the refrigerant gas contained within the pressure vessel to be preheated (simulating the working temperatures and pressures of the compressor) before being ejected over an ignition source by remotely opening one of the boiler valves. The heating element was controlled by feedback from a thermocouple situated at the hottest part of the heating element. The pressure of the vessel was monitored during the heating process.

The ignition source consisted of a resistive wire connected to a power supply. The temperature of the glow wire was be adjusted by varying the current.

Thermocouples were situated 1cm below and 2cm above the glow wire respectively. The thermocouple below the glow wire recorded the temperature of the gas at exit. The thermocouple above the glow wire recorded the temperature of the gas after passing over the glow wire. Both thermocouples were connected to a data logger capable of sampling at 1-second intervals.

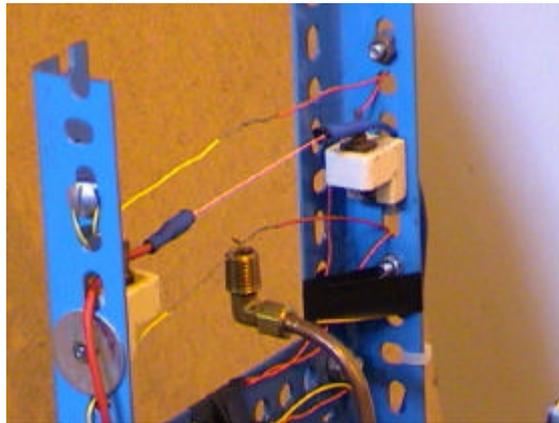
Two HFC134a gas canisters were prepared, one containing pure HFC134a and the second containing HFC134a and 5% by mass SW68 Castrol lubricant (the same lubricant present in the Tua Tona refrigeration plant).



**Figure 3.1b: Schematic of experimental apparatus**

## 3.2 Experimental method

To identify the reference behaviour of the apparatus the pressure vessel containing air only was heated. The boiler valve was adjusted to predetermined positions allowing air to pass over the glow wire at various flow rates. Temperatures of gas below and above the glow wire (as indicated in Figure 3.2) were recorded in three separate experiments. The pre-experimentation enabled the influence of the glow wire to be characterised.



**Figure 3.2: Position of top and bottom thermocouples about a red-hot glow wire**

Pure HFC134a gas was tested first to confirm flammability findings from the literature thus becoming the control experiment. Thereafter the HFC134a/lubricant mixture was tested. The following experimental procedure was followed:

1. The apparatus was situated in a laboratory incorporating a gas extraction facility to prevent any possible exposure of persons to toxic decomposition gases.
2. A vacuum pump was connected to the vessel and the air evacuated from the vessel. Thereafter, the boiler valve was closed.
3. The pressure vessel was filled with HFC134a gas (ambient temperature and corresponding saturation pressure) and the boiler valve closed.
4. The temperature of the vessel was adjusted to 60°C.
5. The temperature inside the pressure vessel was allowed to stabilise.
6. The temperature of the glow wire was adjusted using the power supply.
7. The data logger was set to record temperature data at a 1 second sampling rate.
8. The release pulley on the exit valve was primed and the operator moved some distance away from the test apparatus.

9. The video camera was set to record the scene at the exit side of the apparatus.
10. The exit valve was opened remotely.
11. The gas escaped over the hot wire ignition source.
12. The experiment was repeated using pure HFC134a 3 times followed by 3 repetitions using the HFC134a/SW68 Castrol lubricant mixture.

### 3.3 Results

**Table 3.3: Experimental results**

No.	Experiment description	Visual observations
1	Air only	
2	Air only	
3	Air only	
4	HFC134a only	No flame detectable
5	HFC134a only	No flame detectable
6	HFC134a only	No flame detectable
7	HFC134a with 5% Castrol SW68 lubricant	No flame detectable
8	HFC134a with 5% Castrol SW68 lubricant	No flame detectable
9	HFC134a with 5% Castrol SW68 lubricant	No flame detectable

The averaged pre-experimental temperature variation with time for air was compared with the temperature variation of the pure HFC134a and HFC134a/SW68 mixture. No sharp increase in the temperature of the upper hot wire was found in 3 repetitions of experiments using pure HFC134a and HFC134a/SW68 (mixture) respectively. The implication was that no flame or ignition of pure HFC134a and HFC134a/lubricant mixture occurred under these experimental conditions.

### 3.4 Conclusion

Although rigorous attempts were made to ignite the HFC134a and HFC134a/lubricant mixture at conditions similar to those encountered during compressor failure (passing it over a hot wire ignition source at temperatures in the range 600-800°C) no flammability

was detected. It should be noted that any refrigeration equipment components and bearings experiencing these temperatures would experience catastrophic mechanical failure and hence this represents a highly abnormal condition.

## 4 Discussion

Based on work undertaken in the execution, it is highly unlikely that HFC134a/lubricant mixtures combust under normal and abnormal conditions (temperatures less than 180°C) excluding catastrophic conditions such as plant room fires and total mechanical failure of equipment.

Literature revealed specific laboratory conditions under which HFC134a may become flammable and explosive. Briefly, HFC134a is not flammable at standard temperature and pressure but can become flammable at an elevated temperature of 280°C with a HFC134a/air mixture composition of 13% by volume HFC134a. At maximum HFC134a concentrations, (60 000 ppm by volume) the SABS 0147 code of practice for refrigerating systems suggests that the temperature of any hot surface or flame under these circumstances is at least 100°C less than the minimum ignition temperature, ie 180°C.

Based on the outcome of the accident report for the incident that occurred at Tau Tona, the most likely scenario put forward to explain the explosion was: refrigerant and lubricant escaped past overheating red hot journal bearing surfaces mixed with air, thus providing a heat source and the oxygen needed for combustion to occur. A qualitative experiment was designed and built to investigate this scenario and no flammability occurred.

The addition of small quantities of flammable gas to HFC134a/air mixtures has an effect of lowering the LEL. Under increasing (abnormal) temperatures, decomposition or thermal cracking of the lubricant will begin long before thermal decomposition of HFC134a begins to take place. It is thus interesting to consider the effect of decomposition of the lubricant and consequently the formation of flammable gases on the flammability of HFC134a by the mechanism described. In addition, the presence of rapidly worn aluminium and other metals could play a catalytic role in the reaction. No matter what the exact mechanism, it must be born in mind that these conditions are highly abnormal and catastrophic and must be prevented from occurring in the first instance.

As such, guidelines for a code of practice recognising conditions that may lead to an ignition of HFC134a and ways in which these situations may be avoided or neutralised are presented in Section 5 of this report.

## 5 Recommended guidelines for the safe use of HFC134a underground

### 5.1 Scope

A code of practice regarding the safe use of ammonia (and other refrigerants including HFC134a) as the working fluid in the operation of large refrigeration plants, is presented in SABS 0147:1995. The standard specifies a code of practice for safety, construction, erection, operation, inspection and testing of refrigeration plants, with the main emphasis placed on **refrigeration plants situated in buildings on surface**. Mining applications are referred to Department of Minerals and Energy Affairs and usually emphasis is placed on an issue-based risk assessment. Although SABS 0147 focuses primarily on surface refrigeration plants, it contains considerations that could add value to the risk assessment process.

The guideline considerations listed in Section 5.2 were identified from this research and are suggested for situations not covered in the standards previously discussed. It is suggested that any risk assessment is based on the eventualities that:

- HFC134a can become flammable at elevated temperatures (280°C) when exposed to an ignition source (for example an open flame or overheated bearing).
- Decomposition of HFC134a will result in the formation of highly toxic and instant unpleasant hydrogen fluoride gas.
- HFC134a can displace air and may accumulate in lower sections of the mine

The guidelines listed in Section 5.2 may be used in risk assessments to reduce damage and injury arising from a catastrophic failure of an underground refrigeration plant using HFC134a. The failure may be because of massive leakage of refrigerant, compressor mechanical failure or plant room fires.

## 5.2 Guidelines

1. Preferably ventilate refrigeration plants to return air. Where this is not possible, adopt protective measures in accordance with a risk assessment. Air used in other areas of the mine passing through underground refrigeration plant rooms should be considered in the risk assessments.
2. Depending on the outcome of the risk assessment, quick-seals should be installed upstream of the refrigeration plant and should be shut off in the event of a plant room fire.
3. It is suggested that **refrigerant leak detectors** are installed and interlocked to the system to stop the plant under unacceptably high refrigerant concentrations (0.1 to 1%, depending on the risk assessment). Note that SABS 0147 (and ASHRAE) define an upper concentration limit as 6% HFC134a in air by volume. This would lead to 80% of cardiac sensitisation level.
4. In due consideration of any risk assessment, for a situation where large quantities of refrigerant can escape and displace air (and oxygen), it is suggested that self-contained breathing apparatus or compressed air masks are located at a central position and protective clothing issued accordingly inside and outside the plant room.
5. Under conditions, where the concentration of HFC134a in air can reach an upper limit of 6%, and is exposed to hot surfaces (or flames) exceeding 180°C, an appropriate protective action should be adopted in terms of the risk assessment.
6. Based on risk assessments, consideration should be given to monitoring return air from the plant rooms for the presence of smoke.
7. Ensure that all equipment protection devices are operational by monitored scheduled testing over the course of the year.
8. Ensure that plant machinery is in good operational order and is free from any flammable substances (for example excess oil build-up, waste etc).
9. Flammable gasses such as **methane** or propane reduce the lower flammability limit for HFC134a/air/methane mixtures. It is recommended that the presence of methane in refrigeration plants should be considered in risk assessments. The reader is referred to section 2.1.4 for a quantitative description of this effect.

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## **Appendix 1: Interim report**