TECHNIQUES FOR ANALYSING FUMIGANTS AT ULTRA-LOW CONCENTRATION LEVELS

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INTRODUCTION

Contamination of atmospheres with toxic gases has created problems of great concern to environmental and health authorities. New techniques have revealed the presence of materials that were previously unsuspected and new knowledge on the harmful effects of toxic compounds has pointed up hazards that were not known to exist. The advent of new industrial processes with the consequent proliferation of toxic contaminants has emphasized the need for sensitive instruments and methods that can easily analyse low concentrations of chemicals in atmospheres. For toxic compounds like fumigants, where substantial quantities may be periodically injected into atmospheres and where the general public is already apprehensive of the dangers from pesticides, the need is urgent.

Analysis of gases from systems where a high degree of dilution occurs (as in contaminated atmospheric air) has the inherent problem of separating the small amounts of the contaminants from massive quantities of other compounds i.e. nitrogen and oxygen. The contaminants then must be retained in a way that will be suitable for analysis by some appropriate technique.

A method for concentrating such diluted gases has been developed and used to measure, by gas chromatography, very low concentrations of fumigants (Dumas 1978, 1982, Dumas and Bond 1981). Low levels of the residual gas desorbed from fumigated grain have been thus collected and analysed. The method is also useful for low levels of contaminating gases in atmospheric air.

The procedures for collecting and concentrating fumigants, along with methods for analysing ultra low levels of the gases, are described here.

CONCENTRATING GASES FROM DILUTE SAMPLES

To collect the contaminating gas from the atmosphere a trapping device somewhat similar to the column in a gas chromatograph was used.

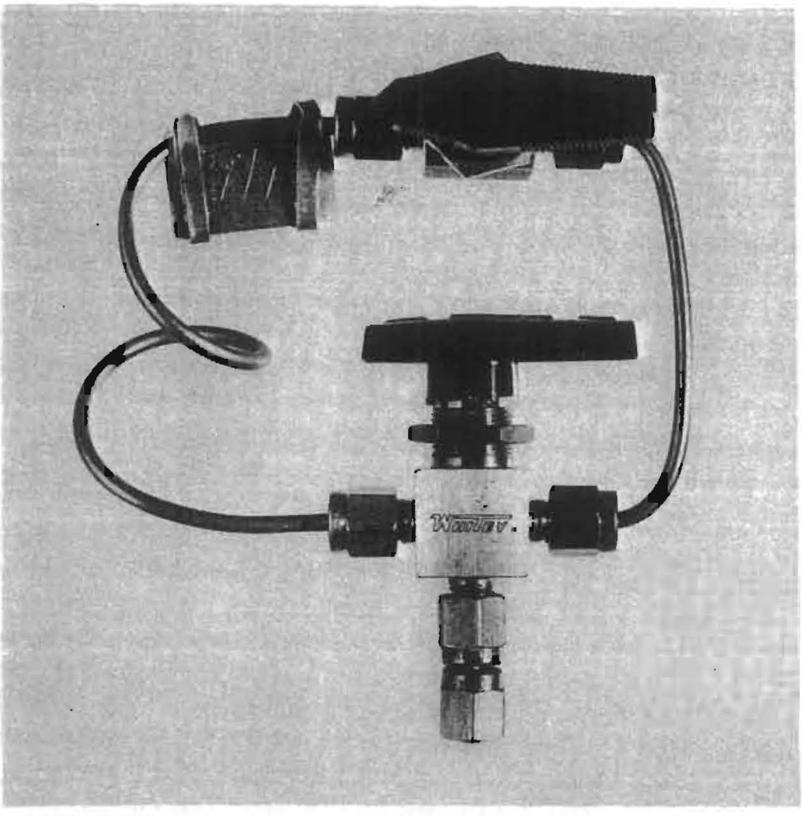

Fig. 1. Trapping device designed for collection and analysis of samples by gas chromatography.

A short length of stainless steel tubing was packed with appropriate sorptive materials and fitted with three way valves plus connections for incorporation in the gas flow system of a GLC. Selection of the sorptive packing material was achieved by cooling the trap with dry ice while it was installed in the GLC and determining the ability of the packing to retain the test gas.

Atmospheric contaminants were collected by passing known volumes of the diluted samples through the trap while it was held in a small foam insulated box filled with dry ice. For analysis the trap was then inserted in the GLC, allowed to warm up to column temperature and the stopcocks were then opened to allow carrier gas to move the sample through the column to the detector.

When contaminated air was under test a syringe was used to obtain and inject the desired quantity. For collection of gas that desorbed from fumigated commodities an appropriate amount of the commodity was retained in a gas-tight container for a specified period of time and then a measured volume of nitrogen was used to flush the desorbed gas from the container and into the trap.

This method was found to be suitable and reliable for collection of ultra-low concentrations of methyl bromide and phosphine, both from samples in air and samples desorbed from fumigated cereals (Dumas 1980, 1982). When wheat treated with phosphine or methyl bromide was analysed for desorbing residues of the gases, levels down to ppt (10^{-12}g) could be detected and measured. Further investigation of the procedure showed that low levels of gases could also be collected at ambient temperatures with a satisfactory degree of accuracy. Consequently the versatility of the method was expanded and its utility for application under field conditions increased.

ANALYSIS OF COLLECTED GAS SAMPLES

Three detectors were found to have the required sensitivity for analysing the low levels of fumigants that were collected by the trapping technique. A flame ionization detector was used for methyl bromide analysis and an alkali flame ionization detector for phosphine. A photoionization detector in a portable GLC (Photovac 10A10) operating at ambient temperature was found to be effectual for analysis of four fumigants under field conditions at levels down to ppb (10^{-9}g), (Bond and Dumas 1982, Dumas and Bond 1982). This detector was also found to be useful for the detection and analysis of low concentrations of formaldehyde (Dumas 1982). Analysis were accomplished by direct injection of 1 ml samples of the gas-air mixtures into the instrument. For lower concentrations a special valve can be supplied with this instrument to incorporate the trapping technique described above and thus further increase its analytical capability.

Details of the above methods have been published in the journals cited below. While the potential capacity for analysing ultra-low levels of gases has been advanced by using the principles and instrumentation described here considerable scope for future development still remains. Several facets of modern technology might be exploited to accommodate the increasing needs for sensitive and precise analytical methods for fumigants.

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Method of trapping low levels of phosphine at ambient temperature for gas chromatographic analysis. J. Chromatog. 206: 384-386.
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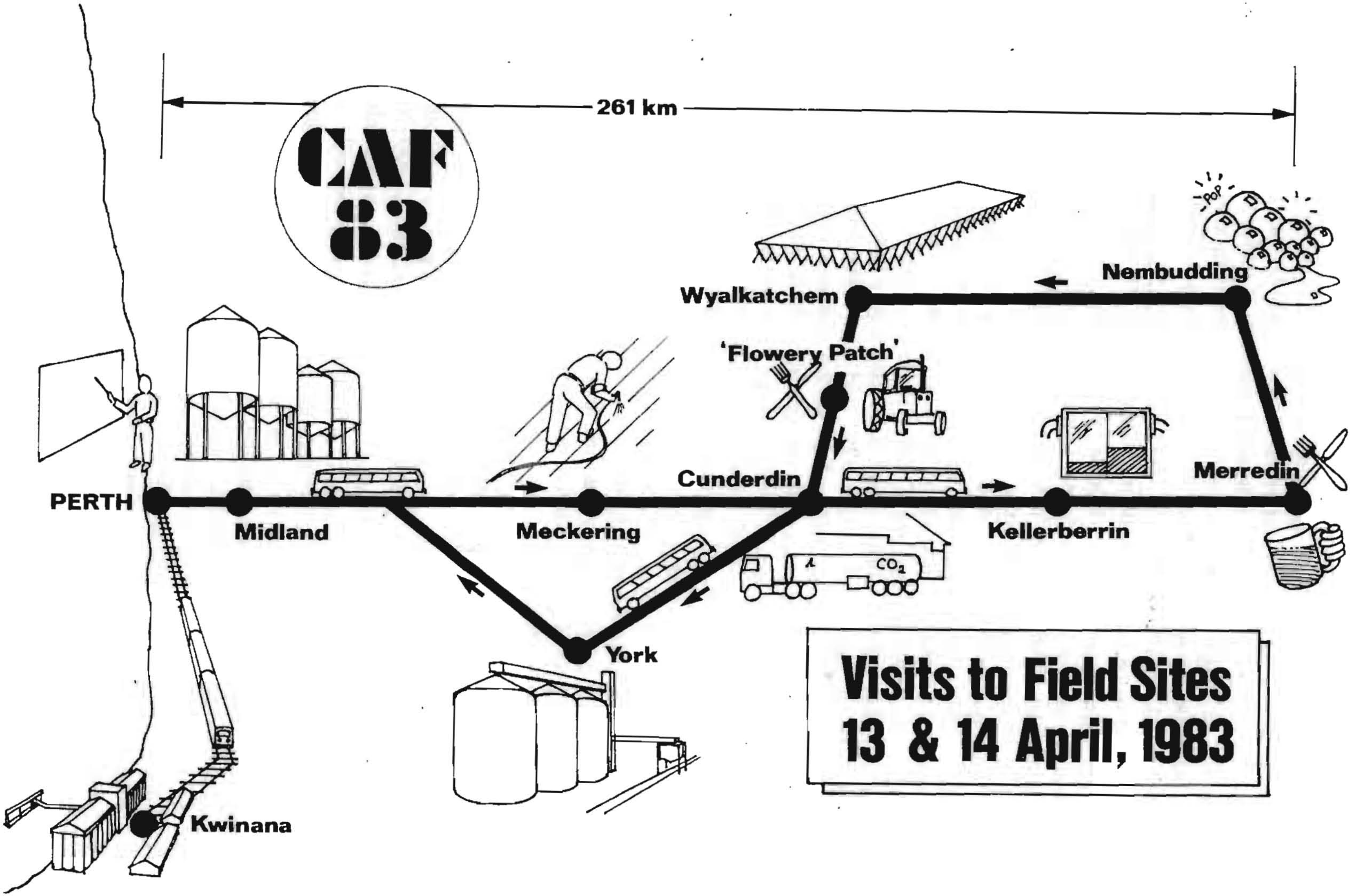
PRACTICAL DEMONSTRATION TOUR OF COUNTRY SITES

The sites visited for the practical demonstrations were selected to provide sequential story of Controlled Atmosphere for the sealing process through to purging with carbon dioxide.

Midland	Farm Silo Expo - the smallest of storages sealed.
Meckering	An average Central Storage System grain store set up to provide an exploded view of progression through the sealing process.
Kellerberrin	Conducting a pressure test on a sealed storage.
Merredin	Overnight stop and viewing a large storage and grain handling equipment.
Membudding	Leak detection.
Wyalkatchem	A less cost storage to cater for above average production.
"Flowery Patch"	A typical broad acre farm. Lunch stop.
Cunderdin	Purging with CO_2
York	Vertical steel storage, sealed during construction.
Kwinana	The largest of the storages sealed and fitted for Controlled Atmosphere.


261 km
CAF
83
Wyalkatchem
Nembudding
POP
'Flowery Patch'
Cunderdin
Merredin
PERTH
Midland
Meckering
Kellerberrin
CO_2
York
Kwinana
Visits to Field Sites
13 & 14 April, 1983

MIDLAND EXPO - ON-FARM TYPE STORAGES USED FOR DEMONSTRATION PURPOSES

This location is the site of 13 on-farm type storages (1 fibreglass the rest steel), each of about 16 tonnes wheat capacity, and established with the co-operation of resident silo manufacturers, to demonstrate to farmers the effectiveness of sealing their seed and feed grain storages when introducing a fumigant (usually phosphine) for total insect control. The demonstrations included the introduction of generated colored smoke - to simulate a fumigant - into both sealed and unsealed silos. This dramatically showed the loss of fumigant to be expected from an unsealed storage and the retention of the gas in a sealed storage. The influence of the weather conditions - sun and wind - and the chimney stack effect of sucking the smoke out of the unsealed storage - was clearly shown as was the internal pressure variations caused by natural heating and cooling. A pressure of 200 pascals was introduced into a sealed silo by use of a standard type vacuum cleaner and the time noted for decay to half life to determine the effectiveness of the seal. The pressure relief vents attached to each silo were explained. For details of on-farm silo sealing refer to Papers 45 and 46.

Photo 1. General View of "Midland Expo".

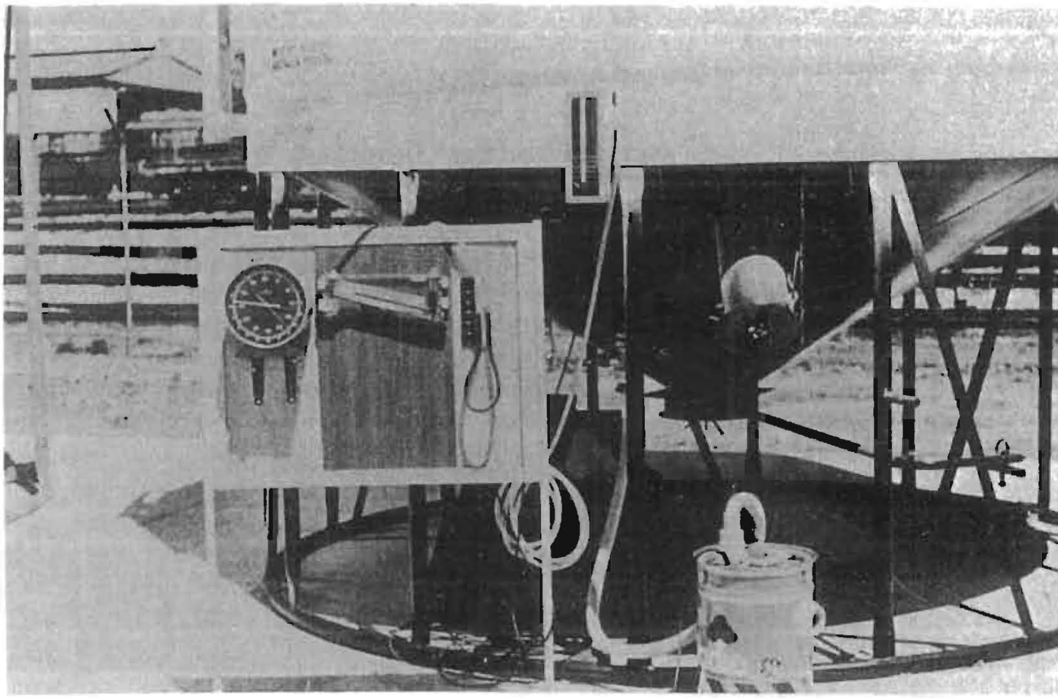


Photo 2. Sealed Farm Silo showing manometer and pressure relief vent.

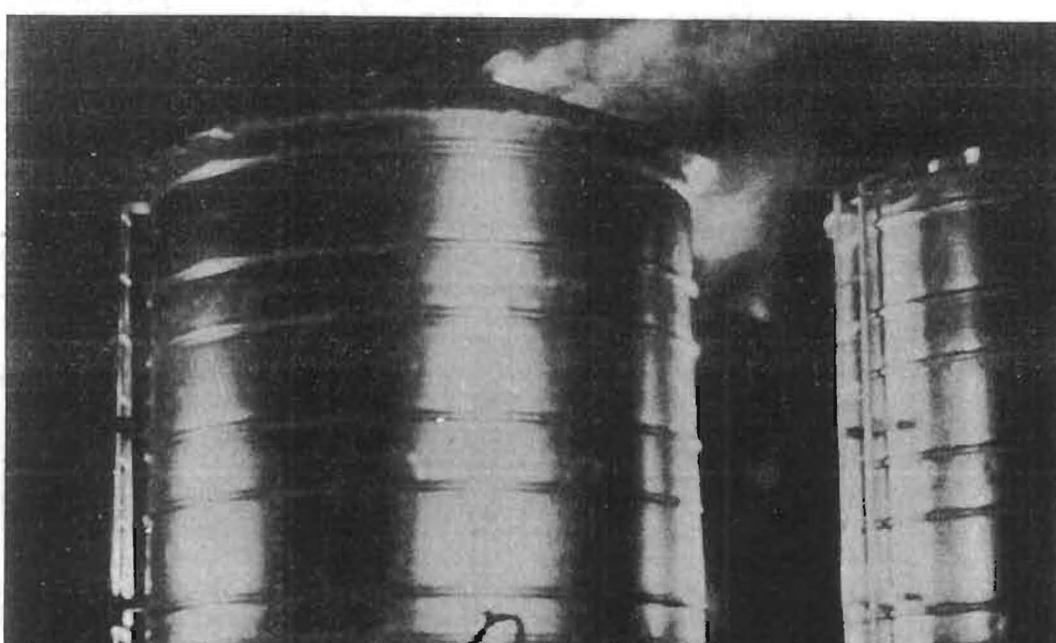


Photo 3. Leakage of fumigant (smoke) from an unsealed farm silo.

MECKERING : HORIZONTAL STORAGE IN PROCESS OF BEING SEALED

The storage visited was a standard 'C' type horizontal silo of 22,000 tonnes wheat capacity, constructed with concrete walls and floors and having a clear-span trussed roof of corrugated galvanised iron cladding. Gable-end walls and side curtain-walls are also of corrugated iron. Of particular interest was the application of rigid polyurethane foam over the internal laps of the steel sheeting and along the gaps formed between the curtain and gable-end walls and the roof and concrete walls of the building. Foam was also applied along the roof ridge areas, around the internal perimeter of doorways, around the fans in each of the end gable walls and the entry point for the overhead conveyors. The spray application of the internal wall sealant was also demonstrated. Other features pointed out were the methods of external sealing of the roof cladding sheets, attention to the concrete floor, door sealing and the final top coat of a heat reflectant material sprayed over all external surfaces. For details of sealing procedures refer to Papers 11, 12 and 13.

Photo 4. Sealing in progress on the end wall of a horizontal silo at Meckering. Note all lap ends of the corrugated iron sheets used to clad the gable-end wall are individually sealed, as are surface cracks evident in the concrete wall.

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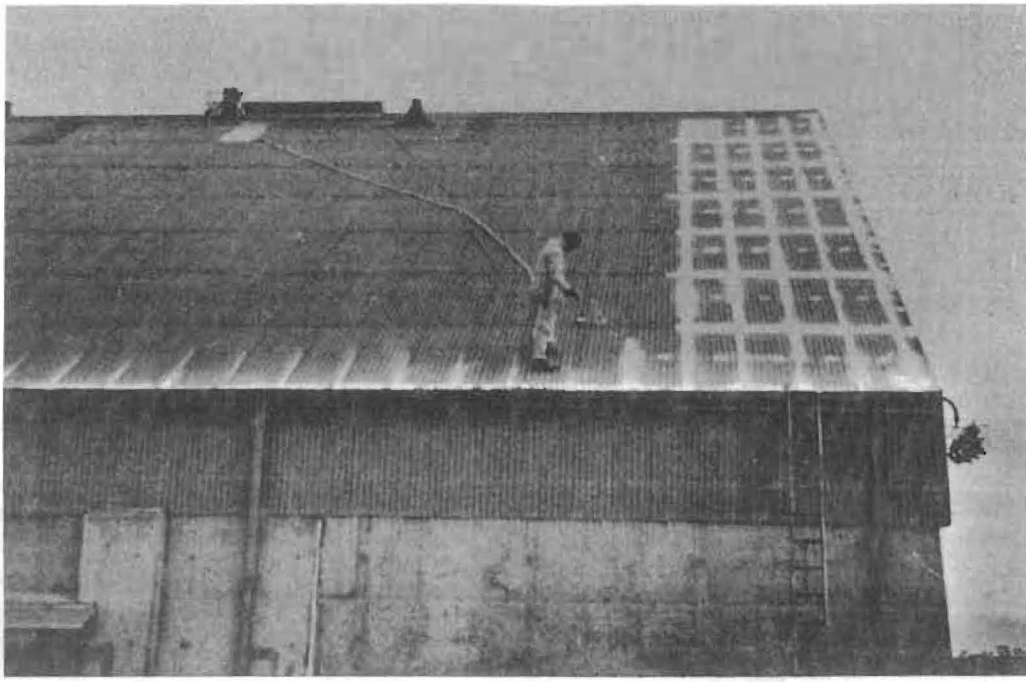

Photo 5. Spray sealing of all lap ends of corrugated iron roof sheets on horizontal silo at Meckering.

Photo 6. Application of final coat of reflectant material over previously sealed roof and wall at Meckering.

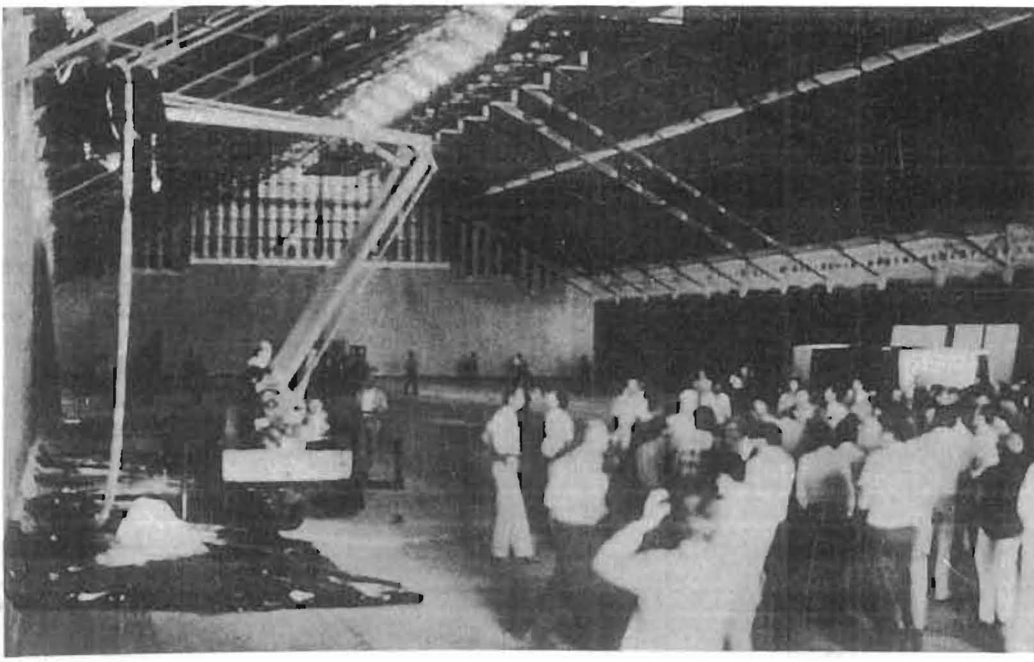

Photo 7. Interior view of Meckering horizontal storage showing applications of polyurethane foam to the roof/wall joints.

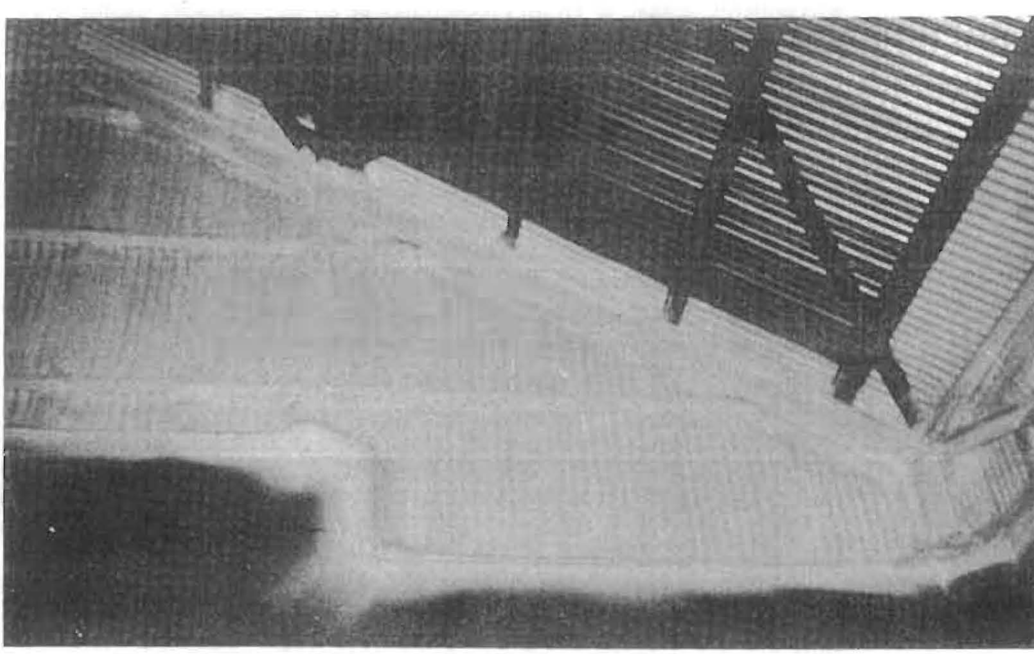

Photo 8. View of a gable end wall at the Meckering horizontal Silo after foaming of all joints and spray sealing of the finishing coat.

Photo 9. Application of foam inside a horizontal storage.

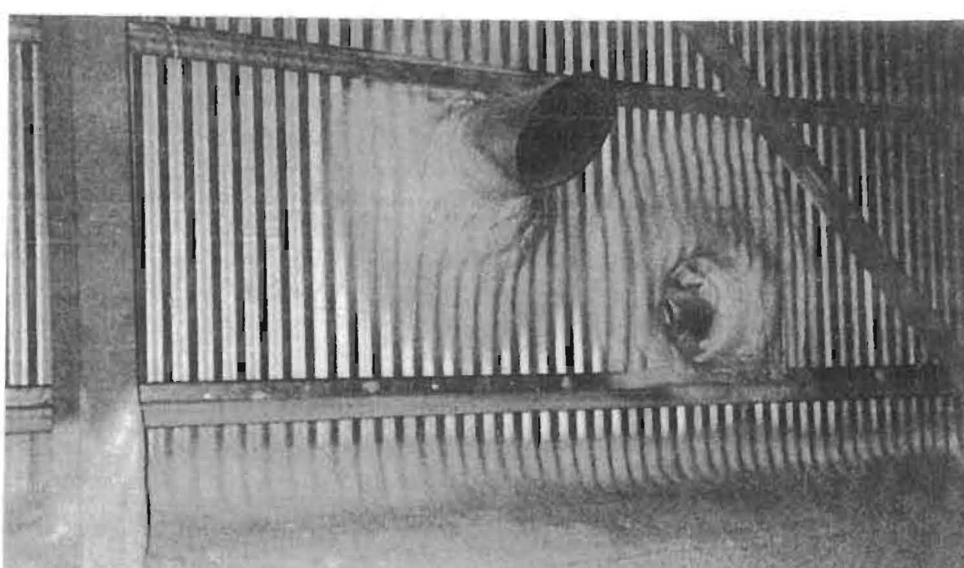

Photo 10. Foam application along an inside wall ledge and around the fan and pressure release duct fitted into a gable and wall.

Photo 11. Sealing inside the roof ridge line of a horizontal storage.

KELLERBERRIN : PRESSURE TEST ON A SEALED STORAGE

The demonstration at this site was of a pressure test of a completely sealed storage - a standard 'A' type horizontal storage of 27,500 tonnes wheat capacity. Before starting the test, the naturally induced pressure inside the storage, shown by the positive pressure on the intake side of the pressure relief vent, was pointed out. This positive pressure is noted during the warming of the internal air spaces by the sun and a reverse negative pressure will occur during the cooling down phase.

One gable end fan was started and a pressure of 200 pascals introduced into the storage, noting the increasing pressure on a manometer and by the imbalance of the light oil in the chambers of the pressure relief vent. After turning off the fan, and resealing the fan aperture, the retention of pressure was clearly demonstrated through an almost negligible decay noted on both the manometer and pressure relief vent over a period of 30 minutes.

At the conclusion of this test a main silo entry door was opened to physically show by sound and feel the force of the pressurised internal air escaping to the external atmosphere. This force was strong enough to blow a piece of heavy cloth material at right angles to the door opening. For details of pressure effects on grain storages refer to Papers 16 and 21.

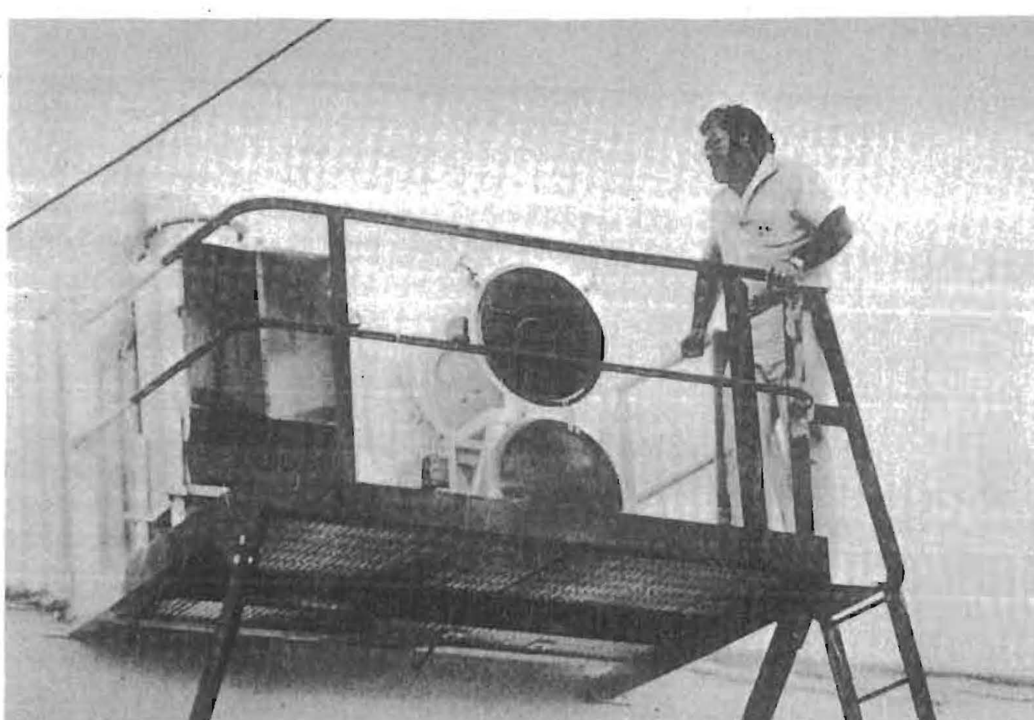

Photo 12. Pressure relief vent and fan built into gable end wall of horizontal storage at Kellerberrin. The fan cover is opened while pressurising the storage and is sealed for the pressure decay and leak detection test.

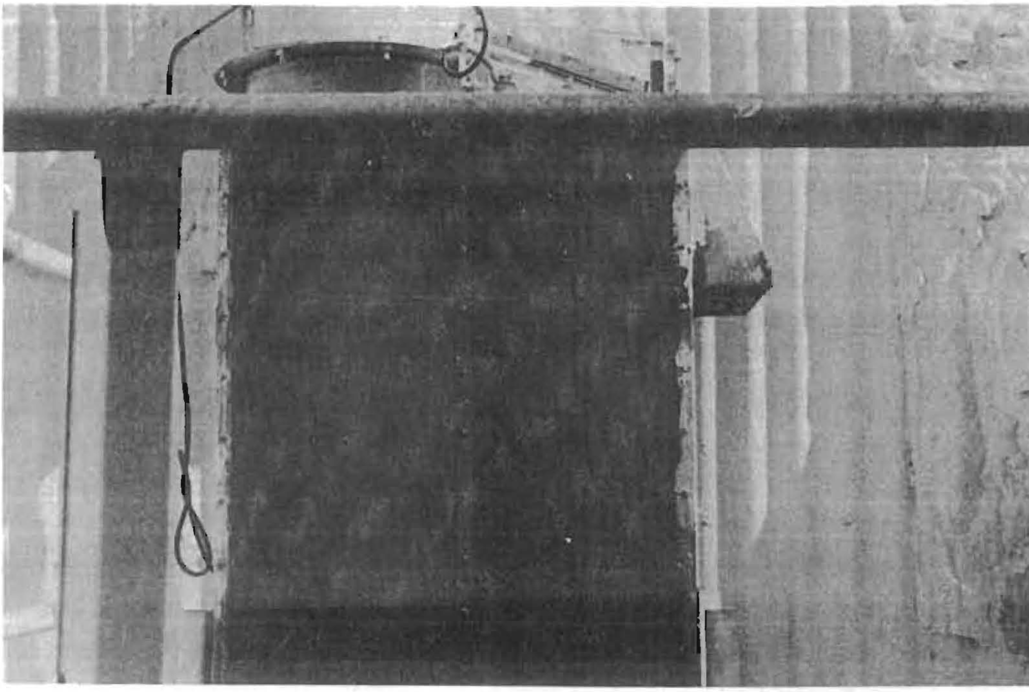

Photo 13. Kellerberrin storage under pressure indicated by difference in fluid level in the pressure vent.

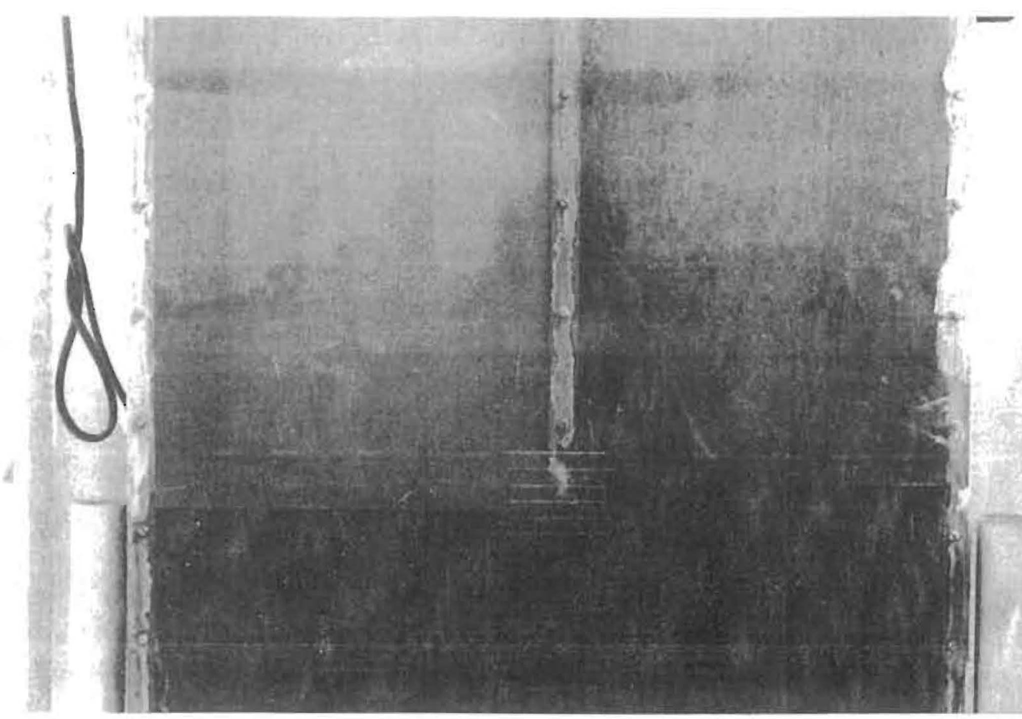

Photo 14. Close-up of a typical pressure relief vent fitted to a horizontal storage.

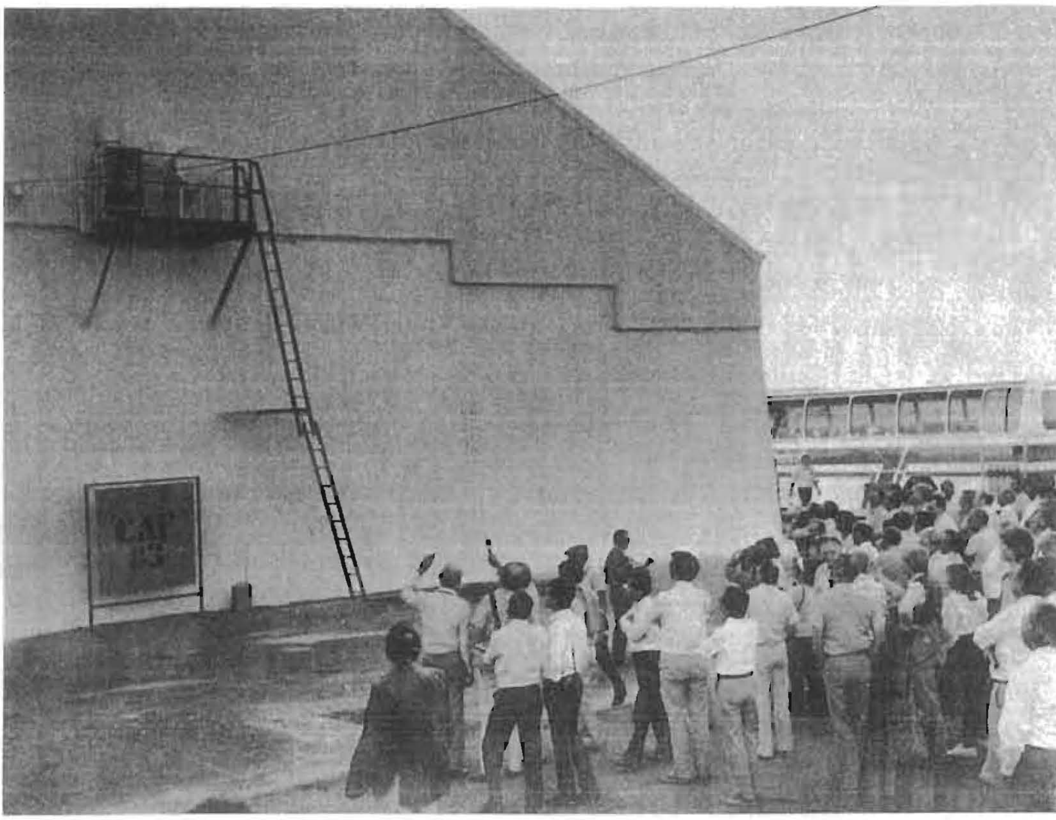

Photo 15. Symposium delegates inspecting pressure testing trial at Kellerberrin.

MERREDIN : STATIC DISPLAY OF COMPANY EQUIPMENT

Various items of grain handling and maintenance equipment were displayed inside an 'E' type horizontal storage (wheat capacity 233,000 tonnes constructed of galvanised iron on inverted Y frame timber wall supports with bitumen floor and corrugated iron roof on trusses mounted on steel columns). The displays included:

a A standard country mobile elevator fitted with spray equipment used for the application of a grain protectant to the grain stream at intake into the older types of storages in the C.B.H. system. These machines are virtually unchanged from the original design developed from a bag elevator in the early 1930's. They incorporate a bucket belt encased in a light sheet steel barrel and driven by a direct drive belt from an 8 horsepower diesel engine. The handling capacity of grain delivered by the farmers motor truck through a self emptying hopper direct to the elevator boot is 60 tonnes per hour. The machine is moved along the storage to progressively fill it through steel chuting leading from the elevator head to the centre of the storage. The elevator is also used to retrieve grain from inside the storage by means of an attached mechanical scoop known as a Clarke Shovel.

b Lobstar - a machine designed to compliment the country elevator for the receival and retrieval of grain in an open bulkhead situation. Screw Augers on the front of the machine under the delivery hopper moves the grain to a central belt conveyor and delivers it to a mechanical thrower to direct the grain to the stack being filled. Retrieval is by removal of the hopper and driving the auger front of the machine into the grain stack for self recovery and loading via the conveyor into motor trucks under the end chute.

c Front-end Loader - These machines are based on an industrial 60 horse-power tractor fitted with a hydraulically operated bucket with a capacity of 1.6 tonnes of grain. They are used to retrieve grain from the horizontal grain storages for delivery to an elevator pit and so out to the transport system. Each machine is capable of outloading from an average storage at a rate of 100 tonnes per hour. A feature of the tractor is the slick tread driving tyres used to minimise damage to storage floors and to spilled grain which otherwise occurs with conventional lug grip tyres.

d Other Items of Equipment used Throughout the System were Displayed as - Trailer mounted high reach work platform: Pest Control specialised wash down unit: Pest Control standard mobile unit with spray equipment, pumps and samples of materials used (herbicides, rodenticides, chemical protectants and fumigants): Standard country truck fitted with crane and clam-shell bucket: Mobile mechanical maintenance workshop unit: High reach portable scaffolding: Sampling equipment for on site testing of grain quality: Safety equipment and photographic displays of the Company over the past 50 years.

The display site was also used as the venue for a social barbecue function held during the overnight stop at Merredin and has been described as "The World's Biggest Grill Room".

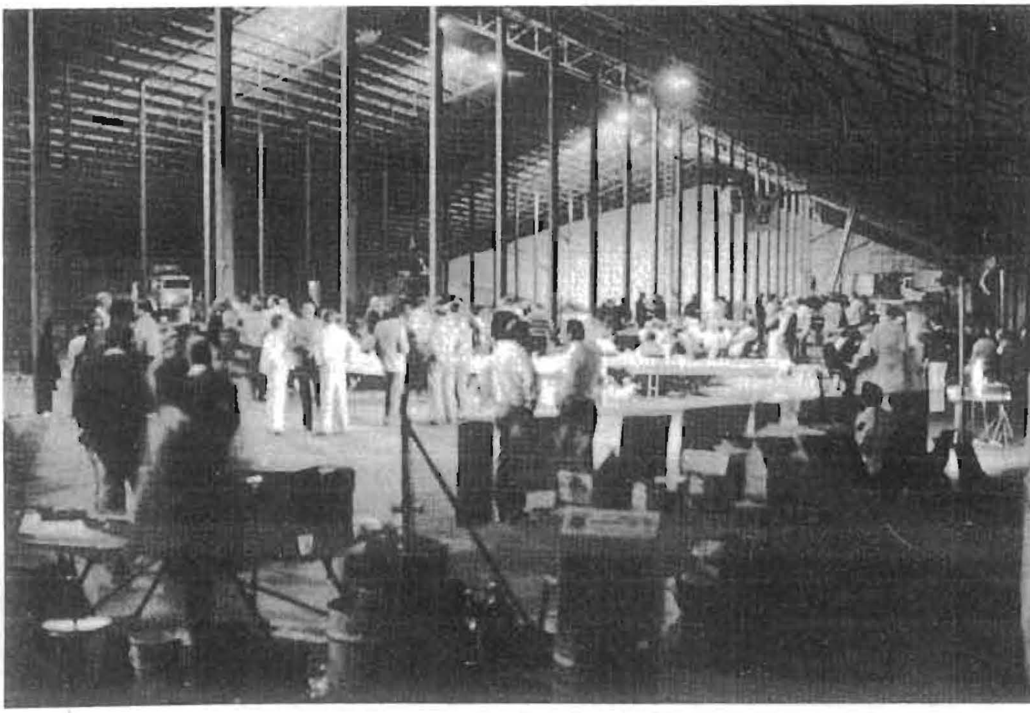

Photo 16. Inside "The World's Biggest Grill Room" - the venue of a social barbeque evening held for Symposium delegates inside a large horizontal storage at Merredin. In the background is a static display of various grain handling machinery and equipment fronting a stack of some 100,000 tonnes of wheat.

NEMBUDDING - SOAP BUBBLE LEAK DETECTION TEST

A field test of leak detection in a sealed and pressurised grain storage - 'A' type horizontal storage of 21,800 tonnes wheat capacity - was demonstrated at Nembudding. This storage was pressurised by using the gable end fans and a weak detergent solution was sprayed over areas of the roof and walls where leaks had been previously detected. The resultant bubbles appearing over the faulty areas enabled the leaks to be pin-pointed and marked for future repairs to the seal. Although other methods of leak detection by use of sophisticated sound, heat and colour measuring equipment have been tried, the simplicity and effectiveness of the "soap bubble" test was shown to be the most viable for our conditions and circumstances. For details of leak detection methods refer to Paper 22.

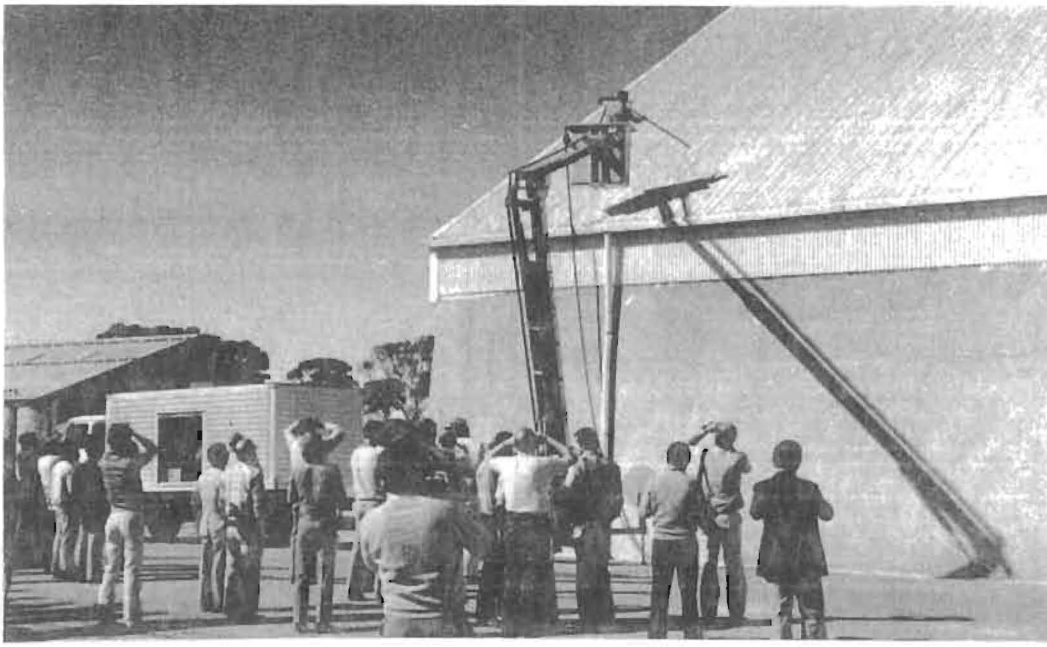

Photo 17. Symposium delegates at a "leak detection" test at Nembudding. After pressurising the storage, a weak detergent solution is sprayed over external surfaces. Escaping air through leaks form bubbles which are then marked for later attention to the seal.

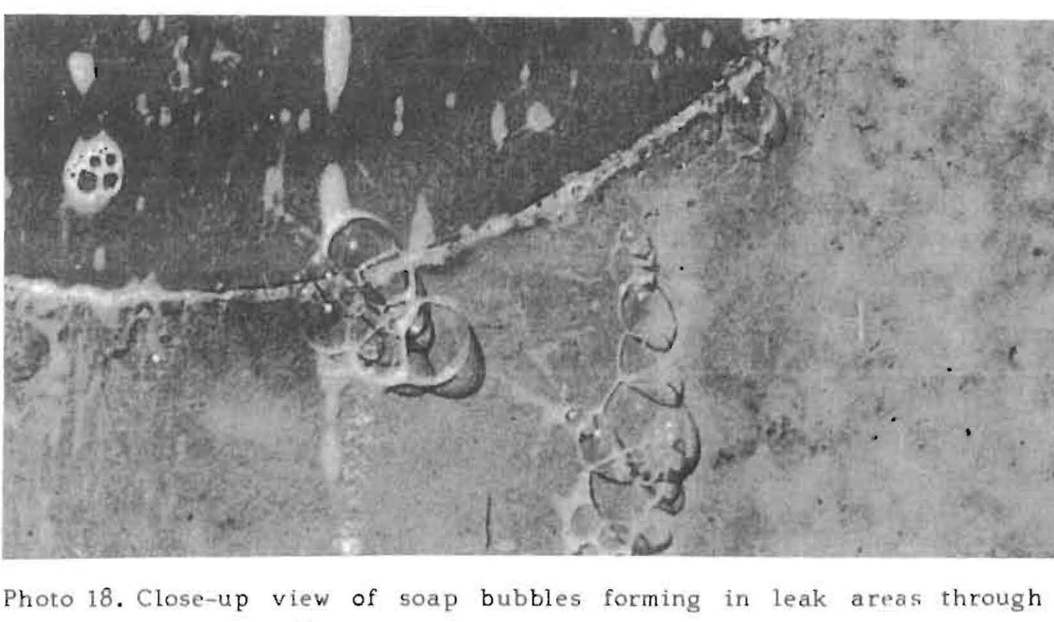

Photo 18. Close-up view of soap bubbles forming in leak areas through a concrete wall.

WYALKATCHEM - SEALED OPEN BULKHEAD EMERGENCY STORAGE.

A sheeted and sealed open bulkhead type storage was demonstrated at this site. The storage consists of a slightly cambered (for drainage) bitumen pad laid on open ground with portable steel frames erected around the perimeter. Grain is loaded into the storage using conventional mobile elevators (or a lobstar and thrower) and the stack is covered with vinyl sheeting anchored with a series of cables. Each sheet is sewn and heat sealed to the next and the covering is then sealed to side sheets placed down the inside of the walls and laid back along the floor under the grain to form a sealed envelope. Small ports are built into the top sheets to allow for sampling and the introduction of a fumigant should this become necessary to control insect activity. This type of storage is used solely as an emergency facility to hold overflow grain in times of good seasons. Its flexibility allows it to be moved from site to site as required. For details of sealing open stacks and the 'bunker' system, refer to Papers 38 and 39.

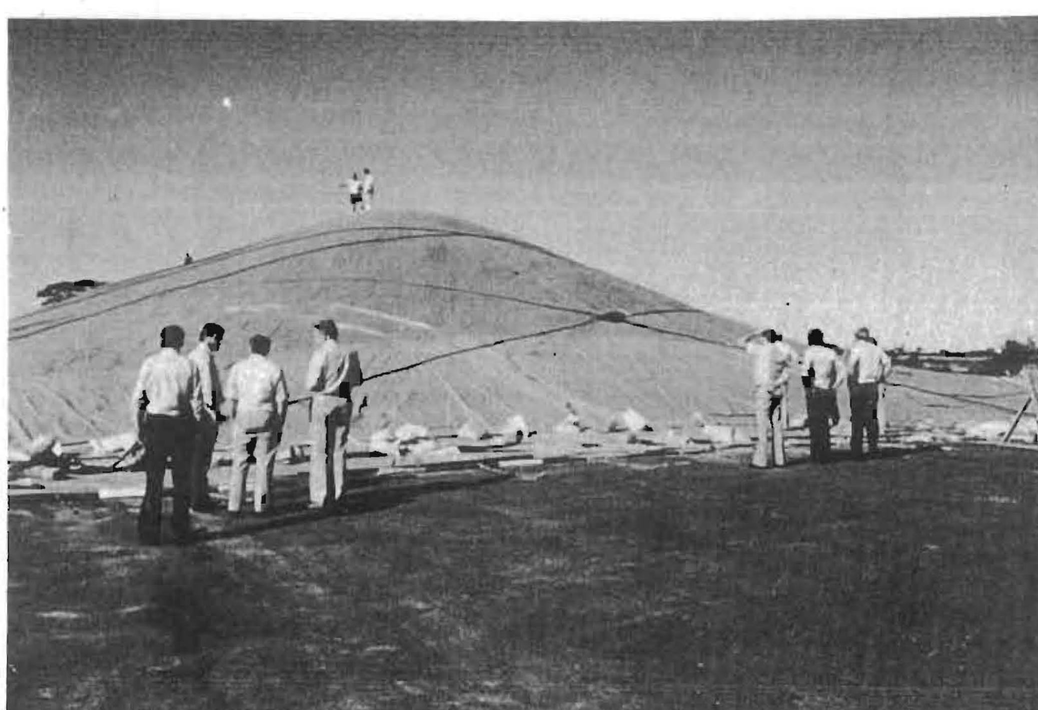

Photo 19. A covered "bunker" storage. Cables are used to tie the PVC sheets to the grain surface to prevent wind damage.

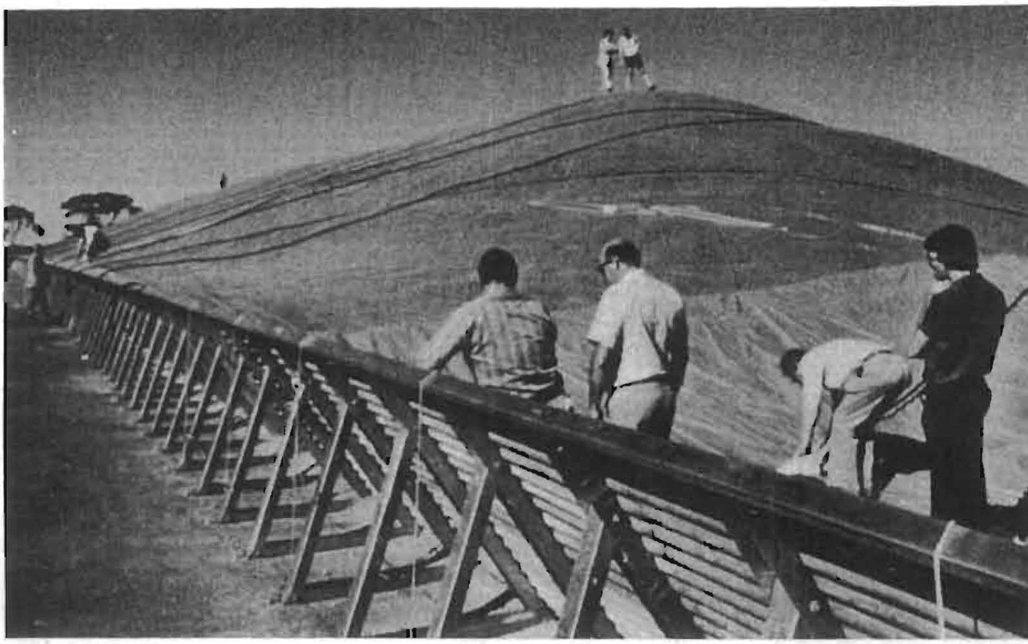

Photo 20. Bunker storage at Wyalkatchem showing the bulkhead type side walls constructed of portable steel frames.

Photo 21. Delegates visit a vintage farm machinery museum inside one of the original grain storages built at Wyalkatchem in 1933.

Photo 22. A brief luncheon interlude at the farm of C.B.H. Director Mr Jack Lundy at Cunderdin. The opportunity was taken to view displays of sheep mustering with dogs, sheep shearing and items of farm machinery used on a typical wheat and sheep farm.

CUNDERDIN : INTRODUCTION OF CARBON DIOXIDE INTO A SEALED STORAGE.

The demonstration at this sealed and fitted storage - a 'C' type horizontal silo 27,700 tonnes of wheat capacity - was the introduction of carbon dioxide gas into a full storage of grain. The liquid CO_2 was supplied to the site by a tanker vehicle and was converted to gas by a vaporiser before being pumped into the storage through perforated ducting laid along the floor. The rate of induction is up to 4 tonnes per hour and a total supply of 48 tonnes is used to give an atmosphere of approximately 75% CO_2. Recirculation of the gas within the storage is by means of ducts and fan which draw the CO_2 from the bottom of the storage and delivers it into the top head-space where it is allowed to spread and permeate back through the grain to the bottom, ensuring an even distribution of gas at all times during the period of fumigation. For details of the use of CO_2 as a fumigant, refer to Papers 5, 6, 7, 19, 25 and 28.

Photo 23. Demonstration of the introduction of CO_2 gas into a sealed storage at Cunderedin. Liquified carbon dioxide is supplied by tanker from where it is pumped through a vaporiser into the storage.

YORK : 'L' TYPE STEEL VERTICAL STORAGES.

A brief inspection of the newly constructed 'L' type vertical steel silo was made at this point. The cells are each of 5,000 tonnes wheat capacity and are fully sealed and coated with a heat reflectant material during construction. They are also fitted for the introduction and recirculation of an inert gas. For details of storage design for C.A. refer to Paper 17.

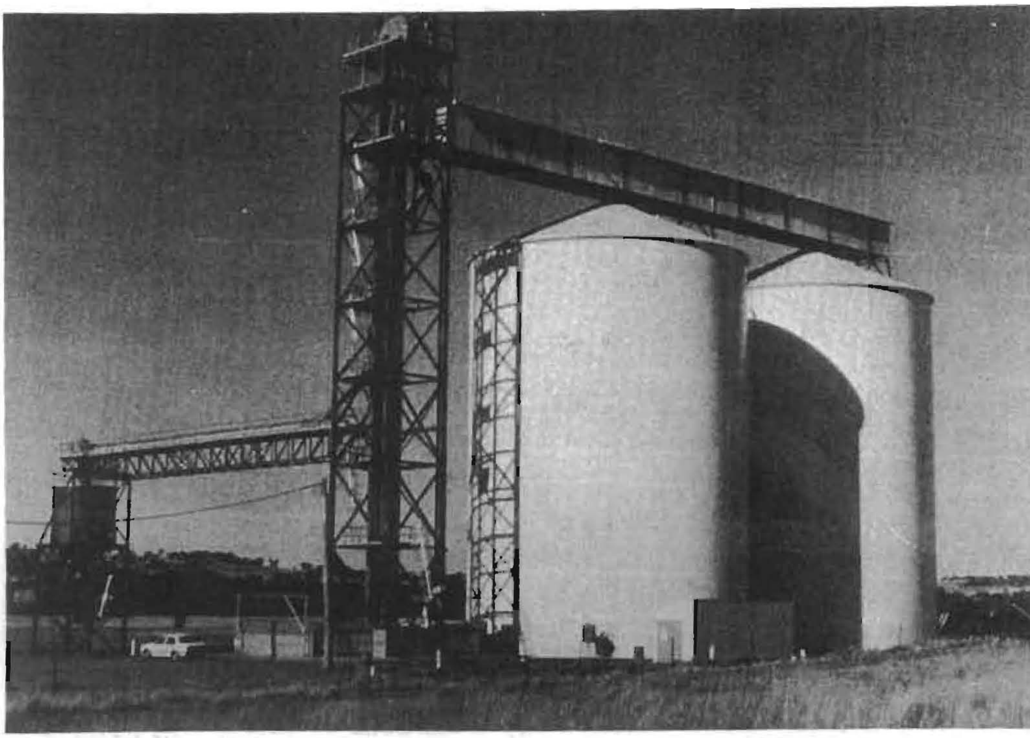

Photo 24. Twin steel vertical cells, each of 5,000 tonnes capacity with a through-put of 300 tonnes per hour at York.

KWINANA : SATURDAY 16TH APRIL 1983

By courtesy of Westrail (the State Government's rail system), a special train carried delegates from Perth through the suburbs to the grain export terminal at Kwinana. Here the largest single storage to be sealed anywhere in the world was inspected.

KWINANA : SEALING AND FITTING OF NO. 1 HORIZONTAL STORAGE.

A very large horizontal storage (wheat capacity 300,000 tonnes) at the Kwinana Grain Export Terminal, completely sealed and fitted for the introduction and recirculation of carbon dioxide, was inspected on the Saturday following the first week of the Symposium. Supplies of carbon dioxide have been arranged from a Nickel refinery, some 3 kilometres from the terminal, where it is produced as a by-product in the refining process. A scrubbing, drying and cooling plant and a pipe line has been constructed to pump the gaseous CO_2 direct to the storage as and when required. Entry is through a plenum chamber and a series of valves through progressively reduced pipes into each of the two under storage tunnels which then act as very large manifolds. A further 32 entry points are supplied along the two side walls to supplement the tunnel entries in uniform swamping of the storage with a calculated 300 to 400 tonnes of gas in a full storage.

Once the storage is filled with carbon dioxide to a concentration of about 40%, the gas will be recirculated by drawing it from the tunnels and floor areas by extractor fans built into the ducting and directing it into the head space above the grain where it will spread and permeate back through the grain to the floor and tunnel areas to be again picked up and recirculated in a continuing movement.

Release of positive pressure built up during the CO_2 swamping action, and of both positive and negative pressures induced by the prevailing weather conditions of sun and wind, is through a series of pressure relief valves connected by ducting to the head space of the storage.

Monitoring of gas concentrations and distribution within the storage is carried out during all stages of the fumigation through tubing and extractor pumps to provide samples of the internal atmosphere for testing with gas analysers. Should concentrations decline to below required levels, a maintenance phase will introduce a further supply of carbon dioxide through the pipe line (estimated 5 to 10 tonnes daily).

When the grain in the storage is required for outloading to ships, the gas clearance phase is commenced to allow safe entry into the storage. The recirculation ducting, with valves reversed, is used to expel gas in the low levels (floor and tunnels) direct to the atmosphere. Large fans built into each gable end of the storage are used, in conjunction with prevailing wind condition, to create an air current from one end of the head space to the other and clear these areas of gas to the outside atmosphere. Blower fans are also used in the tunnel areas to assist the extractor fans in the end ducting to clear this area of concentrations of gas.

When the gas analysers show all areas are safe for re-entry, the seals around the outloading conveyors are removed, entry doors opened and the storage outloaded in the normal manner. Should excessive grain dust remain in suspension in the working areas because of an absence of air movement in the sealed storage, the gable end fans and extractor fans can be used to create an artificial air flow for the removal of grain dust, so minimising any risk of a dust explosion and increasing worker comfort. For details of C.A. in a very large storage refer to Paper 21.

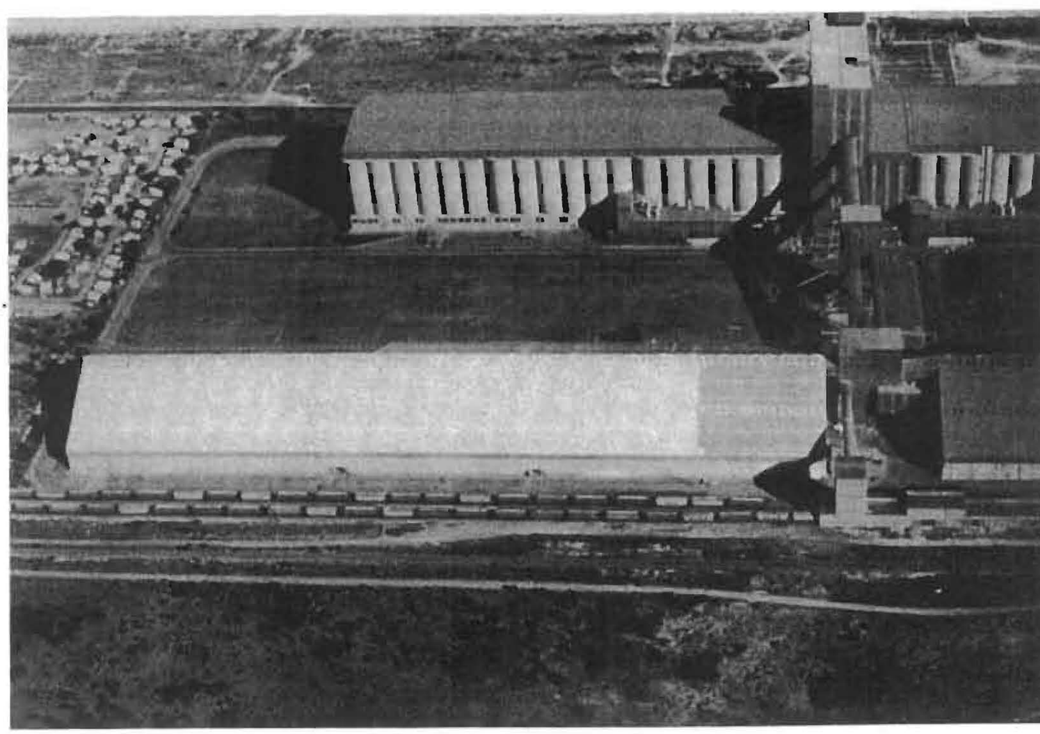

Photo 25. The Kwinana export terminal showing the No. 1 horizontal storage (foreground) during the process of sealing. This storage, of approx 300,000 tonnes wheat capacity, is the largest yet sealed. It is completely fitted with manifolds for the induction of CO_2 gas direct via a pipline from a nickel refinery some 3 kilometres distant. Gas recirculation and clearance systems are provided together with pressure relief vents and a centrally located monitoring system to automatically provide gas concentration readings throughout all areas of the storage.

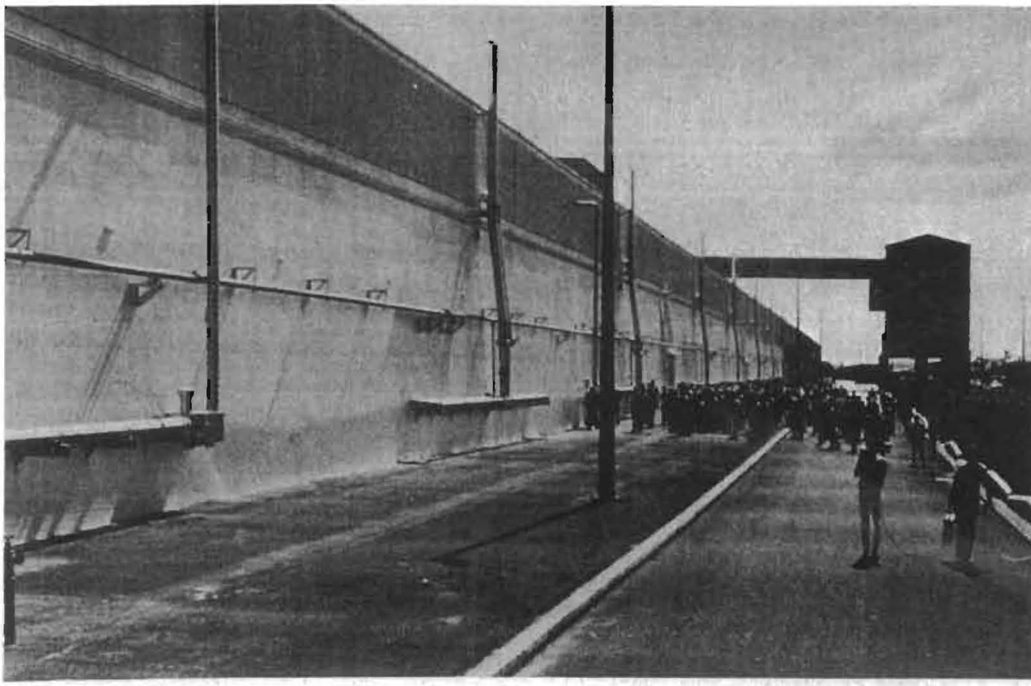

Photo 26. Delegates arriving at Kwinana to inspect the sealed and fitted No. 1 Horizontal storage.

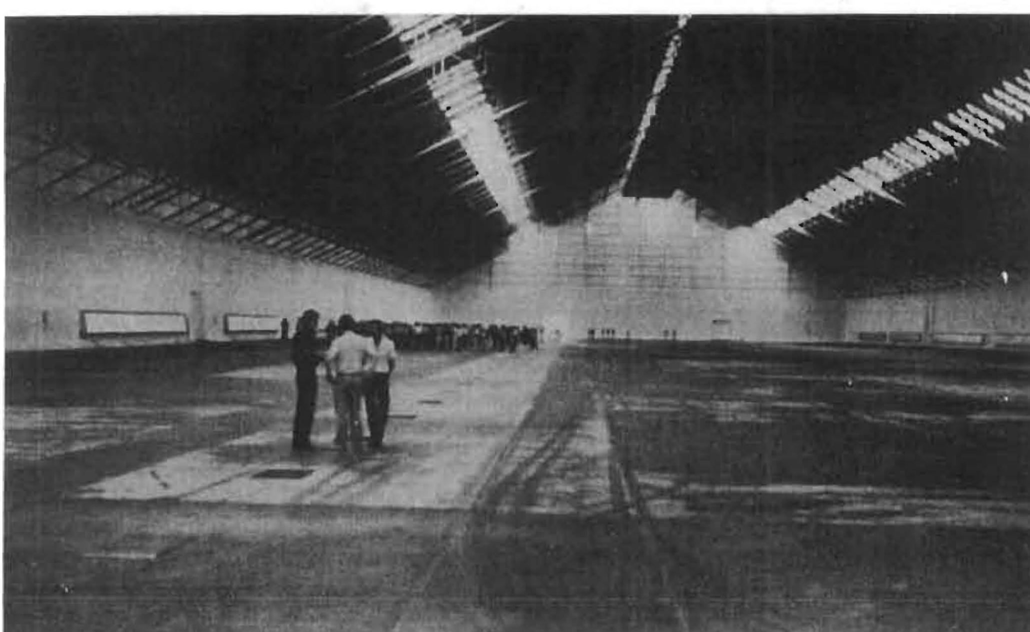

Photo 27 An interior view of the No. 1 horizontal storage at Kwinana.

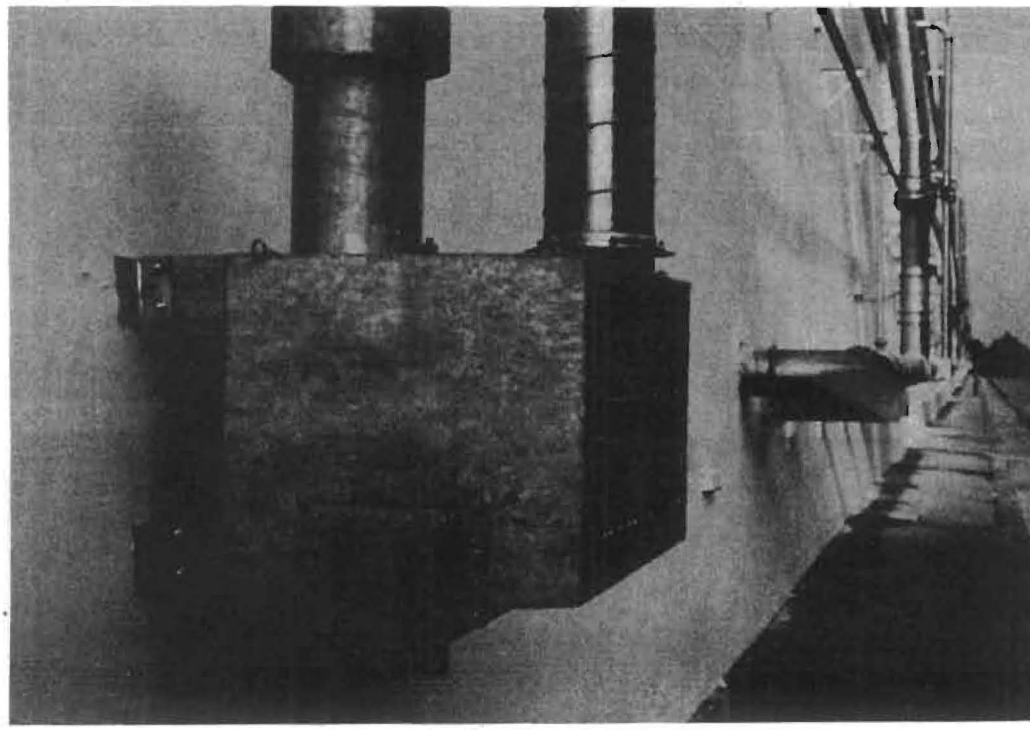

Photo 28. A close-up view of the pressure relief vent fitted at Kwinana. The spiralled ducting enters the storage throught the curtain wall. This allows excessive internal pressure to be vented through an oil bath and out to atmosphere through the short hooded outlet. Negative pressure is relieved by the reverse to this system, allowing air at atmospheric pressure to enter the silo back through the hooded duct, the oil bath and the duct leading to the headspace. The level at which pressure venting occurs may be adjusted by increasing or decreasing the level of oil in relation to the internal baffle fitted between the two chambers.