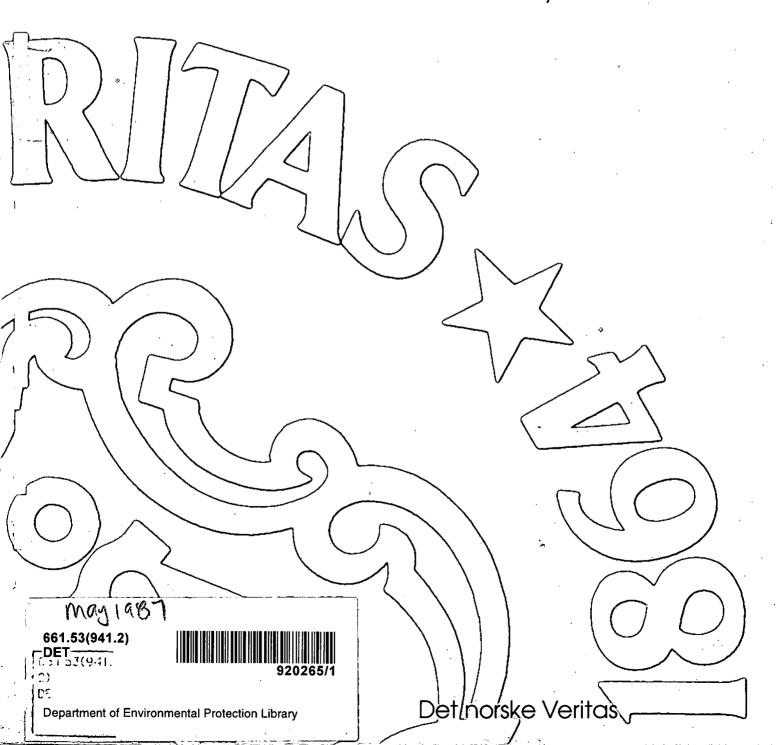


Preliminary Risk Analysis of an

Ammonia/Urea Plant

for CSBP & Farmers Ltd. and Norsk Hydro a.s





DET NORSKE VERITAS



AUSTRALIA, NEW ZEALAND AND SOUTH PACIFIC REGION

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by Det norske Veritas

Report No. 70104 26th May, 1987.

Signed By:

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Chemical Engineer

Approved by:

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PROPOSED AMMONIA UREA/PLANT FOR CSBP/NORSK HYDRO AT KWINANA PRELIMINARY RISK ANALYSIS

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- C. PROPOSED AMMONIA/UREA PLANT EPA GUIDELINES FOR THE PRELIMINARY RISK ANALYSIS
- D. SIMPLIFIED PROCESS FLOW SCHEMES



SUMMARY AND CONCLUSIONS

1.

Det norske Veritas has carried out a Preliminary Risk Analysis for a proposed Ammonia/Urea Fertilizer Plant at Kwinana for CSBP & Farmers Ltd. and Norsk Hydro a.s.

The analysis has examined the proposed process arrangements, storage and export facilities with particular emphasis on factors affecting the site and risk to the public and nearby facilities.

Quantified Risk Analysis techniques have been used to assess the consequences of equipment failure or process malfunction which may present risk to the public and nearby facilities and to estimate the probability of occurrence of hazardous events and their consequences. The results have been compared with the risk assessment guidelines of the EPA and generally accepted criteria for such facilities.

The study has been carried out as an independent assessment in accordance with EPA requirements and DnV's internal requirements for independence and objectivity.

Our conclusions are as follow:

- 1. The study confirms the suitability of the proposed site at Kwinana from the risk criteria viewpoint. Risk levels are found to be within the criteria levels suggested by the EPA for individual risk to residential zones and within generally adopted criteria for individual risk to adjacent industry.
- 2. The risk of lethal concentrations of ammonia gas reaching local population centres is negligible for a range of toxic gas release scenarios, even under the most unfavourable atmospheric conditions.
- For neighbouring industries within the 1×10^{-6} per year risk contour there is a small risk of exposure to accidental release of ammonia for which emergency response procedures will apply. The resulting risk of serious injury or fatality is small, well below that due to other common industrial risks and within criteria levels usually accepted for risk to adjacent facilities from fire or explosion. Most of the industries within the 1 x 10^{-6} contour (i.e. CSBP, KNC) are familiar with ammonia and have in place procedures for emergencies from existing operations.
- 4. Natural gas, hydrogen, urea-formaldehyde and process materials (catalysts, MDEA, water treatment chemicals) do not pose any significant hazard during normal operation beyond the plant boundary.
- 5. Heat flux and explosion overpressure effects do not present a significant risk and damage is likely to be confined within the battery limits of the plant.

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- As the proposed full height concrete bund will contain any liquid ammonia in the (unlikely) event of a serious leak or rupture of the inner steel tank, boil-off will be limited by the amount of heat which can be absorbed from the surroundings in the annular volume. This will limit the total quantity of ammonia vapour released to the atmosphere. The height of any vapour discharge will aid dilution and dispersion downwind to non-toxic levels.
- 7. Failure of the refrigerated ammonia export pipeline from the storage tank to the jetty could result in one of the most serious spillages of ammonia, as the hold-up in the line is of the order of 80 tonnes. The consequences are unlikely to be as far reaching if the spill occurred along the bulk cargo jetty resulting in liquid ammonia flowing into the water. This would result in a rapid boil-off and give rise to a lighter, more rapidly dispersed ammonia vapour cloud. Taking these consequences into account, the resulting risk levels calculated for the loading of an ammonia ship were found to be low and considered acceptable.
- 8. Although the concept of a mobile loading arm is considered reasonable, a permanently installed loading arm at the wharf would further reduce the potential hazards and therefore should be examined further.
- 9. The risks of a shipping accident involving a major release of ammonia whilst navigating to and from the bulk cargo wharf were found to be less than one chance in a million years and can be considered acceptable.
- 10. The proximity of the B.P. Refinery, KNC and CSBP plants has been reviewed and our conclusion is that risks to and from the proposed ammonia/urea plant are below the risk level of 50×10^{-6} per year which is in line with the EPA guideline (September, 1986) for adjacent industry.

In particular the major offsite risks from the refinery to this plant are heat flux and explosion overpressure for which the proposed separation distances and design standards are adequate to avoid domino effects.

11. A quantified assessment of cumulative risk from all industries in the area is beyond the scope of this study. However, as individual risk levels from the proposed ammonia/urea plant do not reach residential areas even at the level of one in a hundred million per year (1% of the criteria level), it can be stated that the proposed plant would not present a significant contribution to cumulative risk levels at residential areas.



The Kwinana Cumulative Risk Analysis Report was not available at the time of preparation of this study but was due for release in late May 1987.

12. Achievement of the risk levels determined in this study is dependent on high standards of engineering operation and maintenance. Det norske Veritas have examined the proposed engineering and operating philosophy, management structure and operations and maintenance safety procedures, and are satisfied that the required standards will be met.



2. INTRODUCTION

2.1 BACKGROUND TO THIS STUDY

In 1985, the W.A. State Government extended to interested parties an invitation to undertake a study of the design, construction and operation of an ammonia plant in conjunction with facilities for the manufacture of urea, a fertiliser used widely in Western Australia and presently manufactured overseas from ammonia. Following the assessment of submissions received, the State Government appointed CSBP & Farmers Ltd (CSBP), and Norsk Hydro a.s (Norsk Hydro) of Norway, to undertake a full feasibility study for the project on an exclusive basis.

The feasibility study was based on a proposal to construct and operate a plant with the capacity to produce about 1,500 t/d of ammonia and about 1,300 t/d of urea, of which approximately two-thirds of the manufactured product would be exported.

Following the submission to the Environmental Protection Authority (EPA) of a Notice of Intent (NOI) in April 1986, the State Government considered that a detailed analysis of suitable sites should be conducted. The proponents (CSBP and Norsk Hydro) complied by commissioning a site selection study to evaluate prospective sites adjacent to the natural gas pipeline. The resulting study found that the environs of Geraldton, Kwinana, Wagerup and Bunbury were the most suitable for detailed study, and that, of these, Kwinana was the preferred site. The results of the site selection study were forwarded to the State Government in confidence in May 1986.

Det norske Veritas carried out the risk assessment for this study, which focussed on the critical risks including major storages, pipelines and ship loading facilities that may be capable of affecting the public in surrounding areas. While based on limited design information and consideration of risks to the public, the studies found the Kwinana site to be the most favourable from the public risk viewpoint and, with proposed relocation of nearby residences, capable of meeting the proposed risk criteria for residential areas.

Following consideration of the NOI, the EPA advised the proponents that, under existing environmental legislation, implementation of the proposed project would have to be preceded by the preparation of an Environmental Review and Management Programme (ERMP). Similarly, the Federal Government, through the Department of Arts, Heritage and Environment, required that a draft Environmental Impact Statement (EIS) be prepared.

The proponents have commissioned Kinhill Engineers Pty Ltd (Kinhill) to prepare this ERMP/draft EIS to assess the environmental factors relevant to the construction and operation of the proposed ammonia/urea plant. Det norske Veritas have been commissioned by the proponents to carry out an independent Preliminary Risk Analysis as a requirement of the ERMP/EIS.

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2.2 STUDY AIMS AND OBJECTIVES

The aim and objective of this study is to subject available information on the proposed plant and operations to a detailed, independent and objective risk analysis to enable:

- 1. Identification and evaluation of potential hazards and their resulting risks in order to assist the safety of the project through understanding of risks and implementation of effective risk reduction measures.
- 2. The proponents to meet the requirements of the EPA and other authorities in respect of planning and approval procedures.

Scope of Work

The work involves the undertaking of a preliminary risk analysis for the proposed Urea/Ammonia plant and will discuss and recommend measures which may be used to minimize risks.

The study addresses all aspects nominated in the EPA guidelines (refer Appendix C) and specifically includes assessments of the following risks:

- Leakage or failure of process equipment.
- Hazards of process, storage and operations proposed.
- Domino effects.
- Export loading.
- Shipping.

The presentation of the results of the risks analysis is cognizant of the EPA requirements for a public document, and the need for a Summary Report.

The information from the hazards analysis may be used to:

- confirm or modify design standards,
- establish operational procedures,
- establish contingency measures,
- inform relevant authorities,
- confirm the selection of a suitable site.

The form of hazards analysis used is based on the requirements of relevant authorities and is similar to those used by Veritas for comparable facilities. The analysis systematically examines the safety of the plant by addressing the following issues:



- The determination of where and how releases, spills or leakages are likely to occur;
- The estimation of the likelihood of failure (frequency) and size of releases, spills or leakages and the probability of ignition;
- Calculation of the consequences of failure including dispersion and diffusion characteristics;
- Development of risk levels relating to people in the area, adjacent facilities or nearest residences.

In view of the preliminary (feasibility) phase of project development in which the study is placed, emphasis is given to conceptual aspects including siting, layout, design philosophy, etc. with input to design and approval considerations. Aspects which are more appropriately dealt with in later stages are identified for attention.

2.3 GENERAL NATURE OF THE PROJECT

The proposal is to establish a manufacturing plant for processing natural gas to form Ammonia and Urea for export and local requirements. The plant would be of current proven design incorporating modern controls for safety and reliability.

The plant would be designed to produce 1500 tonnes per day of ammonia (495,000 tonnes annually) and 1300 tonnes per day of urea (430,000 tonnes per year). Approximately half the ammonia is consumed in production of urea. About one third of the production of ammonia and urea will be utilised for W.A. requirements and the remaining two thirds will be exported.

A refrigerated ammonia storage tank of 30,000 tonne capacity will be constructed.

The proposed site is on land currently owned by B.P. Refinery, Kwinana immediately north of the CSBP fertiliser complex at Kwinana, W.A.

2.4 PHILOSOPHY OF APPROACH TO RISK ASSESSMENT

The potential for major hazard arising in the processing, storage or transportation of hazardous materials warrants special measures to ensure safety of the public, the work force and the plant.

One of the approaches utilised in the development and approval of facilities involving products such as ammonia is Risk Assessment, which requires the use of a range of analytical techniques and calculation methods to identify and evaluate the hazards and risks associated with a process or facility.

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The primary purpose is to ensure that all significant risks are identified and properly evaluated to enable appropriate action to be taken to eliminate or reduce the potential for serious accident. The techniques, while still subject to many limitations and uncertainties, have developed to the stage where much of the risk can be quantified in terms of consequence, probability or frequency of occurrence and resultant frequencies (risk levels) of exceeding designated hazard impact levels.

Consequently, it is now common for risk assessment to be used to assist in the approval process for new plant proposals. The risks associated with a plant are measured against criteria to assist in determining the acceptability of the risk for the proposal involved.

It is essential that risk assessment be carried out in an objective manner by competent analysts who achieve a proper understanding of the processes and risks involved. Because some degree of subjectivity exists in assessing failure modes, selecting failure rate data, determining inputs to calculations and computer programs, and so forth, it is also necessary for the assessment to be carried out free from influences which could result in bias. This is best achieved by ensuring independence of the analysts.

Independence of Det norske Veritas

Det norske Veritas, a recognised international classification society, is established as an independent, self-owned institution. By not having shareholders, and maintaining strict controls over its organisational independence, integrity of its staff and its quality standards Veritas has established a reputation for independence and objectivity. In addition to its internal audits and controls, Veritas independence and objectivity is tested from time to time in inquiries and reviews. Det norske Veritas has no links with the proponents Norsk Hydro a.s. and CSBP & Farmers.

2.5 RISK STANDARDS AND GUIDELINES

2.5.1 EPA GUIDELINES - GENERAL CRITERIA FOR RISKS ASSESSMENT

The Environmental Protection Authority Statement on the evaluation of the risks and hazards of industrial developments on residential areas in Western Australia proposes the following as a guide for assessment of the fatality risk acceptability of new industrial installations:

The Authority has taken note of how decisions on risks are taken in other parts of the world. In the light of that knowledge the Authority will classify decisions into three categories. These are as follows:

- A small level of risk which is acceptable to the Environmental Protection Authority;
- A high level of risk which is unacceptable to the Authority and which warrants rejection; and
- A middle level of risks, which subject to further evaluation and appropriate actions may be considered to be acceptable to the Authority.
- 2. An individual risk level in residential zones of less than 1 in a million a year is so small as to be acceptable to the Environmental Protection Authority.
- 3. An individual risk level in residential zones exceeding 10 in a million a year is so high as to be unacceptable to the Environmental Protection Authority.
- 4. Where the preliminary risk level in residential zones has been calculated to be in the range 1 in a million to 10 in a million a year, the Authority will call for further evaluation of the risks associated with the project. The Authority may then be prepared to recommend that the project be acceptable subject to certain planning and technical requirements.

A major technical requirement will be the commissioning of a Hazard and Operability Study at the detailed design stage of the project. Such a study is an effective technique for discovering potential hazards and operating difficulties at the design stage. Significant reductions of hazards, and in the number of problems encountered in operation, as a result of studies are possible. The Hazard and Operability Study should be undertaken by the proponent with a qualified person, approved by the Authority, who has to certify to the Authority that the study was carried out in a proper manner. This study should explore all feasible ways of reducing risks. The proponent may be required to update the risk analysis, and make the results public.

In addition the EPA proposes that cumulative risk effects be considered as follows:

Cumulative Risk Impacts

Where a number of hazardous industries or activities exist in a region, it is appropriate for a cumulative risk and hazard analysis for existing and proposed developments in the region to be undertaken before assessing new developments in the region. No extra risk would be acceptable where the cumulative risk of existing industry, combined with the assessed risk of the proposed new industry, exceeds the risk levels proposed for new industry (item 5).



2.5.2 EPA GUIDELINES FOR THIS PROJECT

The EPA has provided guidelines for the content of the risk analysis which follow the approach adopted in other recent studies. Appendix C presents these general guidelines which have been used as a basis for this report.



3. PROJECT DESCRIPTION

3.1 SITE LOCATION AND ENVIRONMENT OF THE PROJECT SITE

3.1.1 BACKGROUND

In 1955, a planning study (Stephenson and Hepburn 1955) recommended that the Kwinana district be developed as a major industrial centre. The subsequent industrialization of the area led to the decline of the residential communities of Naval Base and Kwinana Beach, and the development of Kwinana 'New Town', including the residential suburbs of Medina, Calista, Orelia and Parmelia, to house the Kwinana industrial workforce.

3.1.2 RESIDENTIAL

The nearest major residential area to the plant site is Kwinana 'New Town', approximately $2\ km$ inland to the south-east. The town is screened from the industrial strip on the coastal plain by a ridge of well-vegetated dunes.

A smaller isolated pocket of residential development is located at Kwinana Beach. The populations of each of those communities for 1966 and 1981 and estimates for full development are shown in Table 3.1.1.

Table 3.1.1 Population in surrounding communities: 1966, 1981 and at full development

Neighbourhood unit	1966 population	1981 population/dwelling	Full development population		
Kwinana 'New Town'	4,132	12,216/3,936	32,260		
Kwinana Beach	846	310/98	<u> -</u>		
Naval Base	426	421/138	240		

Source: Kinhill Stearns 1986.

Since the Kwinana Beach area was zoned 'Special Industrial' in 1975, under the Metropolitan Region Scheme (MRS) (State Planning Commission 1986), its population has steadily declined. A high proportion of dwellings are unoccupied as a result of Fremantle Port Authority acquisition. Presently, there are only fifteen residents remaining and these are expected to be relocated by May 1987, well ahead of any possible commencement of operations.



Industrial

The existing major industrial operations in the vicinity of the site, together with their maximum on-site workforce, are shown in Table 3.1.2.

Table 3.1.2 Industrial Workforce surrounding site

Company	Type of Industry o	Maximum on-site workforce		
BP Refinery	Oil refining	450		
KNC	Nitrogen production	20		
CSBP	Fertiliser and chemical manufactur	e 420		
WMC	Nickel refining	440		
Coogee Chemicals Pty Ltd	Chemical manufacture	25		
BHP Kwinana	Steelworks	250		
Commonwealth Industrial Gases	Industrial gas production	15		
Co-operative Bulk Handling	Grain terminal	150		
SECWA	Power station	450		
Alcoa	Alumina refinery	1,360		
Total		3,580		

Source: Kinhill Stearns 1986.

Recreational

The Cockburn Sound Environmental Study (Department of Conservation and Environment 1979) recognised that Kwinana Beach and adjacent Wells Park constituted an important recreational resource for residents in the Kwinana area. Even when residential occupation is phased out of the immediate vicinity in 1987, the resource will retain its importance to the greater population of the Town.

Accordingly, a draft coastal management plan (Department of Conservation and Environment 1984) has been prepared for the location to ensure that its attributes are protected and enhanced in the future.

3.1.3 ZONING

The plant site is zoned 'Industrial' under the MRS and is surrounded by 'Industrial'-zoned land to the north, south, east and west. Further to the east, a 1 km wide parks and recreation reserve preserves an attractive landscape buffer between the site and 'Urban'-zoned land at Medina.

The plant site falls within 'Industrial'-zoned land under the Town of Kwinana Town Planning Scheme No. 1.

3.2 METEOROLOGY

Introduction

The climate of Kwinana, as for the entire Perth Metropolitan Area, is characterized by mild, wet winters and hot, dry summers.

The average annual rainfall for the area is 772 mm, which occurs predominantly in winter. The maximum annual rainfall recorded was 1,178 mm, while the minimum was 414 mm. The Perth area is renowned for large volumes of rain falling in a short time, with the maximum rainfall falling in one hour being 48 mm.

Wind Direction

Sea breeze/land breezes predominate in the coastal region around Kwinana. During transition between offshore and onshore breeze, south winds frequently occur (9).

The strongest winds blow from the west and occur mainly in winter when storms from the Indian Ocean affect the coast further South. Offshore easterly winds can reach gale force in summer. The average wind speed is approximately 4 m/s from records at Hope Valley Base Station near the plant site.

The wind speed/wind direction frequency matrix for all stability categories is summarised in Table 3.2.1 overleaf.

Atmospheric Stability

Information on atmospheric stability for Pasquill categories A-F (A = unstable, D = neutral and F = stable) was provided by the E.P.A. from the Hope Valley Base Station for the period 1st January 1980 to 31st December 1980 (11). The information presented is in the form of six wind speed — wind direction frequency matrix tables corresponding to each of the Pasquill stability classes.

From analysing this information nineteen specific sets of stability categories and wind speeds were initially chosen as representative of the area for calculation purposes. After analysis, sixteen sets were selected as shown in Table 3.2.2.

These categories represent approximately 87% of the time with C,D, 4, 5 and 7 m/s representing approximately 55%. These may be taken as representing low night-time winds, average conditions, afternoon strong breezes and occasional high winds.

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TABLE 3.2.1: Wind speed/wind direction frequency matrix for wind data measured at the Hope Valley Base Station over the period 1st January 1980 to 31st December 1980. Wind speed and direction were measured at 10 metres above ground level.

WIND SPI	een.	-					WIND	DIRE	CTION	SECT	OR .							,
RANGE TOTALS		S)	N	NNE	NE	ENE	E	ESE	SE	SSE	S	SŚW	S₩	WSW	W	WNW	NW	NNW
OVER	13.5																	Ø.
12.0 -	13.5										•							Ø.1
10.5 -	12.0	٠							•			Ø.1	Ø.1			Ø.1	•	Ø.3
9.0 -	10.5								.*	Ø.1	Ø.7	Ø.5	Ø.2	Ø.1	Ø.2	Ø.1	Ø.1	2.1
7.5 -	9.0	Ø.1	Ø.1	Ø.1	Ø.1	Ø.1				Ø.2	2.0	1.2	Ø.9	Ø.4	0.5	Ø.3	Ø.2	6.4
6.0 -	7.5	Ø.2	Ø.4	Ø.4	Ø.6	Ø.6	Ø.2	Ø.1	Ø.1	Ø.7	3.0	. 2.8	1.6	1.1	Ø.8	Ø.4	Ø.3	13.2
4.5 -	6.0	Ø.5	Ø.8	Ø.5	1.Ø	1.8	0.8	Ø.5	Ø.8	1.2	2.6	2.7	1.7	1.5	Ø.9	Ø.5 _.	Ø.5	18.3
3.0 -	4.5	Ø.6	2.0	1.6	1.9	2.5	2.9	2.0	3.5	3.3	2.2	1.4	1.1	1.7	Ø.7	Ø.5	Ø.4	28.
1.5 -	3.0	Ø.6	1.6	3.2	2.7	2.8	3.0	3.3	3.2	2.3	1.4	Ø.6	Ø.7	1.1	Ø.6	Ø.4	0.4	27.
Ø.5 -	1.5	Ø.2			-						Ø.2							3.4
TOTALS		2.2	5.2	6.1	6.5	8 Ø	7.2	6.1	7.9	8.0	12.2	9.5	6.5	6.1	3.9	2.3	2.1	

CALMS (LESS THAN Ø.5 M/S): Ø.1%

The percentages do not add up to exactly 100 due to rounding errors.

Table 3.2.2 Stability Categories & Wind Speeds Used in Report

Pasc	Wind Speed M/S	
	**	
	À	2, 4
	В	2, 4
	Ċ .	4, 5, 6, 7
	Ď	4, 5, 6, 7
	E	2, 4
	F	2, 4

Temperature

The air temperature (at 10 m height) varies between $2^{\circ}C$ and $40^{\circ}C$ (9), however, ground temperatures may be higher. High ambient temperatures will cause rapid vaporisation of any spilled liquids and also result in heating of cold vapour clouds, decreasing density and reducing the rate of gravity spreading. A typical ambient temperature of 22.5°C was used for the majority of the risk analysis calculations.

Surface Roughness Length

The surface roughness length is a measure of the friction between the atmosphere and the earth's surface. Surface roughness length may vary from less than 1 mm over calm water, smooth ice, or smooth mudflats to over 1 m for the centre of cities. This proposed site and surrounding terrain is a low lying area surrounded by a variety of landscapes and buildings ranging from minor vegetation to large warehouses and chemical plants. Surface roughness is estimated to be in the range of 0.1 to 0.3 m, therefore a length of 0.2 m was chosen as a compromise value.



3.3 PROCESS DESCRIPTION

A simplified process flow scheme for the proposed ammonia plant is presented at the end of the report. A brief description of the proposed steps is given below. Where specific references to a process are required, the C F Braun ammonia process has been used.

3.3.1 GENERAL

The ammonia process plant is to produce 495,000 tonnes of product from natural gas annually. Of this 248,000 tonnes will be used for producing urea, the balance will be directed to storage and a varying demand of approximately 100,000 tonnes/year will be transferred to the existing Kwinana Nitrogen Company tank for use by KNC and distribution to other domestic users. An atmospheric pressure storage tank of 30,000 tonne nominal capacity will be constructed.

Ammonia is to be exported via tankers specially designed for transporting refrigerated product at atmospheric pressure. Approximately 20,000 tonnes of ammonia will be exported per time requiring 9 tanker visits per year. Product will be pumped through a 250 mm diameter insulated pipeline and loaded onto a tanker using a loading arm. It is proposed to use the Kwinana Bulk Cargo Jetty for the ammonia export operation. The loading arm is to be designed as a mobile unit for relocation and storage back at the plant between tanker visits.

3.3.2 AMMONIA MANUFACTURE

General

Ammonia is manufactured in three basic process steps:

- i) High pressure catalytic reforming of natural gas.
- ii) Purification of gases.
- iii) Ammonia synthesis.

The first two steps involve the production of hydrogen gas, the introduction of nitrogen in stoichiometric proportion and the removal of carbon dioxide, carbon monoxide and water, which are catalyst poisons. Ammonia synthesis involves the catalytic fixation of nitrogen at elevated temperature and pressure and the recovery of ammonia. A brief description of the proposed steps is given below for the C F Braun ammonia process chosen for this study.

Refer also to the Simplified Process Flow Diagrams in Appendix D.



Desulphurisation

The sulphur content of the natural gas feed is reduced to less than 0.2 ppm over the hydrotreater catalyst followed by a zinc-oxide bed in order to prevent temporary poisoning of the reforming catalyst and permanent poisoning of the low-temperature shift catalyst. The feed gas is mixed with recycle synthesis loop purge to provide the hydrogen for hydrotreating. Then it is preheated to about 370°C in the reformer furnace H101 convection section before going to the cobalt-molybdenum and zinc-oxide vessel V105.

Primary Reforming

The desulphurized feed gas is mixed with 3.6 MPa steam, preheated to about 415°C by heat exchange and finally heated to about 600°C in the primary reformer convection section. It then flows to the primary reformer H101 catalyst tubes where the gas and steam react over a nickel catalyst to form a mixture of hydrogen and carbon oxides. The effluent from the tubes (at about 710°C and 3.0 MPa, containing approximately 23 mole % unreacted methane) flows to the secondary reformer R101.

Secondary Reforming

Compressed process air is preheated to about 460°C in the primary reformer convection section and fed into the secondary reformer. In the upper section, oxygen in the air reacts with incoming primary reformer effluent to form carbon oxides and water. The gas mixture then passes down through a bed of nickel reforming catalyst in the lower section, where the heat released by the above oxidation further converts methane to hydrogen and carbon oxides. The methane content of the gas leaving the secondary reformer is about 1.7%.

The effluent from the secondary reformer is cooled from about 880°C to about 388°C for shift conversion. The cooling occurs in a natural circulation secondary reformer steam generator E101 designed to produce 10.3 MPa steam, and then in a steam superheater exchanger E102 where the entire plant (10.0 MPa) steam production is superheated to about 390°C before final superheating in the reformer convection section.

Shift Conversion

The cooled effluent from the secondary reformer steam superheater exchanger flows through a bed of conventional high-temperature shift catalyst in the high-temperature shift (HTS) converter R102 where carbon monoxide reacts with steam to form carbon dioxide and hydrogen. About 65% of the carbon monoxide is converted in the HTS. The gas leaving the high-temperature shift converter at about 445° C is cooled to about 204° C by heat exchange and then flows into the low-temperature shift (LTS) converter R103.

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Most of the remaining carbon monoxide is converted to carbon dioxide, leaving a residual carbon monoxide content of about 0.36% in the converter effluent. The process gas leaves R103 at 233 $^{\circ}$ C and is then cooled to 159 $^{\circ}$ C by 400/450 kPa steam generator E103.

The LTS converter effluent is further cooled to about 75° C by heat exchange. The condensed water is removed in a knockout drum V101 and sent to the process condensate stripper. The process gas is fed to the CO₂ removal section.

Carbon Dioxide Removal

The CO₂ removal system is a two-stage MDEA system licensed by BASF.

The MDEA system consists of a two stage absorber in a single column (T101) a pre-flash unit (first desorber) and a two stage regenerator arranged in two columns (second desorber T103 and stripper T107). Most of the ${\rm CO}_2$ is removed in the bottom section of the absorber using a semi-lean MDEA solution. Final absorption takes place in the top section using a lean solution. The semi-lean solution is not cooled so that most of the heat of desorption is supplied by the heat of absorption. The lean solution is produced by the stripper and its heat input is minimized by a feed/bottoms exchanger E122.

The overhead vapour from the second desorber, which contains the ${\rm CO}_2$ product, is cooled in an air cooler E121 where most of the steam is condensed. ${\rm CO}_2$ -rich gas then flows to the urea plant with the surplus vented at atmosphere.

The gas leaving the top of the absorber T101 (containing about 800 ppmv ${\rm CO}_2$) is scrubbed with water over wash trays, followed by a demister to remove traces of MDEA.

Methanation

The overhead gas from the carbon dioxide absorber T101 is preheated to about 316°C in heat exchanger E105 (methanator effluent) and, if required, by heat exchange with saturated 10.3 MPa steam in the methanator start-up heater E117. It then flows through the methanator where remaining carbon oxides react with hydrogen over a nickel catalyst to form methane and water. Residual carbon oxides in the methanator effluent are less than 10 ppm vol.

In preparation for drying the effluent is cooled by heat exchange with methanator feed (E105), air (E106) and finally with ammonia refrigerant (E107). Condensed water in the cooled gas is removed in a knockout drum V102 and sent to the process condensate stripper. The gas from this drum goes to the driers in the cold box.



The methanator, its feed-effluent exchanger and the related piping are designed mechanically for an operating temperature of 425° C. This provides an extra margin to protect the unit from upsets in the CO₂ removal system. It also makes it possible to operate the plant at reduced throughput when the low temperature shift converter is out of service.

Drying

Most of the water in the methanator effluent is removed in the knockout drum V102 following the chiller E107. The temperature of this stream is set to remove as much water as possible without freezing in the methanator effluent chiller.

The chilled gas from the knockout drum V102 goes to a drier containing solid desiccants sized to remove ammonia, residual carbon dioxide, and water in a 24 hour drying cycle. Dry waste gas from the purifier is used for both regeneration heating and cooling.

The regeneration facilities are designed for a 12 hour cycle to provide a comfortable safety margin. Before the purifier is in operation, it is possible to regenerate the driers with gas from the drier effluent.

Cryogenic Purification

Drier effluent is cooled to about minus 130°C in the cryogenic purifier by heat exchange with the purified syngas and purifier waste gas. It then flows through a turboexpander where energy is removed to develop the net refrigeration required for the cryogenic unit. The expander effluent is further cooled and partially condensed by exchange to minus 175°C and then enters the rectifier column.

Essentially all the methane and 60% of the argon coming to the purifier is removed along with the excess nitrogen as rectifier bottoms. About half of the 10 ppmv or less of carbon monoxide is also removed. The partially evaporated liquid leaving the rectifier overhead condenser is reheated and vaporised by exchange with purifier feed and then leaves as purifier waste gas. About 30% of the waste gas is used to regenerate the syngas drier and then flows to reformer fuel. The remaining waste gas is compressed in a waste gas compressor for use as gas turbine fuel.

The purified 3 to 1 hydrogen to nitrogen ratio syngas from the top of the rectifier overhead condenser tubes is reheated by exchange with purifier feed to about plus 2° C and flows to the syngas compressor C102 suction.



Compression C102

The purified syngas at about 2.3 MPa is compressed in three stages with two air-cooled inter-coolers E118/119. Recycle gas at about 16.3 MPa is added to the syngas at the third stage. The combined gas leaves the compressor at about 17.6 MPa and flows directly to the ammonia synthesis converter R106 after preheating.

Ammonia Synthesis

Ammonia is produced in two fixed-bed converters R105/6 arranged in series with inter-cooling. Both converters contain conventional, promoted iron ammonia synthesis catalyst. Combined feed gas from the syngas compressor C102 is preheated by exchange with the first and second converter effluents and is fed to the first converter R105. The effluent from the first converter R105 is cooled by heat exchange with its feed gas and goes to the second converter R106. The effluent from the second converter R106 contains about 16 mole % ammonia.

Converter Effluent Cooling

Heat is recovered from the converter effluent by generating 10.3 MPa steam, and then by converter feed preheat. The effluent is then cooled to about 30°C with an air-cooled converter effluent condenser E111. Ammonia condensation begins in this cooler at about 42°C . The effluent is then cooled to about 24°C by heat exchange with recycle gas in E120 and then to about 4°C by two stages of refrigerant chilling in E112/-113. The resulting liquid ammonia product is recovered in the high pressure separator V103 and is then let down to about 3.5 MPa in the letdown drum V104.

Inerts

The total inert gas in the fresh syngas entering the syngas compressor is only about 0.28 mole %. This is essentially all argon and helium. About 16% of the inerts in the syngas feed entering the synthesis loop dissolves in the ammonia leaving the primary separator V103. The rest is purged continuously in a small stream representing about 4% of the syngas feed. About 70% of the dissolved gases are flashed off in the letdown drum V104, and together with the purge stream are sent to the ammonia scrubbing and stripping unit for ammonia recovery.

Refrigeration And Product Separation

Ammonia is condensed from the converter effluent stream by chilling at two levels, 12°C and 2°C , with ammonia refrigerant. The plant is designed to produce all of the ammonia as anhydrous liquid at -33°C . It will also produce warm liquid and warm vapour as required.

The ammonia compressor supplies the cooling for the ammonia product as well as the cooling requirements of the ammonia process. The compressor is a two-case, steam turbine-driven machine with intermediate feeds. The ammonia vapour is ultimately compressed to about 1.5 MPa. The compressed ammonia is condensed in an air-cooled ammonia condenser and then flows to the warm section of the refrigeration accumulator.

The cold liquid ammonia from the refrigeration accumulator is used as refrigerant for the high-level chiller. During normal operation, liquid ammonia product at about 20° C is drawn from the warm end of the refrigeration accumulator for direct feed to the urea plant.

Steam System

The steam system operates at four pressure levels. They are 10.0 MPa, 4.0 MPa, 3.6 MPa and 400/450 kPa. Steam is generated at 10.3 MPa using ammonia plant process heat recovery. It is then superheated to 500° C in the secondary reformer effluent steam superheater exchanger and in the convection section of the primary reformer. This supplies all of the steam requirements of the ammonia plant, the power requirements of the CO_2 compressor and any excess of steam will generate electric power. Steam is available from during plant start-ups from an on-site start-up boiler.

3.3.3 UREA MANUFACTURE

General

Urea is produced from liquid ammonia and gaseous carbon dioxide at about $170-190^{\circ}$ C and 13.5-14.5 MPa according to the following reactions:

$$2 \text{ NH}_{3} + \text{CO}_{2} = \text{NH}_{2} \text{ CO}_{2} \text{ NH}_{4} + \text{H}_{2} \text{O}$$
 (1)

In the first reaction the carbon dioxide is converted into ammonium carbamate; the reaction is fast and exothermic.

In the second reaction the ammonium carbamate decomposes to form urea and water. This second reaction is slow and endothermic. About 60% conversion of CO_2 into urea is obtained.

The reaction mixture then flows to a series of decomposers where the pressure is reduced and unconverted ammonium carbamate is decomposed by heat. The resulting ammonia and carbon dioxide, as well as the excess of ammonia originally charged, are ultimately recycled.

The urea solution is concentrated by flash evaporation and pumped to the granulation section where solid granules are produced in a fluidized bed.

SALE VERTICAL

Urea plant production will be 1,300 tonnes per day.

Urea Process Plant Description

$\mathrm{NH_3}$ and $\mathrm{CO_2}$ Compression

Ammonia liquid (NH $_3$) is pumped from the battery limits to the urea plant HP pump, P-201, through the preheater, E-202, in which the NH $_3$ is heated to approximately 60°C with waste heat.

The NH $_3$ is pressured to about 17.0 MPa and is delivered to the HP carbamate condenser, E-207, via the HP ejector, J-201.

Off-plot carbon dioxide (CO $_2$) flows together with air into centrifugal CO $_2$ compressor C-201 where the pressure of the CO $_2$ mix is raised to about 14.5 MPa.

The hydrogen present in the ${\rm CO}_2$ mix is reduced by catalytic combustion to a concentration of less than 100 ppmv; the catalyst used consists of platinum on a carrier. Part of the air is used for this catalytic combustion, the remainder is necessary for maintaining an oxidising atmosphere in the synthesis and high pressure recovery equipment for protection against corrosion. The dehydrogenised ${\rm CO}_2$ mix is cooled down to $120^{\rm O}{\rm C}$ and fed to the bottom of the HP stripper E206. This dehydrogenisation has the advantage that the off-gases contain so little hydrogen that they are well outside the explosion limits of hydrogen-air mixtures.

Synthesis and High Pressure Recovery

The ${\rm CO}_2$ gas mix flows to the HP stripper, E206, a falling film type shell and tube heat exchanger, where it flows counter-currently against the reaction mixture leaving the urea reactor, R202.

Unreacted NH $_3$ is stripped from the reaction mixture and some decomposition of carbamate (to NH $_3$ + CO $_2$) takes place in E206. Stripped solution then flows to the recirculation section for further removal of NH $_3$ and carbamate.

Stripper overhead vapours flow to the HP condenser E207 where they mix with ammonia feed and the carbamate forming reaction takes place. Heat liberated by the reaction is used to generate L.P. steam in E207, and the pressure on the shell (steam) side is used to control the degree of carbamate conversion.



The condensed and remaining non-condensed ammonia and carbon dioxide flows to the bottom of the reactor R202 where the conversion of carbamate into urea takes place. The reactor volume provides sufficient residence time to approach equilibrium. The heat required for the conversion as well as that needed for raising the temperature of the solution in the reactor is supplied by further reaction of NH $_3$ and CO $_2$ to form carbamate.

To improve the contact between the gaseous and the liquid phases and to avoid backmixing, 10 sieve strays are installed.

The reaction mixture descends through the downcomers to the stripper E206; the inerts introduced with the carbon dioxide and the non-converted NH $_3$ and CO $_2$ leave the reactor via an overhead line to the HP scrubber, E-208. The HP scrubber comprises a shell and tube heat exchanger in the lower part and a packed bed in the upper part.

In the lower part of the HP scrubber the majority of the NH $_3$ and CO $_2$ reacts to form carbamate, the heat of reaction being removed by tempered cooling water.

In the upper part of the HP scrubber the gases leaving the bottom section are counter-currently contacted with the carbamate solution pumped from the recirculation section. The gases (containing N $_2$ and O $_2$ and insignificant concentrations of NH $_3$ and CO $_2$) are purged to the atmosphere via atmospheric inert purge scrubber, T-203.

The tempered cooling water is in turn cooled by the urea solution in the recirculation heater and recycled to the HP scrubber. The condensed carbamate mixed with the carbamate solution flows to the HP ejector J201A/B.

The ammonia feed is at a pressure such that sufficient head is induced in the HP ejector to transfer the carbamate solution from the HP scrubber E208A/B to the HP carbamate condenser E207.

Recirculation

In this section essentially all of the non converted ammonia and carbon dioxide are recovered from the urea/carbamate solution leaving the bottom part of the stripper E206. This solution is expanded to 300 kPa via a level control valve.

As a result of this expansion, part of the carbamate left in the solution decomposes; the required heat is supplied by the solution, resulting in a temperature decrease. The gas-liquid mixture is sprayed onto a bed of pall rings in the rectifier column T201.

The urea-carbamate solution circulates from the bottom part of T201 to heater E-209 where its temperature is raised to $130-135^{\circ}$ C, as a result of which more carbamate is decomposed.

SKE VE STEEL

The heat required is supplied mainly by the tempered cooling water from the HP scrubber, the balance being supplied by LP steam. In the separator (i.e. the base of the rectifying column) the gas is separated from the liquid phase.

The gases flow to the bottom section of the rectifying column to be cooled by the urea-carbamate solution, which will cause part of the water vapour contained in the gases to condense.

The urea solution leaving the bottom part of the rectifying column flows to a flash tank, D-202, via a level control valve.

Together with the gases from the desorption section (T204), the gases leaving the rectifying column flow to the lower section of the LP carbamate condenser E-210. $\rm NH_3/water$ solution from the top part of E210A/B flows to the base of the LP scrubber T-202 where unreacted $\rm NH_3$ gas is scrubbed from the inerts using process condensate, which circulates through T202 via LP scrubber cooler, E-225.

Process condensate is supplied to the LP scrubbing system in order to control the concentration of NH $_3$ and CO $_2$ in the carbamate solution. The pressure is controlled at about 250 kPa.

From the level vessel of the LP carbamate scrubber the concentrated carbamate solution flows to the HP carbamate pump, P-202, where the pressure is raised to about 14.0 MPa and it is recycled to the HP scrubber. The rate of pumping is controlled by the pump speed.

Urea Storage And Evaporation

The solution from the rectifying column T201A/B enters the flash tank D202A/B, where a slight vacuum is maintained by E-215 and the ejector of the 1st-stage evaporator.

Due to this pressure drop a considerable amount of water vapour as well as some ammonia will evaporate from the solution (urea content of about 72%) which then flows into urea storage tank TK-202.

The urea solution transfer pump P-221 transfers the urea solution to the 1st-stage evaporator, E-212A/B, in which it is heated up to 125-130 $^{\circ}$ C under a partial vacuum.

In E212 the concentration of the urea solution is increased to about 95/96%. The temperature of the outgoing solution is automatically controlled by varying the LP steam supply. The liquid-vapour mixture from the 1st-stage heater is separated in D-203. Vapour from this separator is condensed in a 1st-stage evaporation condenser E215A/B.

Urea solution from the 1st-stage evaporation separator D203A/B is pumped to the granulation section.



Urea Granulation

Urea solution at a concentration of about 96% and at a temperature of about 136° C is fed to the granulator.

In order to improve the granulation characteristics of the solution and the handling properties of the urea granules, formaldehyde is added to the urea solution.

The formaldehyde is added in the form of a liquid urea formaldehyde precondensate. This is a product which allows a higher concentration of formaldehyde to be transported and stored as a liquid.

In the granulator, BL 301, solution is sprayed at a pressure of about 300 kPag onto granules suspended in a fluidized bed.

The solution injectors located in the bed require low pressure atomization air supplied by the blower B-302 and heated in the atomization air heater E-301 to above the urea crystallisation temperature.

Ambient air is used as a fluidizing gas, with no dehumidification being required.

Atomization and fluidization air are extracted from the top of the granulator, together with some entrained dust, washed in a wet scrubber T301 and discharged by fan B-305 through a stack.

Urea dust entrained with air amounts for the whole plant to 4.5% of plant production and is recovered as a 45% solution which is recycled to the urea plant. The washing process uses condensate from the urea plant.

The granulated product on the vibrating extractor flows to the fluidized bed cooler BL 302, which uses ambient air supplied by the fluidization fans B-303/4 as cooling medium. Air exhausted from the cooler contains some dust which is washed in a low pressure-drop scrubber T302 and vented through a separate stack.

In the event ambient air is particularly cold or damp the preheater may be used. Similarly if ambient air is particularly warm a chiller can be used.

Urea granules cooled down to the required temperature are lifted by the bucket elevator CR 301 to the screening section F301 A/B where they are separated into three fractions.

Undersize granules are recycled directly to the granulator BL301; oversize granules are first crushed in a roll mill SR 301 and then fed back to the granulator to be used as a seed material to initiate granulation. The on-size fraction is sent to storage.



Granules grow by slow accretion of urea droplets onto the seed material supplied by the crusher. The average droplet diameter being much smaller than the final diameter of the granules, thousands of drops contribute to the build-up of one single granule. The average build-up time of a granule amounts to several minutes.

Product average diameter is controlled by screen sizes and roll mill adjustment. Internal devices (weirs and baffles) are installed in the granulator in order to reduce backmixing; these devices provide a means of adjusting granulator selectivity and to vary the width of the product granulometric curve.

The plant will be designed for fertiliser grade urea (average particle diameter from 2 to 4 mm).

Dust Emission And Recovery

There are three main locations where urea dust laden air is produced

- 1. the granulator BL 301,
- fluid bed cooler BL 203,
- 3. the various dedusting points (i.e. elevator CR 301 top, roll crusher SR 301, screens F301A/B and discharge points on the conveyor belt) which are serviced by the dedusting fan duct.

The air exhausted from BL 301 entrains fine urea dust and is directed to T301 where it is scrubbed with dilute urea solution.

Urea dust is recovered in the scrubber tank and the solution (concentration of around 45% urea) is recycled to the urea synthesis plant.

Urea dust is also recovered in the scrubber T302 from the cooler BL 302 and from the dedusting fan pick-up points.

Waste Water Treatment

Process condensate from the vacuum condenser, E-215, containing NH $_3$, CO $_2$ and urea, is pumped from the NH $_3$ watertank to the first desorber, T204, via the desorber heat exchanger, E-218.

In T204 the bulk of the NH $_3$ and CO $_2$ is stripped off with steam. The stripper overhead stream is condensed and sent to the urea plant and to T204 as reflux.



The stripper bottoms are partly cooled by the incoming stripper feed in E-218 and pumped to the granulation scrubber circuit. Heat required for total evaporation of the waste water is supplied by the granulator air, the evaporator condenser and by a make-up steam heater E-216. The urea solution circulating around the granulator scrubber T-301 is concentrated to about 45% wt of urea and is fed to the urea storage tank TK-202.

3.3.4 REFRIGERATED AMMONIA STORAGE

The proposed ammonia plant is to produce 1,500 tonnes per day of which 750 tonnes will be delivered to the refrigerated storage tank, including about 300 tonnes which will be transferred to the Kwinana Nitrogen Company tank.

The storage tank will have a nominal capacity of 30,000 tonnes and designed for atmospheric storage of ammonia at -33.4°C; the structure will consist of a single steel wall clad with a 75 mm thickness of polyurethane insulation and an outer concrete dyke 600 mm thick to the full height of the tank. A weatherproof cover spans the annular space between the tank and bund wall. This design has the advantage of low maintenance, low heat in-leakage and minimal susceptibility to damage by wind, rain and projectiles. The tank foundations incorporate electric heating elements to prevent ground freezing and causing frost heave.

Foam glass insulation is to be provided underneath the tank floor together with a heating coil. The insulation system is to be designed for a heat leakage rate of 0.04%/day of the tank's contents.

The bottom load bearing insulation system comprises a layer of foam glass blocks installed with a vapour barrier. Laminated timber blocks will be used to transfer the high loads under the tank shell to the foundations.

The tank dimensions are approximately 45 m in diameter with a height of 30.5 m. The self-supporting stiffened domed roof will be designed for a live load of 1.2 kPa. Suspended roof insulation will be 100 mm thick mineral wool.

The tank is to be designed for an internal pressure of 6 kPa and a vacuum of $\emptyset.5$ kPa. The annular space between the outer concrete wall and the steel tank will be covered and sealed with steel plate. This roof is designed to have a weak joint to enable relief of excess pressure generated as a consequence of main tank failure. The temperature within the annulus is expected to be $5-10^{\circ}$ C below ambient. A foam riser system, connected to a portable foam generator, is to be provided.



Temperature and level controls will operate together with vapour detection monitoring of the annulus space. Specific details on instrumentation are not available.

The refrigeration system is specified to condense ammonia vapours generated by heat in-leakage into the tank, cooldown of the export line to the jetty and during tank filling. The system consists of two 100% compressors with air cooled condensers each designed for the normal holding duty. Any non-condensable gases present in the vapours are purged from the condensers.

3.3.5 EXPORT SYSTEM

EXPORT PUMP

Two export pumps are to be installed, both capable of delivering 626 tonnes per hour. Information on pump pressure rating has not been provided; for calculation purposes a pressure of 2,000 kPa has been assumed (this pressure rating will provide conservative results).

The pumps will be controlled from the control room and can be stopped from activation of the load-out Emergency Shut Down (ESD) system. Suction and discharge lines will be fitted with pressure and temperature indicators with remote readings in the control room.

PIPELINE FROM PLANT TO WHARF

Two pipelines are proposed from the plant to wharf i.e. a 250 mm diameter liquid line and a 100 mm diameter vapour line. Each pipeline is approximately 1800 m.

Detailed information on pipeline design is not available at this stage. However, the materials used will be suitable for the operating temperature of -33° C and comply with Australian Standards.

The ammonia export facility is designed to load ships at a rate of 15,000 tonnes per day. Two pumps, each sized for the maximum design pumping rate, are provided. The loading line terminates at a flange on the south pier of the jetty where it can be connected up, via a spool piece, to a trailer mounted ship loading arm. The mobile loading arm is necessary so that there is no interference with normal activities on the jetty while no ammonia export takes place. The export line is provided with an automatic isolating valve at the shore end of the jetty.

A vapour return line is provided from the jetty direct to the tank in order to cool down the export line. The vapour is recompressed by the tank's refrigeration system as required to control storage tank pressure. It is assumed that vapour generated during loading operations will be handled by the compression and liquifaction units on the ships themselves.

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Facilities are also provided to send liquid ammonia directly to the urea plant and to domestic ammonia users via the existing Kwinana Nitrogen Company (KNC) 10,000 metric tonne storage tank and distribution system. The pump is designed for a rate of 45 t/h so that it can satisfy both demands simultaneously. The cold liquid ammonia for the urea plant is heated by an indirect steam heater to 5° C.

Integration with the existing KNC facility is limited to provision of a line for sending product ammonia from the 30,000 tonne ammonia tank to the KNC storage tank and the connection from the new storage tank into the existing distribution system outlined above. Aside from tapping into lines, no other modifications are envisaged to the existing facilities.

The ammonia storage area is served by an ammonia flare to handle intermittent and emergency discharges in a safe and environmentally acceptable manner.

The proponent estimates that both pipelines will be used for approximately 315 hours per year (approximately 200,000 tonnes per year).

MARINE LOADING ARM

Ammonia is to be exported via tankers specially designed for transporting refrigerated product at atmospheric pressure. Approximately 20,000 tonnes of ammonia will be exported per time requiring 9 tanker visits per year. Product will be pumped through a 250 mm diameter insulated pipeline and loaded onto a tanker using a loading arm. It is proposed to use the Kwinana Bulk Cargo Jetty for export of ammonia. The loading arm is to be designed as a mobile unit for relocation and storage back at the plant between tanker visits.

A trailer mounted mobile loading arm is proposed for loading ammonia onto a tanker. The arm is to be designed for a flow rate of 625 tonnes per hour at -33° C. A 250 mm diameter liquid line with a 100 mm diameter vapour return is proposed. The liquid line is to be a solid connection to the tanker's manifold with a hydraulically operated Speed Seal quick connect/disconnect coupling. Isolation valves are proposed at the base of the arm for connection to the wharf pipelines. In addition 38 mm diameter drain valves are to be provided on the liquid line.

The loading is estimated to be operational for 315 hours per year.

3.3.6 NATURAL GAS PIPELINE

Natural gas flows to the plant via a metering station to be located in the neighbouring KNC complex.

The line size is 300 mm N.B. and supply pressure varies from 4 to 5.6 MPa. Methane is the major component (about 87%), the proportion of other gases varying with the degree of upstream LPG removal.

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In the event of a pipeline failure between the metering station and the plant, automatic protection would be given by an excess flow valve at the metering station. Manual protection in the form of block valves at the metering station and battery limits would be used to isolate the gas supply.

There is currently no emergency protection system for the line between the proposed plant metering station and the SECWA Kwinana junction.

However, within the next 12 months SECWA propose to instal a telemetric system linked to their control centre with trip valves located in the Kwinana junction station, so in the event of line failure downstream of the Kwinana junction station a low pressure trip would be activated terminating supply to the plant.



4. FACTORS AFFECTING THE SITE AND RISK TO PUBLIC AND NEARBY FACILITIES

4.1 PROPERTIES OF PROCESS MATERIALS

From reviewing preliminary process information, the following process materials are of interest in this study:

- Ammonia.
- Urea.
- Methane (in natural gas).
- Carbon monoxide.
- Chlorine.
- Urea formaldehyde solution.
- MDEA.
- Various catalysts.

Information relevant to this study on the above process materials is contained in Appendix A.

4.2 POTENTIAL HAZARDS ASSOCIATED WITH AMMONIA AND UREA PLANTS

4.2.1 IN-PLANT HAZARDS

Principal hazards encountered in ammonia and urea plants may be grouped as follows:

- i) Chemical: particularly ammonia and hydrogen (see 4.2.2 below for details).
- ii) Operating Conditions:
 - High pressure (e.g. 17.6 MPa in synthesis converter).
 - High temperature (e.g. 710°C in primary reformer).
 - Low temperature (e.g. -175°C in cryogenic purifier).
- iii) Pressure System Components:
 - Furnaces.
 - Compressors.

The use of high pressure greatly increases the amount of energy available in the plant. In an atmospheric pressure plant stored energy is mainly chemical, but in a high pressure plant there is the additional energy of compressed permanent gases and of fluids kept in the liquid state by pressure, such as ammonia.



High pressures are generally associated with high and/or low temperatures. Although high pressures in themselves do not present serious problems in material specification, the use of extreme temperatures or corrosive products (e.g. carbamate) does.

With high pressure operation the problem of leaks becomes much more serious, as the pressure difference gives rise to a greater fluid loss for a given hole size.

Problems associated with high temperatures in the ammonia plant are:

- creep,
- hydrogen embrittlement.

The above phenomena could lead to tube rupture which could result in leaks/tube fires in the combustion section.

For low temperature operation the potential problems are:

- low temperature embrittlement,
- impurities in the process fluids which may come out of solution as solids (unlikely to be a problem in this complex).

For ammonia and urea plants the materials requirements to handle the above operating conditions are well understood, and covered by the relevant engineering codes and standards.

4.2.2 CHEMICAL HAZARDS

As this preliminary risk analysis is primarily concerned with the impact of the complex on the surrounding environment, discussion of hazardous events will focus on those chemicals which will be present in quantities large enough to cause potential problems outside the site if a release occurs.

Appendix A describes the detailed properties of process materials in the proposed complex: physical and chemical properties and, where relevant, flammability and toxicity data.

The main hazards arise from loss of containment of pressurised gases or liquids (refrigerated or stored under pressure). Resulting vapour clouds mixing with surrounding air may be dangerous, both from the potential environmental effects of the spreading of the materials and also from the possibility of a flammable mixture being ignited.



i) Ammonia

Ammonia is a toxic and also a flammable material. The TLV of ammonia is 25 ppm. Concentrations of about 1700 ppm are dangerous for a half-hour exposure. It can be smelled at a concentration of about 20 ppm.

The flammable range of ammonia is 15-28% vol. in air. The minimum ignition energy is 100 MJ, which is high. Ammonia is flammable, therefore, but not readily so.

Vessels containing liquid ammonia where high release rates would result from failure have the highest potential to cause offsite damage as dense clouds of ammonia vapour may be formed.

As the normal boiling point of ammonia is -33.4°C , it is stored either as a refrigerated liquid at -33°C and slightly above atmospheric pressure or at higher temperatures and correspondingly higher pressures. At the proposed Kwinana plant bulk storage will be in an atmospheric pressure 30,000 tonne refrigerated vessel. Liquid ammonia will also be present at various combinations of pressure and temperature in the refrigeration section and at other intermediate stages of the process plants e.g. V418, the high level chiller, contains the highest on-site liquid inventory of 12.3 tonnes.

Sections of the process where ammonia is present as vapour are also examined, although the quantities are generally small compared with liquid inventories and releases are likely to be less dense.

In section 5.2 various possible ammonia release events are considered and in subsequent sections the likely behaviour of resultant vapour clouds is described and modelled as part of the consequence and risk level assessment.

Ammonia is fully miscible with water. This creates the hazard that if there is water in a vessel containing ammonia vapour, the latter may dissolve, so that a vacuum is formed and the vessel collapses inwards.

Materials of construction for ammonia depend on the operating temperature. While mild steel may be used at ambient temperatures, special steels are necessary at low temperatures to avoid embrittlement.



Ammonia is corrosive even in trace amounts to copper, zinc, silver and many of their alloys. It is necessary, therefore, in handling ammonia to avoid the use of valves and other fittings which contain these metals.

Under certain conditions ammonia can react with mercury to form explosive compounds.

Impurities in liquid anhydrous ammonia, such as air or carbon dioxide, can cause stress corrosion of carbon steel. This is largely inhibited, however, if the ammonia contains 0.2% water and this water content is therefore specified for some applications. Stress corrosion is also completely inhibited at -33° C.

ii) Methane

Methane is not stored on site but is present as the principal component of the natural gas feed and in (reducing) quantities in the desulphurisation, shift conversion and methanation sections of the ammonia plant.

A release of methane may result in the formation of a dense cloud, as sudden reduction in pressure will result in cooling of the gas and surrounding air. Low pressure or relatively slow release will not involve this cooling, the gas will be lighter than air and will dilute below flammable concentrations more rapidly.

Methane is not toxic except as a simple asphyxiant. It is flammable between 5 and 15% (vol.) in air. When unconfined it is not explosive but it can explode if confined.

iii) Hydrogen and Flammable Mixtures

Hydrogen exists in varying quantities as a component of flammable gas streams throughout the ammonia complex presenting the potential for explosions either internal (resulting from ingress of air) or external (from leaks). The impact of such explosions is likely to be local, however the secondary or domino effects (such as damage to a liquid ammonia vessel) could result in offsite harm.

In the reactor sections of urea plants two explosions are reported to have occurred involving explosions, which were thought to be caused by ignition of hydrogen and oxygen present in the gas streams. No injuries were sustained in these incidents.

iv) Carbon Monoxide

This gas is not present in sufficient amounts to warrant quantification of risk but releases may initiate other unwanted events.

v) Chlorine

Chlorine may be used for water treatment, using sodium hypochlorite, dichloroisocyanate or pure chlorine. If liquid chlorine is used it may possibly be stored in a number of 920 kg pressurised drums for use in water treatment. As chlorine gas is denser than air and toxic at low concentration levels, the consequences of a chlorine release are considered in section 5.4.

vi) Urea-formaldehyde Solution

Urea-formaldehyde solution has a pungent, irritating odour and exposure limits for formaldehyde are low (IDLH = 100 ppm). The planned storage quantity (300 tonne, as a 37% solution) is not particularly hazardous in isolation and a release resulting from a mishap in the process area is unlikely to cause problems offsite.

vii) Urea

Urea will be produced as white granules and stored in storage bins up to 100,000 te and loaded into ships by a conveyor system. As it is a relatively non toxic material and not combustible, it is not considered to present a serious degree of risk to humans on or off site. It may be harmful to aquatic life in high concentrations if a spill into Cockburn Sound from the jetty or from a shipping accident occurs.

A CSBP & Farmers Safety Data Sheet for Urea is included in Appendix A.

viii) MDEA (n-MethylDiEthanolAmine)

Several systems for CO₂ removal from process gas are in use, utilising different chemicals, generally with similar characteristics. A typical example in a system utilising MDEA is described as follows. MDEA will be used for CO₂ removal from process gas. The initial fill is 350 tonne and the annual consumption will be approximately 6 tonne/year, therefore it will not be necessary to maintain large quantities in storage.

Methyldiethanolamine is an alkaline liquid of low oral toxicity, and a moderate irritant to the skin and eyes.

The low vapour pressure of the liquid at ambient temperatures means that hazards due to inhalation or skin contact with the vapour are slight. The alkalinity of mists or droplets may irritate the respiratory tract.

The liquid is believed to present a very low toxic hazard during normal handling operations. However, both gloves and eye protection should be worn.

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DNV.CS 26/05/1987 MDEA may be stored in carbon steel or stainless steel containers, preferably under dry nitrogen to prevent oxidative degradation and colour development. Contact with aluminium, copper, zinc and magnesium alloys should be avoided.

MDEA is flammable. In the event of fire, water, dry chemical powder or carbon dioxide may be used.

ix) Catalysts

I.C.I. Product Safety Data Sheets for process catalysts are included in Appendix A. These substances do not pose any particular hazard during normal operation, although precautionary measures are necessary to minimize dust exposure during handling, particularly for catalysts where nickel compounds are present.

Catalyst	Application	Main Compounds
Catalyst 50-2	Hydrodesulphurisation	Nickel & Molybdenum oxides
Catalyst 32-4	Sulphur removal	Zinc oxide
Catalyst 57-3	NG Steam reforming	Nickel oxide
Catalyst 54-3	Secondary steam reforming	Nickel oxide and aluminium oxide
Catalyst 54-4	Secondary steam reforming	Nickel oxide
Catalyst 15-4,15-	5 High temp. shift catalyst	Iron and chromium oxides
Catalyst 53-1	Low temp. shift catalyst	Copper and zinc oxides
Catalyst 11-3	Methanator catalysts	Nickel oxide
Catalyst 35-4	Ammonia Synthesis catalyst	Magnetite

4.2.3 OPERABILITY HAZARDS

In-plant failures leading to the releases discussed above could be caused by:

- mechanical or material failures,
- utility failures,
- operational mishaps,
- start-up/shut-down mishaps

Detailed treatment of operational failure cases will be covered in hazard and operability (HAZOP) studies carried out when detailed design information and drawings are available. For this preliminary analysis, frequencies of potential hazardous events are estimated using historical failure rates for mechanical or material failures in conjunction with fault trees and event trees (see sections 5.2 and 5.3).



4.2.4 PRODUCT EXPORT

4.2.4.1 Ammonia export

Failure of the ammonia export pipeline will result in the release of refrigerated ammonia on land or water. Similarly, failure of the marine loading arm will spill ammonia on the jetty, ship or water. Spills of ammonia onto the water surface generally do not result in heavy fog-like clouds of ammonia and the resultant ammonia vapours disperse buoyantly, presenting a smaller area of risk. In any case, spills over the water are further removed from population centres and other industrial sites compared with releases on land.

In Sections 5.3 and 5.4 a range of ammonia release scenarios in the ammonia export system are analysed.

4.2.4.2 Urea export

A spill of urea granules from the conveyor export system would present no particular hazard to humans, although if spilled into the sea it would dissolve rapidly and is harmful to aquatic life in high concentrations.

4.2.5 SHIPPING HAZARDS

The number of export ship movements is small (approximately 9/year ammonia and 15/year urea cargos) the likelihood and consequences of a shipping mishap are examined in Section 5.3.7.

4.2.6 OTHER RISK EVENTS

4.2.6.1 Risk from other facilities

The adjacent facilities comprise fertiliser and chemical manufacture and storage, petroleum refining and nickel refining.

Reasonably close proximity between the facilities is desirable for the following reasons:

 integration of interconnected facilities where it is advantageous to minimise pipeline lengths e.g. to KNC and the jetty.



 providing compatible land use within zones where residential or public access is not desirable due to the risk of ammonia release.

However the proximity of adjacent plants should be such that no additional risk due to "domino" effects is created. The risk contours and separation distances for fire, explosion overpressure and missile effects from explosion indicate that with the proposed site arrangements, risks of domino effects are so low as to be negligible.

The proximity of the B.P. Refinery, KNC plant and CSBP plant has been reviewed and our conclusion is that risks to and from the proposed ammonia/urea plant are below the guideline risk levels of 50×10^{-6} per year for adjacent industry.

In particular the major offsite risks to industry from the refinery are heat flux and explosion overpressure for which the proposed separation distances and design standards are adequate to avoid domino effects.

While theoretically the proximity of the KNC plant and CSBP fertiliser storage is close enough for missile damage in the event of major explosion, such an event is assessed as being of extremely low probability with the risk of serious damage to any critical plant being non-credible i.e. less than 10^{-0} per year. Such low risks are not overlooked in the study but are considered in the failure frequencies applied in the risk analysis.

In the event of fire or toxic gas release from adjacent facilities there will be provision for evacuation of personnel in the plant either to safe indoor locations or to offsite areas until it is safe to return to the plant. If necessary the plant will be shut down to avoid unsafe conditions (refer section 4.3.4.).

Other industries in the vicinity of the plant have been considered for possible risks to the plant and found to be of adequate separation to minimise any risk.

4.2.6.2 Aircraft risks

Commercial aircraft are not allowed to fly over the Kwinana area, therefore aircraft risk to the proposed ammonia urea plant is negligible. Small aircraft may occasionally fly over the site and could present a crash risk. The resulting frequency of this event is likely to be very small and is considered not to present a significant increase in risk levels to the plant.

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4.2.6.3 Vehicle impact

Vehicle impact to plant equipment or export pipeline could cause damage resulting in the release of chemicals.

The design and layout of the plant will provide protection against damage and avoid the placement of equipment in vulnerable positions where impacts from vehicles could occur. The final plant design should be examined to ensure that the potential for damage from vehicle impact is minimised.

The export pipeline will be shielded with barriers wherever there is a potential for vehicle damage.

4.2.6.4 Earthquake

From reviewing Australian Standard 212-1979, the area where the plant is to be located is classified as Zone A. In accordance with recommended practice, the plant will be designed to a higher standard than required for normal structures.

4.2.6.5 Sabotage/wilful damage

We do not attempt to quantify the probability of sabotage or wilful damage to the proposed plant. However security measures will be provided at the plant including fencing and security patrols. During ship loading the export pipeline will also be regularly inspected.

4.3 REVIEW OF OPERATING PHILOSOPHY AND SAFETY MANAGEMENT

4.3.1 NORMAL AMMONIA/UREA PLANT OPERATION

The plant will be operated via a centralised computer control system from which all process parameters can be monitored. Alarms will be highlighted immediately on this system allowing the operator to take corrective action or shutdown the plant. Additional instrumentation will shutdown the plant automatically via the interlock system should conditions develop which present a risk to process equipment or operating personnel.

Operating the plant under normal conditions involves very little manual work. Instrument readings not available in the control room will be checked regularly and corrective action taken.



4.3.2 AMMONIA PLANT OPERATIONS

Normal Start-up

To start the plant it has to first be purged free of oxygen. Nitrogen is used for this, and the plant is heated to near reaction temperature by circulating nitrogen through catalyst beds and other process equipment.

The catalysts are delivered in an oxidised state and must be reduced by hydrogen before use. The reduction is by a strict and careful procedure. The reduction involves primary and secondary reformer, high and low temperature shift, methanation and ammonia synthesis catalysts.

Heating up of process equipment will include firing of the primary reformer and the steam systems with natural gas.

Natural gas and steam are let into the process plant, and the catalysed reactions start. Shortly afterwards the process air compressor is started and air let into the process in the secondary reformed. The oxygen will be burned completely and the production of steam by the process boilers will increase.

The plant will be maintained at 40 to 50% load and the process gas is flared until the proper analyses are obtained in order to allow the ammonia synthesis section to be brought on-line. The ammonia synthesis compressor, driven by a steam turbine, can now be started. At the proper synthesis catalyst temperature the process gas is let into the ammonia synthesis loop. Synthesis loop pressure and temperature are increased and the synthesis reaction starts. As more process gas is routed to the ammonia synthesis the flaring will be reduced and eventually stopped normally about 12 hours from the admission of natural gas to the process plant.

Front end input of feedstock is increased and balanced with ammonia production up to the desired production level.

Total start-up time with unreduced catalysts will normally be approximately 3 days. After shorter shutdowns when air is not let into the process equipment, start up time will be less than two days.

Normal Shutdown

To shut the plant down, feedstock load is reduced to a minimum (about 40% load) set by secondary reformer burner temperature and synthesis reactor temperature. The synthesis gas compressor is stopped and the process gas flared. The reformer firing is reduced accordingly to reduce steam production and process gas temperatures. The process air compressor is stopped and the process gas temperatures and feedstock are further reduced.



When temperatures are down to a minimum for catalyst operation, natural gas feedstock is shut off, and flaring stops.

The process is purged with steam for a short period and then shut off.

Nitrogen is then let in to purge the catalysts and process equipment of water vapour and traces of process gas. A normal shutdown takes approximately 6 hours.

If any of the catalyst reactors have to be entered, they have to be cooled down. Depending on catalyst volume, this may add another 6 to 24 hours to the shutdown time.

4.3.3 UREA PLANT START-UP, OPERATING AND SHUTDOWN PROCEDURES

Prior to start of the urea plant the equipment is purged free from oxygen. The vessels are then filled up with water to normal liquid operation levels and water is circulated through the plant. Ammonia and carbon dioxide are drawn from the ammonia plant, compressed and fed to the urea plant. Steam is admitted to heat up the reactants and production commences.

Some important protective measures are taken to safeguard the plant equipment and to reduce risk during operation.

The carbamate solution present in the high pressure part of the plant is corrosive. In order to protect the equipment a small quantity of air (oxygen) is fed into the carbon dioxide gas. In order to prevent oxygen and hydrogen forming an explosive mixture in the inert purger, a catalytic system for hydrogen removal from carbon dioxide gas is incorporated. This has been in operation successfully since 1978 in other such plants.

Small quantities of hydrogen present in the feed gas are removed down to less than 100 ppm (vol) and the hydrogen content of the gas flowing from the catalytic reactor is continuously monitored. The remaining air and some ammonia and carbon dioxide is purged from an inert purger at the top of the urea reactor.

The inerts purge scrubber T203 (see Urea Plant Description 3.3.3) is designed in such a way that in the unlikely event of an explosive gas mixture (hydrogen and oxygen) forming and igniting only relatively cheap internal components would be damaged. The explosion energy would be dissipated with no external damage occurring.

Several operators of similar plants experienced explosions in the scrubber prior to the introduction of the catalytic hydrogen removal process. The process designers state that since this time (1978) they know of only one incident in which the scrubber internals were damaged, causing a downtime of several days for repair.



Proper materials are selected for the urea synthesis loop to guard against carbamate solution corrosion. High quality stainless steels used for construction are maintained in a "passive" or un-reactive state by maintaining an oxidizing atmosphere through the addition of air, as noted above.

The operation of the plant can be fully controlled from the central control room. Three main parameters are monitored and controlled:

- Ammonia/Carbon dioxide ratio
- Pressure
- Stripping efficiency

The start-up time is about 3 hours from admitting ammonia and carbon dioxide to the plant.

For shorter disruptions of the process (up to 24 hours) the plant can be "blocked in". That means that the synthesis section of the plant is left under pressure after ammonia and carbon dioxide supply have been shut off. This allows easy and short restart to take place without having to drain the carbon dioxide, which has to be done if longer shutdowns are envisaged.

Normal shutdown procedure includes stopping ammonia and carbon dioxide feed to the plant and decomposing the ammonia carbamate solution into ammonia and carbon dioxide. The ammonia is condensed and kept in an ammonia tank in the plant or returned to the ammonia storage. The plant is put on water circulation and purged free of any process gases. The urea solution already formed is kept in a urea solution tank.

4.3.4 EMERGENCY SHUTDOWN AND INTERLOCK SYSTEM

The plants, being dependent on high and regular throughput, will be highly instrumented and computer controlled. Further the plants will be equipped with interlock systems which upon initiation from carefully selected process or equipment performance criteria will ensure a safe emergency shutdown of the plant.

All such essential input signals to the interlock system will be based on a 2 out of 3 voting system which ensures that failure in the instruments themselves should not lead to unnecessary shutdowns and on the other hand that any real situation is dealt with properly.

The instrument system itself will have a power supply independent from the regular supply (via batteries). The control of shut off valves will have a fail safe action system (open or closed) according to the emergency shutdown plant.



The automatic emergency shutdown by the interlock system only goes into action if the operators of the plants are not reacting to or do not have the time to react to the pre-alarms on process or equipment signals coming to the control room.

The philosophy for the automatic or manual shutdown procedure is developed based on maximum safety of the operators and equipment and the minimum disturbance to the environment.

Detailed procedures will be developed and written for those situation.

4.3.5 ENGINEERING AND OPERATING PHILOSOPHY

The operational philosophy and the incorporation of safety features of the plants start with the selection of technologies to be used in the production of urea and ammonia. For both products there exist well proven technologies from a range of suppliers. The final choice of one supplier above another is to be determined on the basis of site specific requirements as well as commercial reasons.

The detailed design of the plants will incorporate the extensive knowledge of both CSBP and Norsk Hydro to this type of process industry as well to Australian industrial operations. In the design phase major emphasis will be placed on the following areas:

- material specifications,
- operability of the plant,
- hazard and operability studies,
- plant and project outlay,
- approval of potential vendors for equipment and material.

In the procurement and construction phase, close attention will be paid to the quality control systems both in vendors equipment fabrication as well as in the construction of the plant itself.

The commissioning and operational phase is preceded by recruitment and training of operators and staff both for operation and maintenance of the plant. Both theoretical and practical training courses will be given by experienced staff.

Detailed operational and maintenance procedures will be developed for use in the training and the operational phase.

The pre-commissioning and commissioning phases will include cleaning and testing of all parts of the plants, then part systems and finally the whole plant based on the philosophy that all parts and systems have to be tested to conditions similar to operation conditions prior to actual operation. For the initial operation phase some critical positions in the plant organisation will be doubled with experienced personnel (if those are not to be found locally).

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In the actual operation of the plant emphasis will be put on continuous training of the operators in understanding and handling the plant in all situations. Particular exercises will be combined with planned start up and shutdown situations.

The maintenance of the plants is another important aspect influencing the operation philosophy and safety features. The operation of the project includes handling of both flammable and toxic gases at elevated temperatures and pressures. It is a major task for both the operation and maintenance personnel to keep a close watch on any potential leaks of gas or liquids or equipment malfunctions which might lead to hazardous situations.

To assist in this task the plants will be equipped with gas monitoring systems and equipment condition monitors either permanently installed in specific places or as part of a mobile surveillance routine.

Any abnormal operating circumstances will be recorded and dealt with in a proper manner which might vary from immediate shutdown to corrective maintenance actions whilst operating. Again routines/instructions for dealing with those situations are described in operational and maintenance manuals which are part of the training programmes.

Other specific safety features not included in the above description the following are:

- Nitrogen supply system

Nitrogen is utilised to purge the process plants free from any flammable gas and must be readily available. The plant will have a continuous supply from a nitrogen gas distribution system in the Kwinana region as well as from a plant storage of liquid nitrogen equipped with separate evaporator capacity to ensure safe and quick handling of hazardous developments in the plant.

- Fire water system

The plant will be equipped with a separate fire main system with permanent hydrants situated at selected spots around the plant area together with foam generators in areas of the plant where ammonia leaks can occur.

This fire main will be supplied directly from production bores backed up by the public water supply system in the Kwinana region.



4.3.6 MANAGEMENT STRUCTURE

The Project will have an independent organisation for the operation and maintenance of the plant backed up by a Management Agreement with CSBP & Farmers Ltd. and a Technical and General Assistance Agreement with Norsk Hydro a.s.

In the setting up and operation of this structure the Project will be able to draw on the extensive experience of both companies in relation to management of operations in the Kwinana region and that of operation of the ammonia/urea industry in particular.

This will include setting of policies in the following areas:

- industrial relations,
- safety and health,
- recruitment and training,
- public relations,
- environmental control.

4.3.7 OPERATIONS AND MAINTENANCE SAFETY PROCEDURES

In the Kwinana region there are at present two ammonia plants, one of which is operated by CSBP, and the Project should benefit from drawing on the existing operation and maintenance experience. In addition, the Norsk Hydro group operates a number of modern plants in Europe and elsewhere and has within its organisation a wealth of experience which will be made available to the Project as required.

In the recruitment and manning schedules drawn up for the Project's operating organisation, the time and sequence are directed by the need to train recruited personnel properly prior to the commissioning. The training of senior personnel (including the shift supervisor level) is intended partly to be conducted in licensors plants, partly in Norsk Hydro plants and also on site with qualified instructors.

It is intended that the operating staff will be trained initially by the senior operating personnel using a physical model of the plant as well as detailed operation and maintenance instructions. The operating and maintenance instructions will be developed especially for the plants and take into account all details required to operate the plants including start up, normal operation, normal shutdown and all emergencies. Although standardised, the instructions will need to take into account the detailed design features and the installed equipment specifications. The training will be repeated at planned intervals to ensure that all personnel are fully familiar with the operations.



Maintenance procedures are an important aspect of safe plant operation. Specific routines and controls will be developed for all types of maintenance operation to be carried out in the plants. They will involve the use of written work permits for each job where all safety procedures will be specified and how they are to be controlled, actual work to be done and how the item attended to is to be tested before recommissioning.

When alterations to existing equipment or installation are suggested, detailed check procedures on the design, including hazard and operability analysis, will be performed and approved before requisitions are issued for the work.

This particular procedure is required to ensure that safety standards set by the hazard and operability analysis carried out in the detailed design phase of the plant are maintained.

The routines on the plant and equipment checks, which will be carried out both continuously by the operators and periodically by the plant inspectors, will ensure that any unsafe or environmentally unacceptable leak or operating condition is detected and corrected. It is the plant management's clear responsibility to ensure that all agreed routines are carried out and to make all personnel (including outside contractors working at site) aware of all the operational and personnel safety requirements on the site. Such requirements include familiarisation with and adherence to all operational, safety and work routines as well as personal safety requirements.

First aid facilities will be maintained on site with the assistance of a trained nurse. The close proximity to the existing CSBP & Farmers operations makes it logical to combine the two site requirements and thereby strengthen the total coverage.

4.3.8 EMERGENCY PROCEDURES

Apart from the emergency procedures worked out for the specific operational requirements, prior to the commissioning of the plants, procedures will be developed to cover the requirements of the site.

These will include the following items:

- definition of emergencies (e.g. fire, gas leaks),
- organisation of emergency control teams,
- escape routes and assembly points for personnel,
- liaison requirements with local and State authorities,
 SECWA and the general public,
- warnings to fire brigades and hospitals.

Prior to the implementation of these procedures they will be submitted to all relevant public authorities and nearby industrial operations for comments. Copies of the procedures will be made available to all bodies affected.

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5. RISK ASSESSMENT

5.1 METHODOLOGY

The methodology adopted for the study followed the usual procedure for risk analysis of hazardous installations, as follows:

- a) Hazard identification using engineering knowledge, experience and systematic review of proposed plant process and operations.
- b) Risk estimation including assessment of probability or frequency of release events and their various consequences and assessment of those consequences in terms of impact and areas affected.
- c) Risk assessment in terms of both frequency (or likelihood) of occurrence and the impact resulting as compared with criteria of acceptability.

The criteria adopted are those proposed by the EPA which relate closely to those adopted in NSW, U.K. and Europe. The risk assessment utilizes risk contouring of the cumulative risks from the project to indicate risk levels within land use zones, particularly residential areas, public access areas and neighbouring industrial sites.

d) Conclusions developed to report the significance of risk levels and particular risk events. The conclusions address the study objectives, review the adequacy of the proposal and will form a basis for further examination as the project details are finalised.

Recommendations as to appropriate risk reduction or control measures are also evaluated and developed in the course of the study.

5.2 IDENTIFICATION OF POTENTIAL HAZARDOUS EVENTS

Table 5.2.1 identifies potential hazardous events which will be subject to consequence analysis.

As stated in Section 4.2, the main hazards in the complex arise from loss of containment of chemicals which may form dangerous vapour clouds.



Releases of ammonia are the most serious hazardous events and a number of possible release quantities are treated in some detail in Section 5.4, Consequences of Hazardous Events. Clearly it is not possible to consider every combination of failure mechanism and release rate/spill size for each vessel containing ammonia, therefore on-plot vessels are chosen with inventory sizes of at least 1 tonne of ammonia and consequence calculations performed for a major leak and catastrophic rupture.

Tables 5.2.2 and 5.2.3 list all the vessels containing ammonia inventories of more than one tonne in the complex.

Also considered are events leading to ammonia releases in the off-plot areas: refrigerated storage tank mishaps, ammonia export and shiploading systems, and shipping.

Failure of the natural gas pipeline is considered and releases of chlorine gas are examined as events which may cause off site harm.

5.3 ESTIMATION OF LIKELIHOOD OF HAZARDOUS EVENTS

5.3.1 FAILURE RATE DATA

After identification of hazardous events resulting from leakage sources, it is necessary to provide an indication of the frequencies of occurrence per year.

Spill frequencies are estimated by evaluating the proposed design concept, and using reported incident statistics and/or fault tree analysis, to develop failure rates for the respective equipment items and systems. The base equipment failure rate data used in this study are presented in table 5.3.1.

5.3.2 PROCESS AREA

The following chemical release events were analysed in the process area:

- i) Rupture and major leak from 5 vessels containing more than 1 tonne of ammonia at various combinations of pressure and temperature.
- ii) Rupture of a 1 tonne vessel of warm, pressurised ammonia forming a dense cloud of dense ammonia vapour. This case is a conservative representation of a small vessel failure not covered in i) above.



TABLE 5.2.1: Potential Hazardous Events Examined in Risk Analysis

Location	Event(s)
Natural Gas Feed Line	Major leak or rupture
Ammonia Plant	Major leak or rupture - vessels of warm, pressurised liquid ammonia.
Ammonia Plant	Major leak or rupture - vessels of refrigerated ammonia at -33° C.
Urea Plant	Major leak or rupture - urea reactor system (leading to ammonia release).
Refrigerated Ammonia Storage Tank	Failure of inner steel tank (leading to release of liquid to bunded volume).
Ammonia Export Pump	Major release from pump when operating.
	Valve rupture while pump is operating (including both suction and discharge valves with associated gasket/flange joints between valves and pump).
	Major leak from valve while pump is operating.
Ammonia Pipeline from Plant to Wharf	Major leak or rupture in pipeline.
	Major leak or rupture in ESD operated isolation valve at start of wharf.
Ammonia Marine Loading Arm	Major leak or rupture.
Shipping Channel	 Ship to ship collision. Grounding. Contact damage with fixed structure. Fire/explosion onboard. Tank material failure.
	(Leading to release of ammonia or urea).
Water Treatment Plant	Major leak or rupture in liquid chlorine drum.



TABLE 5.2.2: Ammonia Plant - Ammonia Inventories (greater than 1 tonne)

Equipment or Line Item	% of Ammonia	Temperature °C	Phase Liquid or Vapour	Ammonia Quantity (tonnes)
				·
Primary Separator	100	4.4	Liquid	3
Let Down Drum	100	4	Liquid	3
Refrigeration Accumulator	100	30	Liquid	10.7
Intermediate Flash Drum	100	-13	Liquid	2
Heat Exchanger	100	12	Liquid	12.3
Atmospheric Flash Drum	100	-33	Liquid	4
Heat Exchanger	100	. 12	Liquid	3.7
Atmospheric Storage Tank	100	-33	Liquid	30,000

TABLE 5.2.3: Urea Plant - Ammonia Inventories

Equipment or Line Item	Ammonia %	Temperature °C	Other Major Components	Phase Liquid or Vapour	Ammonia Quantity (Tonnes)
Reactor	38.2	183	CO ₂ , Urea, Water	Liquid	77.0
HP Condenser	47.5	167	CO ₂ , Water	Liquid	9.1
LP Carbamate Condenser	30	109	CO ₂ , Water	Liquid	3.1
NH ₃ Water Tank	4.8	44	Water	Liquid	20.0



- iii) Rupture and major leak from the HP and LP condenser systems in the urea plant to release ammonia vapour.
- iv) Rupture and major leak from the urea synthesis reactor, releasing ammonia vapour.
- v) A full bore rupture and a major leak from the natural gas feed line between the metering station (located at the KNC plant) and the ammonia complex.

Frequencies of occurrence for these events were derived from the base failure rates in Table 5.3.1.

5.3.3 REFRIGERATED AMMONIA STORAGE

Refer to Section 3.3.4 for a full description of the storage tank facilities.

Based on the design information available at this stage, preliminary fault tree evaluations have been undertaken. It is estimated that a major release of vapour from the storage tank is calculated to be less than one chance in fifty thousand years.

5.3.4 EXPORT PUMP

Safety Control Assumptions

The pumps will stop automatically on activation of the Emergency Shutdown (ESD) system. They will be fitted with pressure differential alarms between suction and discharge.

Ammonia vapour detectors will be strategically positioned around the pump and valves and set to operate ESD system at a specific concentration level.

In addition if a no-flow signal is received from flow switches installed on the discharge flow meter, the ESD system will be activated.



TABLE 5.3.1: Failure Rates Used In This Study

Component	Type of Failure	Failure Rates	References
	•		•
Valve	Minor	$1 \times 10^{-6} / \text{hr}$) $1 \times 10^{-8} / \text{hr}$)	
	Major	$1x10^{-8}/hr$)	12
	Rupture	$1x10^{-9}/hr$	
Gasket/Flange	Minor	0.3x10 ⁻⁶ /hr) 1.4x10 ⁻⁸ /hr) 1.5x10 ⁻⁹ /hr)	
Joints	Major	$1.4 \times 10^{-8} / \text{hr}$	12
	Rupture	$1.5 \times 10^{-9} / hr$	
Pipework	Minor	1.6x10 ⁻⁸ /km hr)	
	Major	$5.7 \times 10^{-9} / \text{km hr}$	12
	Rupture	1.6x10 ⁻⁸ /km hr) 5.7x10 ⁻⁹ /km hr) 1.14x10 ⁻⁹ /km hr)	•
Pump	Major release	1.14x10 ⁻⁸ /hr	4
	while pumping	•	
Pressure Vessels	Catastrophic	1x10 ⁻⁵ /yr	12
Turbine	Disc fragments	0.3x10 ⁻⁶ /hr	, 2
Refrigerated	Failure leading	31.9x10 ⁻⁶ /yr	Fault tree
Storage Tank:	to ammonia released		analysis
Full Height	into annulus		
Bund Wall			
Loading Arm	Major Release	11.5x10 ⁻⁶ /yr	Fault tree
-	* .		analysis

Release Events

The following product release events have been evaluated

- major release from pump when operating,
- valve rupture while pump is operating,
- major leak from valves when pumping.

From calculation of the above release events, the risk frequencies are calculated to be:

Major release from pump when operating



Valve rupture while pump is operating (including both suction and discharge valves with associated gasket/flange joints between valves and pump).

One chance in less than six hundred and forty thousand years.

Major leak from valves while pump is operating.

One chance in less than sixty six thousand years.

5.3.5 PIPELINE FROM PLANT TO WHARF

Two pipelines are proposed from the plant to wharf i.e. a 250 mm diameter liquid line and a 100 mm diameter vapour line. Each pipeline is approximately 1800 m.

Safety Control Assumptions

The liquid and vapour lines will include the following safety controls:

- Comprehensive quality assurance programme covering manufacture and installation of pipelines, pipeline supports and valves.
- Valves to be welded to pipework.
- Isolation valves at end of each pipeline which will automatically close on operation of ESD system.
- Pressure monitoring of pipeline during operation for automatic monitoring of pipeline and activating ESD valves on sudden pressure drop.
- Insulation.
- Provision of safety relief valve.
- Pipeline patrol throughout the tanker loading operation.
- Corrosion protection of pipeline.

Release Events

The following release events are being considered for the plant to wharf pipeline:



pipeline failure.

- leakage of isolation valve at start of wharf.

From evaluation of the above release events the following risk frequencies have been calculated.

Pipeline

Major leak or rupture has been calculated to occur at less than once in 250 thousand years.

ESD Operated isolation valve at start of wharf

Major leak or rupture has been calculated to occur at less than once in 280 thousand years.

5.3.6 MARINE LOADING ARM

Safety Control

DnV recommend that the following safety features be incorporated:

- Comprehensive quality assurance programme covering manufacture and installation of loading arm.
- Comprehensive set of procedures covering every aspect of the tanker loading operation.
- All other activity on the wharf ceases throughout tanker loading operations. Only electrical equipment approved for hazardous areas will be permitted to be energised during loading of ammonia. Procedures to warn against and prevent non-approved activities during loading will be implemented.
- Emergency shutdown shore-based system which will automatically activate the Speed Seal emergency release coupling and close the wharf isolation valves.
- All valves to be welded onto pipework.
- Isolation valves at end of liquid line to be automatically closed on operation of ESD system.
- An operator to be stationed at the wharf throughout the entire loading operation.



- Vapour connection to be provided at base of liquid arm. This is purely for pipeline chilling before loading and product evaporation after loading. The tankers to be used will have their own refrigerated system and are capable of handling any vapour generated during loading.

Based on fault tree evaluations of the proposed loading operation, failure event frequencies are calculated to be less than one chance in 70 thousand years.

5.3.7 SHIPPING HAZARDS

Approximately 9 ships per year are to load ammonia and 15 urea ships per year at the bulk cargo berth. Ships using the berth would enter Cockburn Sound. Water depth varies from approximately 19 m to 13.4 m at the berth. An ammonia tanker approaching would be under compulsory pilotage with the assistance of two tugs until it is berthed. The same would apply on departure. It is anticipated that berthing and departure would be during daylight hours only. All ammonia tankers would be under radar surveillance from the Fremantle Port Authority.

Hazardous Events

The following events may lead to tank rupture whilst a vessel is underway to/from the loading berth:

- ship to ship collision,
- grounding,
- contact damage with fixed structure,
- fire/explosion onboard,
- tank material failure.

Each of these is considered below:

Event

Risk Evaluation

Ship to Ship Collision

Ship traffic to/from the berth is in general controlled by the Fremantle Port Authority. Small vessels may not be subject to traffic control, however such vessels will not be restricted by their draught and will for their own safety keep away from the tanker. In any case, such vessels are of a size which will cause minimal damage to a tanker if a collision should occur.



Event

Risk Evaluation

Should the tanker collide with a larger vessel, it is estimated that tank rupture on a gas carrier would occur in 1-5 per cent of all collision incidents.

However, due to the compulsory pilotage and tug assistance and the anticipated restrictions relating to daytime entry, it is calculated the probability for a massive spill due to collision is non-credible, probability of occurrence less than one chance in a million years.

Grounding

The approach to the berth appears not to be a difficult navigational problem.

a result of a occur as Grounding may technical failure onboard (engine failure, steering gear failure, etc.) or as a result of mismanoeuvring (human error such as wrong misunderstandcourse setting due to problems, communication ing/internal incorrect interpretation of wind and sea current effects, erroneous position fixing, etc.).

The event is considered unlikely in view of the navigational controls available and the requirements for compulsory pilotage and tug assistance. Should it occur, it is not likely to cause serious damage to the vessel since the seabed is primarily sand bottom and the speed of the impact would in most cases be low. Thus, we conclude major spills due to grounding are non-credible, i.e. the likelihood of occurrence is less than 1 chance in 3 million years.

Contact Damage

Damage to the tanker due to violent contact with the berth could arise from sudden wind squalls which would cause additional short crested waves and could cause the tanker to approach at too high a speed. Appropriate tug assistance and berth fendering would minimise impact damage, with the major release event considered as non-credible, i.e. the likelihood of occurrence is less than 1 chance in 5 million years.

Event

Risk Evaluation

Fire/Explosion

From failure rate adopted from past accident experience with pressure vessels and the safety record of liquified gas carriers it is assessed that the fire/ explosion frequency resulting in major spills is insignificant whilst manoeuvreing to/from the berth.

Tank Material Failure

From fault tree analysis assessment tank rupture due to tank material failure is set to 1 x 10^{-10} per hour per tank, with gas carriers having 3 cargo tanks on average. Thus, the spill frequency becomes noncredible whilst manoeuvreing the vessel to and from the berth.

None of the events that may occur during ship approach to/departure from berth is considered to constitute a significant level of risk in the area of concern, particularly when compared with the events that could occur at the berth or onshore in the proposed ammonia plant.

5.4 CONSEQUENCES OF HAZARDOUS EVENTS

5.4.1 GENERAL

In Quantitative Risk Analysis it is necessary to estimate the likely hazard distance which results from a failure event. For escapes of compressed or liquified gases mathematical techniques are used to model the behaviour and spread of resultant gas clouds, producing estimates of gas concentration for a range of credible releases and weather conditions. Concentration values are then used to estimate the areas where there is a risk of fire/explosion (in the case of a flammable gas) or where harmful doses of toxic gas could result.

5.4.2 BEHAVIOUR OF AMMONIA RELEASES

It is possible for an ammonia release to form a gas cloud which is heavier than air, despite the fact that pure ammonia vapour is less dense than air at ambient temperature. A heavy gas cloud behaves differently from one of neutral density in several important respects:

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- It spreads upwind as well as downwind.
- It is flatter in shape.
- The mechanisms of mixing with air are different.

Whether or not a particular ammonia release forms a cloud which is heavier than air depends on a number of factors:

- Initial conditions of the gas or liquid (pressure, temperature).
- Nature of the release (failure mechanism).
- Temperature and humidity of ambient air.

Ambient air conditions are important because if the gas is cold it chills the air and causes moisture in the air to condense and form a mist. For this study a conservative (i.e. pessimistic) assumption is made that at least some proportion of any ammonia released will form a dense fog with air, this proportion depending on the nature of the release. A different set of assumptions and calculations for initial cloud characteristics have been applied to the following types of spill:

- i) Refrigerated liquid jet.
- ii) Refrigerated liquid on land.
- iii) Refrigerated liquid on water.
- iv) Pressurised (warm) liquid jet.
- v) Pressurised vapour jet.
- vi) Rupture of pressurised vessel.

For each of these categories the initial density, temperature, composition and geometry of the source can be defined, and an appropriate gas dispersion model used to estimate subsequent behaviour of the vapour cloud or plume.

5.4.3 BEHAVIOUR OF METHANE (NATURAL GAS) RELEASES

Methane, the major constituent of natural gas, is much lighter than air at ambient temperature but the cloud given by cold methane and air may be denser than air. A full bore rupture of the feed gas pipeline would most likely result in jet dispersion producing a buoyant cloud or plume. For a smaller leak jet dispersion may apply or, if the jet momentum is dissipated, a dense vapour cloud may result from thermodynamic effects (chilling of the vapour/air mix). For failures of the natural gas line both dispersal mechanisms are considered in the calculation of hazard distances for flammable mixtures.



For this risk analysis gas supply line failures in the section between the (KNC) metering station and the ammonia urea plant are examined, a line length of about 500 metres. The action of the flow limiting valve and the (future) SECWA shut-off valve will limit the initial gas release to the hold-up in this section of line.

5.4.4 BEHAVIOUR OF CHLORINE RELEASES

At normal temperatures and atmospheric pressure chlorine is a dense (heavier than air gas) with a characteristic pungent odour which can be smelled down to a level of about 3 ppm. It is extremely toxic to humans and acts as a respiratory irritant. Concentrations of 40-50 ppm are dangerous for short-term exposure.

Because it is dense relative to air (relative density = 2.5) chlorine leaks may form dense clouds which flow along the ground before dilution with air leads to buoyant dispersion.

Although chlorine supply and storage details are not yet finalized for this proposal, it is assumed that standard 920 kg liquid chlorine drums would be used to produce chlorine gas for water treatment.

Three main classes of release are considered:

1. Total failure of full cylinder

This is a very unlikely event but the consequences would be potentially disastrous particularly if wind direction is toward the populated areas.

2. Release from pipework, pigtail or valve

Releases in the range $0.01 - 1 \, \text{kg/s}$ even for short duration (up to several minutes) would have serious effects and are evaluated for likelihood of occurrence and resultant risk levels.

3. Minor releases or leaks

Releases in the range of up to say .01 kg/s even for sustained periods are very unlikely to present serious risk at inhabited areas except under exceptionally adverse conditions ie very stable atmosphere with calm to slight breeze.

In this preliminary analysis we consider the first 2 classes which, although less likely than the third, are considered to present the most significant external risk at the site considered.



The basis of release rate calculations are in accordance with usual methods for calculating releases of gas and gas liquids. The release rates apply to initial release conditions and are appropriate for the dispersion calculations and for short term toxic effects to be considered.

5.4.5 GAS DISPERSION MODELS DESCRIPTION

Field experiments on dense gas dispersion and observation of accidental releases have established beyond doubt that the dispersion of dense gases follows a different mechanism from that of neutrally buoyant clouds, therefore mathematical models developed particularly for heavier than air gases must be used in assessing atmospheric dispersal.

Several calculation methods are used by DnV to model dispersion (both dense and buoyant).

i) ARCON 3

ARCON 3 (Air Relative CONcentration) is a DnV in-house computer program for modelling the dispersion of a continuous plume of buoyant vapour. Relative concentrations are calculated using standard Gaussian diffusion parameters for a range of (Pasquill) atmospheric stability categories.

ii) DENZ

DENZ is a computer program for the dispersion calculations of dense toxic or explosive gases in the atmosphere. It was developed by the U.K. Atomic Energy Authority (A.E.A.) and is used for instantaneous or "puff" release cases.

111) CRUNCH

Also developed by the U.K. A.E.A., this program models continuous releases of denser-than-air vapours into the atmosphere.

iv) A number of other short-cut gas dispersion techniques, such as nomograms and data tables applying to individual gases, are used as a back-up for the above programs.

Assumptions of the Heavy Gas Dispersion Models

- The dispersing cloud or plume moves over flat terrain or water.
 - The ground (or water) has constant roughness and thermal properties.

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- There are no obstructions to the wind or moving cloud.
- The contaminant gas undergoes no chemical or physical reaction during dispersion.
- The cloud has a flat top and the concentration of contaminant is uniform across the cloud.

In an instantaneous or "puff" release, the cloud can be expected to adopt a pancake shape and spread radially relative to its centre while simultaneously moving with the wind. This shape has been observed in a number of field experiments. The idealised cloud shape for the model is assumed to be a vertically oriented cylinder with flat-top and of radius R and height H, both of which change as a result of gravity spreading and air entrainment.

In the case of a continuous release, the cloud is a narrow plume which spreads laterally due to gravity. The plume is assumed to be steady and rectangular in cross-section (box) with its axis along the wind direction.

Figure 5.1 illustrates idealised plume/cloud shapes for both models. When specific conditions of cloud spreading and/or cloud concentration are satisfied, the models then treat dispersion as buoyant (or Gaussian).

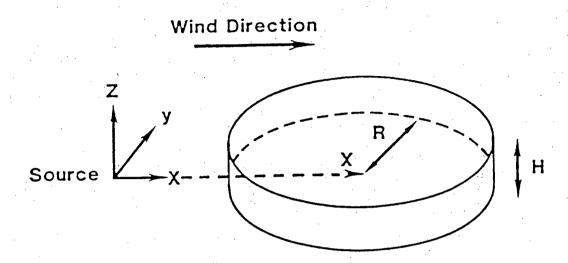
Where there is some doubt about the nature of the release (e.g. whether it is instantaneous or continuous) both DENZ and CRUNCH runs are carried out for the release quantity and the conservative (pessimistic) results taken for hazard distances.

Toxic Gas Dispersion Risk Contour Model Description

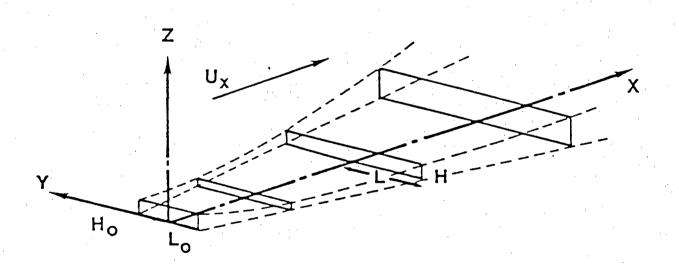
The risk analysis method treats toxic gas dispersion in the following steps:

- 1. Analyse release scenarios to examine the significant factors affecting gas release volumes, conditions, flow rates durations and dynamics.
- 2. Select sets of release conditions and resulting release rates to represent the range of release risk including worst credible release scenario, minor releases and continuous release.
- 3. Select suitable dispersion models for the release conditions including buoyant or dense gas models and instantaneous or continuous release models as most appropriate.





Cloud shape for Instantaneous Release



Cloud shape for Continuous Releases

Figure **5.1** Box model cloud representation



- 4. Analyse meteorological data to determine predominant conditions as well as the most unfavourable (but credible) conditions for consequence calculations over a range of representative classes of conditions.
- 5. From the consequence and dispersion results prepare suites of data for risk contour modelling. The Veritas risk map program utilises gas dispersion information including the shape and dimensions of hazard zones under the various representative classes of meteorological conditions for each release event.
- 6. The dispersion results are ranked and analysed against the meteorological data to provide a basis for determining the meteorological conditions which will produce particular hazard zones and ranges and the resulting frequency of occurrence functions are derived. After analysis of stability, wind speed and direction to confirm suitability of the data for the range of significant gas release scenarios, the meteorogical data is input to the risk map program. The data is represented by wind direction probabilities for sixteen directions and a cumulative probability function for stability and wind speed ranging from the most unfavourable conditions to all conditions.
- 7. In the risk map program each point (usually on a 45 x 60 grid) is checked for proximity to each potential release point and the risk frequency, if any, for exceeding the hazard level is determined and summated. The risk frequency at the point will depend on release frequency, the probability of conditions occurring under which the hazard level would reach the point concerned, and the wind direction probability. The shape of the hazard zone including upwind, downwind and crosswind distances at each grid point is accounted for in the program by cloud hazard zone shapes determined from the gas dispersion results. By utilising the actual hazard zone shapes, more accurate risk levels are determined than by simpler methods used in some other programs.
- 8. Individual risk of fatality is then assessed using the probit equation described in 5.5.2 and 5.5.3 at the risk criteria levels (1 and 10 in a million per year).
- 9. Individual risk contours are then plotted for two levels of lethality as follows:
 - 50%, which is the usual level adopted for fatality risk assessment in the population generally. This level is relevant to an average individual and to the workforce in adjacent industrial areas.
 - 5%, which is a more conservative level being used for risk to the more vulnerable sections of the population in residential areas.



The contours therefore show the expected frequency of a potentially lethal exposure to an individual at greatest risk.

5.4.6 GAS DISPERSION MODEL RESULTS

Ammonia Releases

Table 5.4.6.1. gives DENZ results for a 9840 kg dense cloud of ammonia, one of the release sizes considered in the process plant. The range figure is the calculated maximum downwind distance for a particular concentration level. Three representative weather categories are shown.

Table 5.4.6.2 gives CRUNCH results for two ammonia flow rates and three representative weather categories.

For details on the toxic effects of the ammonia concentrations used see Appendix A. A full discussion of the concentration/time (i.e. dosage) effects of ammonia releases is given in Section 5.5, Assessment of Risk Levels.

TABLE 5.4.6.1: DENZ Results for 9840 kg Ammonia Cloud

Ammonia in Cloud kg	Weather Category		nd Range 1,700 ppm m	500 ppm m
		· · · · · · · · · · · · · · · · · · ·		
9840	В4	413	946	1528
•	D4	492	1119	2680
	F2	551	1344	4285

Note: 10,000 ppm - LC50

1,700 ppm - LC5

500 ppm - IDLH

See Glossary for definitions, and Appendix 1,

Table 1 for further details.



TABLE 5.4.6.2: CRUNCH Results for Continuous Ammonia Releases

Release	Weather Category	10,000 ppm Range	1,700 ppm Range	500 ppm Range
kg/s		, m	m	m
5	. B4	58	194	245
5	D4	215	515	1040
5	F2	356	1060	2230
9.2	В4	26	181	326
9.2	D4	144	352	690
9.2	F2	493	1500	3220

TABLE 5.4.6.3: DENZ Results for 1423 kg Instantaneous Methane Release

Weather	Downwi	nd Range
Category	U.F.L.	L.F.L.
	m	m
D4	34	130
F2	23	111

U.F.L. = Upper Flammable Limit = 15% vol. in air. L.F.L. = Lower Flammable Limit = 5% vol. in air.

Methane Releases

Dispersion calculation results for an instantaneous release of 1423 kg of methane from the plant feed line are given in Table 5.4.6.3. DENZ is used to model the formation of a dense methane/air vapour cloud.

CRUNCH computer runs were carried out for the continuous release of 4.7 kg/sec of methane forming a dense fog. These indicated that the downwind range of the lower flammability limit was less than 80 metres for all weather categories considered.

Both the DENZ and CRUNCH results indicate that even if a dense cloud of methane/air vapour formed from a release (an unlikely occurrence) the downwind ranges for a flammable cloud would be in the order of 100 m or less. These results, combined with the fact that the ignition of a methane cloud is likely to result in a flash fire rather than an explosion, lead to the conclusion that the consequences of a catastrophic failure of the gas feed line would not result in off-site damage.

Chlorine Releases

Note that chlorine dispersion calculations were carried out for three toxic concentrations:

 $LC_{50} = 500$ ppm, IDLH = 50 ppm, TLV = 1 ppm Appendix 1, 4.1 gives further details.

Calculations were performed for three representative weather conditions B3, D4 and F2.

Tables 5.4.6.4/5 summarise the results for the DENZ and CRUNCH runs.

- 1. From Table 5.4.6.4 it can be concluded that in the case of a total failure of a full (920 kg) drum the cloud would travel long distances, even under the most favourable dispersion conditions eg. B3, range is 372 metres at the 500 ppm level.
- 2. CRUNCH results (Table 5.4.6.5) indicate that for the weather categories chosen the 50 ppm level does not stretch beyond the 200 metre range for a 0.3 kg/s release except for stable conditions (F2). However for the higher release rate (0.6 kg/s) the 50 ppm range exceeds 200m for category D4 as well as F2.

TABLE 5.4.6.4: DENZ Results for 920 kg Instantaneous Chlorine Release

Weather Category			Downwind Range 50 ppm 500 ppm	
		· m	m	
7.7			770	
В3		755	372	
D4		1441	688	
F2		3554	1115	



TABLE 5.4.6.5: CRUNCH Results for Continuous Chlorine Releases

Release	Weather Category	500 ppm Range	50 ppm Range	TLV Range
kg/s		, m	m	m
0.3	В3	55	117	614
0.3	D4	68	17Ø	1080
0.3	F2	233	602	5430
Ø.6	В3	78	159	862
0.6	D4	98	242	1588
Ø.6	F2	330	875	8 km

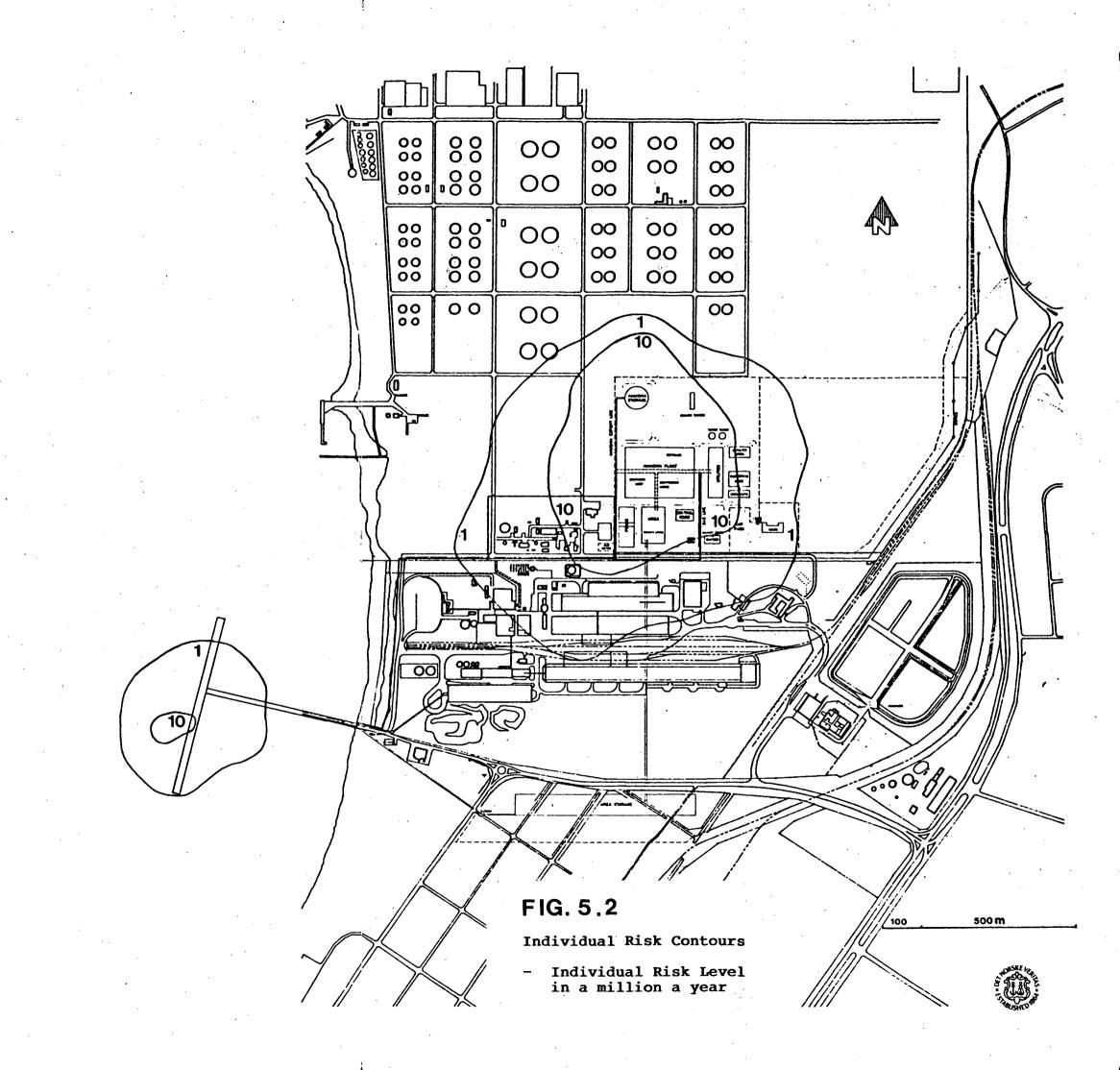
5.5 ASSESSMENT OF RISK LEVELS

5.5.1 INDIVIDUAL RISK CONTOURS

Individual risk contours for toxic gas releases are shown in Figure 5.2. The contours represent the boundaries for risk to an individual in terms of expected frequency of a potentially lethal exposure as follows:

- One event in a million years $(1x10^{-6}$ per year) the guideline level proposed by the EPA below which the risk may be considered acceptable for risk to the public in residential areas.
- Ten events in a million years $(10x10^{-6} \text{ per year})$ the EPA guideline level proposed as unacceptable for risk to the public in residential areas.

As individual susceptibility to toxic gas exposure varies considerably, we have considered a range of lethality and shown an average figure in our analysis.



The contours indicate locations which present a risk to an individual at that point. The actual chance of a person being exposed also depends on the time spent at the location. The contours assume the greatest possible exposure of an individual continuously present 100% outdoors.

In the industrial areas at or above the 1×10^{-6} level, the individual risk (per year) to an employee will be approximately one quarter of the level shown when the normal shift period is taken into account. The majority of people would be expected to survive the exposure to the hazard levels considered, particularly as emergency response actions to avoid inhalation of toxic gas and to provide medical treatment will reduce risks of fatality below the levels stated.

The contours show that the one in a million risk level does not approach residential areas or other areas where individuals at particular risk would be expected to reside or visit frequently for significant periods.

It can be seen from the map that the risk drops rapidly with distance from the main processing plants, the 1×10^{-6} /year boundary is within 250 to 300 m of the plant boundary and the only areas where the 10×10^{-6} /year level is exceeded are within 100 m of the processing plants and in the immediate area of the jetty head and jetty loading point.

5.5.2 TOXIC CRITERIA

Inhalation of toxic gases will have effects ranging from mild irritation to death and the concentrations, effects and exposure periods for ammonia and chlorine are presented in Appendix A.

Toxicity is proportional to both concentration and time of exposure, but the relationship is non-linear. As the level of concentration rises the exposure time for a degree of toxic effect drops rapidly.

Generally the toxic dose is estimated using a formula of the type:

 $L = TC^n$ where L = toxic dose

T = time of exposure

C = concentration

n = constant depending on type of gas.

= 2 - 2.5* for ammonia

= 1.67 - 2.5* for chlorine

* constant used in this study

This formula is used to calculate L by integrating the concentration over the time intervals of exposure. From the heavy gas dispersion model results the cloud concentration profile and velocity are known for a particular downwind position hence, in the case of a DENZ cloud, the toxic dose L is calculated as the cloud, passes over a point, with the peak concentration at the cloud centre.

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A statistical technique called probit analysis is then used to estimate the percentage of the population affected by a particular toxic dose.

The probit number is a measure of the percentage of the population affected, and is calculated using the equation, from reference (4), as follows:

Pr = a + b ln Lwhere a = -30.6b = 1.38 for ammonia

Other probit equation values have been proposed recently (reference 16) which suggest that the lethal concentrations at the LD5 and LD50 levels may be up to 2 to 3 times higher (ie. ammonia is less toxic) than we have assumed. We have conservatively adopted the equation which generally assumes higher toxicity although we concede that this may overestimate the risk.

5.5.3 EXAMPLE OF RISK LEVEL CALCULATION

Toxicity assessment results for a 9840 kg ammonia DENZ cloud at the maximum calculated range for a 10,000 ppm concentration are given in table 5.5.3.1.

From the table it can be seen that in the range of predicted distances (400 to 650 metres) for a 10,000 ppm ammonia concentration the exposure times and dosages are generally not high and the figures for percentage of population seriously affected are mostly below the 1% level.

The worst case is F2, stable, low wind speed conditions and the resultant slow moving cloud would affect 10% of the population i.e. a 10% fatality level. For this weather category the predicted maximum range is 550 metres, and from the risk contour map, the frequency of occurrence of this concentration is less than 0.1x10⁻⁶ per year i.e. less than 1 chance in 10 million per year. It can therefore be concluded that although the consequences of such a cloud reaching 550 metres downwind would be serious, the risk of this happening is negligible. As this is one of the worst cases for dispersion and the range considered does not reach the closest centres of population, the conclusion is that population centres will be exposed to a negligible risk from toxic releases from the proposed plant.



TABLE 5.5.3.1: Toxicity Assessment for 9840 kg Ammonia Cloud

Cat	Cloud Velocity m/min	(1) Cloud Radius m	Dosage ppm ⁿ -min	10,000 ppm Range m	Time	Probit	(2) Population Affected %
B4	240	264	1.3x10 ¹⁰	413	2.1	1.7	<0.1
C5	300	•	1x10 ¹⁰		1.7	1.3	<Ø.1
D4	228	294	1.5x10 ¹⁰	492	2.5	1,9	Ø.1
				499			
E4	210	353	2x10 ¹⁰	649	3.2	2.3	0.5
D8	522	207	5x10 ¹⁰	495	.75	0.4	<0.1
F2	96	457	5.6x10 ¹⁰	551	9.5	3.7	10

⁽¹⁾ To cloud concentration 10,000 ppm.

5.5.4 POSSIBLE INCREASE IN PLANT CAPACITY

Experience has shown that it may be possible to increase the ammonia production rate beyond the 1500 t/d nominal capacity of the plant to about 1750 t/d by debottlenecking during the life of the plant. This, a usual practice within the industry, is essentially fine tuning of the plant following examination of the plant characteristics and performance, and involves minor changes in process parameters.

The effects on risk should be negligible to slight. The maximum adverse effects would be limited to a few increased hazard distances from the process plant of less than 10% and increase in frequency of major releases would vary from nil, for storage and process area, to a maximum of 50% in the case of the export pipeline and ship loading.

These increased levels would remain well below the criteria levels and are considered acceptable.



⁽²⁾ At 10,000 ppm range (max 649 m)
(Note nearest population centre is 3,000 m).

5.6 DISCUSSION OF "ACCEPTABILITY" OF RISK LEVELS

5.6.1 INDIVIDUAL RISK

The proposed category of individual risk level of less than one in a million a year is in line with individual risk levels proposed in planning assessments in other states and recommendations of expert committees and study groups in the U.K., Europe, U.S.A. and Australia as being sufficiently low to be accepted without concern.

The individual risk criteria is one of the most useful criterion for site and preliminary risk assessment. For toxic risk assessment it is necessary to determine the concentrations and times of exposure that will result in risk of fatality. The methods and data adopted in this study are described within the report and are in accordance with generally accepted quantified risk assessment (QRA) procedures.

In this study the individual risk level is assessed and shown by means of risk contours around the facility. It should be observed that levels in residential areas are well below the risk level of one in a million per year. For a cumulative risk level assessment, it is necessary to quantify risk levels from other industries which is beyond the scope of this study. Individual risk levels from the proposed ammonia/urea plant do not reach residential areas even at the level of one in a hundred million per year (1% of the criteria level). In the event of cumulative risk in excess of the criteria it would therefore seem reasonable to look to more significant contributors for risk reduction action.

5.6.2 OTHER RISK FACTORS

Risk levels to centres of population have been examined and due to the distances to residential and other major population centres the risk of fatality in these areas is negligible. In the case of neighbouring industries within the 1×10^{-6} per year risk contour there is a small risk of exposure to accidental release of ammonia for which emergency response procedures will apply. The resulting risk of serious injury or fatality is so small as to be well below that due to other common industrial risks and within criteria levels usually accepted for risk to adjacent facilities from fire or explosion.



6. CONCLUSIONS AND RECOMMENDATIONS

6.1 RISK ASSESSMENT CONCLUSIONS

6.1.1 TOXIC RISK

i) From the risk contour map and calculations of maximum toxic dose it is concluded that the risk of lethal concentrations of ammonia or chlorine gas reaching local population centres is negligible for a range of toxic gas release scenarios. This is the case even for weather conditions most unfavourable to swift dispersion of vapour clouds.

For neighbouring industries within the 1×10^{-6} per year risk contour there is a small risk of exposure to accidental release of ammonia for which emergency response procedures will apply. The resulting risk of serious injury or fatality is small, well below that due to other common industrial risks and within criteria levels usually accepted for risk to adjacent facilities from fire or explosion.

- ii) Urea-formaldehyde risk of toxic exposure beyond the plant boundary is insignificant even with catastrophic failure of the storage tank.
- iii) Urea does not present a toxic risk to humans, although it is harmful to aquatic life in high concentrations.
- iv) Other process materials (catalysts, MDEA, water treatment chemicals) do not pose any particular hazard during normal operation and even if released to the atmosphere, would not cause any harm off site.

6.1.2 EXPLOSION AND FIRE

Natural Gas

Normally methane, the main constituent of natural gas, does not explode on ignition, however if the vapour is in a confined space, as in a furnace, it could explode. If the gas supply line to the ammonia urea plant leaked in such a way as to form a dense hydrocarbon/air vapour cloud (an unlikely mechanism) the predicted downwind concentration of gas would remain in the flammability range only for about 100 metres, after which buoyant dispersion would occur. If the flammable cloud ignited a flash fire rather than explosion would most likely take place, confining any damage to the area covered by the cloud.



It is assumed that furnace safeguard systems will be designed to ensure that the natural gas fuel is shut off by a trip system in the event of a flame out or other furnace failure events.

Hydrogen

From the design information available the impact of any explosion involving hydrogen and flammable mixtures is likely to be local. A catalytic hydrogen removal step will be installed to remove traces of hydrogen from carbon dioxide feed to the urea plant. This will prevent oxygen and hydrogen from forming an explosive mixture in the inert purger of the urea synthesis section, an area where explosions have occurred in the past in similar plants.

Heat flux and explosion overpressure effects do not present a significant risk and damage is likely to be confined within the battery limits of the plant.

6.1.3 STORAGE TANK

As the proposed full height concrete bund will contain any liquid ammonia in the (unlikely) event of a serious leak or rupture of the inner steel tank, boil-off will be limited by the amount of heat which can be absorbed from the surroundings in the annular volume. This will limit the quantity of ammonia vapour released to the atmosphere, and most likely result in a buoyant vapour cloud or stream. Any tank isolation valves should be situated inside the concrete bund in order to guard against uncontrolled release if a valve failure occurred.

To provide early warning of ammonia releases and enable prompt emergency action to minimise vapour emissions (e.g. through the application of foam), vapour detectors should be provided in the annular space.

6.1.4 EXPORT PIPELINE

Failure of the refrigerated ammonia export pipeline from the storage tank to the jetty could result in one of the most serious spillages of ammonia, as the hold-up in the line is of the order of 80 tonnes. The consequences are unlikely to be as far reaching if the spill occurred on water, as rapid boil-off would give rise to a lighter, more rapidly dispersed ammonia vapour cloud. DnV has discussed the routing of the line with the proponents and are satisfied that the line will be adequately protected from outside damage. The nature and positioning of any protection to be provided will be examined in detail at a later stage.



In order to minimize the quantity of ammonia released from a pipeline failure, an isolation valve is to be placed in the pipeline at the start of the wharf.

The resulting risk levels calculated for the loading of an ammonia ship were found to be low and considered acceptable.

6.1.5 SHIP LOADING

The use of a non-dedicated wharf for loading hazardous chemical products presents a few problems which have been analysed in this study. A mobile loading arm, to be transported to the wharf and installed prior to the ship arrival is considered to be satisfactory provided that the design is of an equivalent safety level to fixed installations complying with a comprehensive installation programme and commissioning is prepared and implemented every time the arm is to be used.

Although the concept of a mobile loading arm is considered reasonable, a permanently installed loading arm at the wharf would reduce the potential hazards of transportation and installation and therefore should not be disregarded as an option if found to be feasible.

6.1.6 SHIPPING

Risks from ammonia ships have been analysed together with the Port of Fremantle regulatory requirements. The risks of shipping accident involving a major release of ammonia whilst navigating to and from the bulk cargo wharf were found to be less than one chance in a million years and can be considered acceptable.

6.1.7 GENERAL ITEMS

Operability Hazards

DnV has been informed that the operators of the proposed complex plan to carry out hazard and operability studies at the detailed design phase when process and instrumentation drawings are being finalized.

Emergency Procedures

The operators intend to develop a full set of emergency procedures prior to commissioning of the plants for submission to the relevant public authorities and nearby industrial operations for comments.



6.1.8 RISK TO/FROM ADJACENT FACILITIES

The proximity of the B.P. Refinery, KNC plant and CSBP plant has been reviewed and our conclusion is that risks to and from the proposed ammonia/urea plant are below the risk level of 50×10^{-6} per year which has been used as a guideline for adjacent industry.

In particular the major risks to the plant from the B.P. refinery and vice versa are heat flux and explosion overpressure for which the proposed separation distances and design standards are adequate to avoid domino effects.

While theoretically the proximity of the KNC plant and CSBP fertiliser storage is close enough for missile damage in the event of major explosion, such an event is assessed as being of extremely low probability with the risk of serious damage to any critical plant being noncredible i.e. less than 10^{-6} per year.

6.1.9 CUMULATIVE RISK

A quantified assessment of cumulative risk from all industries in the area is beyond the scope of this study. However, as individual risk levels from the proposed ammonia/urea plant do not reach residential areas even at the level of one in a hundred million per year (1% of the criteria level), it can be stated that the proposed plant would not present a significant contribution to cumulative risk levels at residential areas.

6.1.10 OTHER RISK FACTORS

Residential Areas

The dispersion and toxicity effects of toxic release from the plant have been assessed at concentration levels and dosages capable of causing average lethality to the population exposed.

Even under the most unfavourable atmospheric conditions, concentrations sufficient to cause fatality in exposed people do not reach residential areas. Under the most adverse conditions of maximum credible release, very stable low wind speed and wind directly toward residential areas, the normally recommended procedure of going indoors until the gas emergency has passed would ensure that discomfort and risk of injury was minimised.



Adjacent Industry

In the case of neighbouring industries within the $1x10^{-6}$ per year risk contour there is a small risk of exposure to accidental release of ammonia for which emergency response procedures will apply. The resulting risk of serious injury or fatality is so small as to be well below that due to other common industrial risks and within criteria levels usually accepted for risk to adjacent facilities from fire or explosion.

6.2 DISCUSSION OF SAFETY ASSUMPTIONS

The study has assumed that the following safety measures will be implemented:

- 1. Design to appropriate codes and standards.
- 2. Hazard and operability studies to examine detailed design and operation.
- 3. Check on final design to verify consistency with assumptions made in Risk Analysis.
- 4. Quality Assurance on critical items.
- 5. Commissioning procedures.
- 6. Adequate safety organisation and resources.
- 7. Emergency procedures to be developed.
- 8. Regular safety audits.

6.3 RECOMMENDATIONS

Achievement of the risk levels determined in this study is dependent on a high standard of engineering operation and maintenance. Accordingly, the engineering and operating philosophy, management structure and operations and maintenance safety procedures proposed will need to be developed and implemented effectively.

We recommend that objectives for safety, reliability and quality be developed and approved at an early stage in the project and monitored at a senior level to ensure safety of the plant.



- 2. We recommend that an emergency response plan be developed to provide effective understanding of credible accident scenarios within the plant and adjacent facilities and the necessary responses in terms of plant and personnel. In view of the short time available for response, planning and training for immediate recognition of emergencies and evacuation to safe areas for toxic releases is essential. The plan should be implemented before start-up and tested at regular intervals.
- 3. A plan for public safety and awareness should be developed. Procedures for road closure and evacuation and warnings to stay indoors should be developed, implemented and tested.



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GLOSSARY

Continuous Release

The escape of a hazardous substance at a flow rate which is sustained for a prolonged period.

Dense Gas Cloud

A gas cloud which is heavier than the surrounding air.

This may be for the following reasons:

- The pure gas is denser than air.
- Aerosol droplets are formed.
- Low temperature effects e.g. condensation of moisture in air to form fog with the gas.

Dispersion

The process of dilution of a hazardous substance by the surrounding fluid.

Dose

Amount of a toxic substance to which person is exposed. It may be the quantity ingested, absorbed or inhaled or it (a function of) concentration and time in an area of interest.

Explosion

A release of energy which causes a pressure discontinuity or blast wave.

Flash Fire

The combustion of a flammable vapour and air mixture in which the flame passes through that mixture at less than sonic velocity, such that negligible damaging overpressure is created.

Flash Fraction

The fraction of a superheated liquid that will vaporise under adiabatic conditions on depressurisation to atmospheric pressure.

Frequency

The number of occurrences per unit of time.

Full-bore Rupture

Major failure of a pipeline at least equivalent in size to the cross-sectional area of the pipe.

Guillotine Failure

Complete severance of a pipeline or vessel connection; a particular type of full-bore rupture.

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Hazard

A physical situation with a potential for human injury, damage to property, damage to the environment or some combination of these.

Hazard Analysis

The identification of undesired events that lead to the materialisation of a hazard, the analysis of the mechanisms by which these undesired events could occur and usually the estimation of the extent, magnitude and likelihood of any harmful effects.

Hazardous Substance

A substance which because of its chemical properties, will be a hazard if released from a process or storage.

IDLH (Immediately Dangerous to Life or Health)

The concentration of a substance at which exposure will lead to acute or chronic effects.

Individual Risk

The frequency at which an individual may be expected to sustain a given level of harm from exposure to specified hazards.

Instantaneous Release

The escape of quantity of a hazardous substance over a short time span usually a few seconds.

Jet Flame

The combustion of material emerging with significant momentum from an orifice.

LC 50, LC 5

Lethal toxic concentrations at which 50% or 5% respectively of a typical population would be killed.

LD 50, LD 5

Lethal toxic dose at which 50% or 5% respectively of a typical population would be killed.

Lower/Upper Flammable Limit (LFL/UFL)

That concentration in air of a flammable substance below/above which combustion will not propagate.

Neutral Density Gas Cloud

A gas cloud which has a density equal to that of the surrounding air.

Passive Dispersion

A dispersion process dependent only on atmospheric conditions in which the properties of the dispersing material do not affect the local turbulence.

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Probability

A number in a scale from 0 to 1 which expresses the likelihood that one event will succeed another.

Risk

The (degree of) possibility of loss or damage to human, environment or material values. Both the probability of the occurrence of such losses and the extent of the loss determine the risk, which increases with increased probability or extent of loss. When risk is quantified it is usually expressed as:

- the probability of occurrence of an unwanted event with given consequences in a given period, or as
- expected loss in a given period.

"Period" could be exchanged by "time interval", "number of cycles in use", "dose", "person-years" or similar. Such quantities are usually termed as "exposure".

Quantified Risk Assessment Q.R.A. The quantitative evaluation of the probability of hazards events and the likely harmful consequences together with the value judgments made concerning the accuracy and validity of the results.

Threshold Limit Value-Time Weighted Average (TLV) The time-weighted average concentration for a normal 8-hour workday or 40-hour work week to which nearly all workers may be exposed, day after day, without adverse effect.

Toxic

The property of substances which, when introduced into or absorbed by a living organism, destroys life or injures health.



Appendix A Properties of Process Materials



AMMONIA

1.1 PHYSICAL PROPERTIES

At ordinary temperatures and atmospheric pressure anhydrous ammonia is a pungent colourless gas. It can be liquefied by a moderate increase in pressure or by lowering its temperature to minus 33°C.

Ammonia can readily be detected in the atmosphere by smell, at concentrations as low as 20 ppm v/v. It is extremely soluble in water and some organic solvents, heat being liberated during solution. The main physical constants are as follows:

Atmospheric Boiling Point	-33.3°C
Freezing Point	-77.7 ⁰ C
Critical Temperature	132.4 ⁰ C
Critical Pressure	11420 kPa
Latent Heat (1 atm, minus 33°C)	1370.7 kJ/kg
Liquid Density	$682.8 \text{ kg/m}^3 (33.7^{\circ}\text{C})$
Vapour Pressure	888 kPa (21 ⁰ C)
Vapour Density	Ø.707 kg/m ³ (25 ⁰ C)
Flammable Limits (% by volume in air)	16-25%
Auto Ignition Temperature	651 ⁰ C

Ammonia (NH $_3$) is a colourless, pungent, gas with a normal freezing point of -77.7 $^{\circ}$ C and a boiling point of -33.3 $^{\circ}$ C. It is stable at ordinary temperatures but decomposes to hydrogen and nitrogen at elevated temperature.

Ammonia is a fairly reactive gas; it reacts readily with a large variety of substances. High temperature oxidation to form nitrogen and water is one of the more important reactions. This reaction can be effected by many metal oxides, for example copper oxide.

Chlorine reacts with ammonia to give nitrogen and ammonia chloride.

Other reactions of possible significance are ammonia plus phosphorus vapour at red heat (possible fire conditions) to give nitrogen and phosphine sulphur vapour and ammonia to give ammonium sulphide and nitrogen; sulphur with anhydrous liquid ammonia to give hydrogen sulphide and tetranitrogen tetrasulphide and ammonia and carbon at red heat to give ammonium cyanide. The compounds mentioned are either poisonous, unstable, can react with air to produce other noxious materials, or are all of the aforementioned.

1.2 HEALTH HAZARDS

At low concentrations in air ammonia vapour irritates the eyes, nose and throat. Inhalation of high concentrations produces a sensation of suffocation, quickly causes burning of respiratory tracts and may

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result in death.

Liquid anhydrous ammonia causes severe burns on contact with the skin, while its effect on being swallowed would be to cause severe corrosive action on the mouth, throat and stomach.

Severe eye damage can be caused by exposure to high gas concentrations or direct contact with the liquid.

TABLE 1: Health Hazards

Vapour Concentration ppm Vol/Vol	General Effect	Exposure Period
*25	Odour, detectable by most persons.	Maximum for 8 hour working period.
100	No adverse effect for average worker.	Deliberate exposure for long periods not permitted.
400	Immediate nose and throat irritation.	No serious effect after 1/2-1 hour.
700	Immediate eye irritation.	No serious effect after 1/2-1 hour.
1,700	Convulsive coughing. Severe eye, nose and throat irritation.	Could be fatal after 1/2 hour.
2,000 - 5,000	Convulsive coughing. Severe eye, nose and throat irritation.	Could be fatal after 1/4 hour.
5,000 - 10,000	Respiratory spasm. Rapid asphyxia.	Fatal within minutes.

This is the present Threshold Limit Value (TLV). 1 ppm = 0.72 mg/m^3

For this study, the following toxic concentrations have been used in dispersion calculations:

10,000 ppm - LC50 1,700 ppm - LC5 500 ppm - IDLH

(See Glossary for definitions).

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2. UREA

2.1 PHYSICAL PROPERTIES

Urea is a granular white solid with the following physical properties:

Melting point 132.7°C

Boiling point Decomposes before boiling Specific gravity 1.335

Molecular weight 60.6

Flammability noncombustible solid

formed; it explodes spontaneously in air.

NOTE: When mixed with hypochlorites, nitrogen trichloride is

2.2 HUMAN HEALTH

No recommended exposures limits were found in the literature.

3. METHANE

Molecular Weight 16.04
Boiling Point (at 101.3 kPa) -161.5° C
Freezing Point -182.5° C
Density Liquid (-160° C) 422 kg/m³
Vapour Specific Gravity 0.55
Flammable Limits (in air) 5.0% - 15.0%
TLV Not pertinent*

methane is an asphyxiant and the limiting factor is available oxygen.

Reference: Chemical Hazard Response Information System - U.S. Coast Guard.

4. CHLORINE

4.1 PHYSICAL PROPERTIES

At normal temperatures and atmospheric pressure chlorine is a dense (heavier than air) gas which has a greenish yellow colour at very high concentrations. Chlorine has a characteristic pungent odour which can be smelt down to a level of about 3 ppm. The main physical constants are as follows:

```
70.9
Molecular Weight (Cl<sub>2</sub>)
                                                             -34.05° C
Boiling Point (at 101.3 kPa)
                                                           -100.98° C
Freezing Point (at 101.3 kPa)
Density Cl<sub>2</sub> Gas (0° C/101.3 kPa)
                                                               3.214 \text{ kg/m}^3
Relative density, \text{Cl}_2/\text{air} (0° C/101.3 kPa) Density Liquid \text{Cl}_2 (0° C/370.2 kPa)
                                                               2.486
                                                               1.467 \, kg/l
Liquid/Gas Volume Relationship 1 vol. liquid = 456 vols. gas
                                                             at 0° C/101.3 kPa
Latent Heat of Vapourisation at -34.05°C
                                                             288 kJ/kg
                                                             666 kPa
Vapour Pressure at 20°C
TLV (8 Hr Time Weighted Average for
                                                          1 ppm = 2.9 \text{ mg/m}^2
      occupational exposure)
                                                         50 ppm
IDLH (several minutes to 30 minutes)
                                                      500 ppm
LC<sub>50</sub> ( "
```

Chlorine is not flammable in air but is itself an oxidant in many ways comparable with oxygen. Organic compounds may have flammability limits in chlorine rather similar to those which they have in oxygen. Reactions between organic compounds and chlorine are generally highly exothermic and tend to go to complete chlorination, often with some violence.

Wet chlorine corrodes mild steel rapidly, therefore stringent precautions are necessary to ensure mild steel systems are kept dry.

4.2 HEALTH HAZARDS

Chlorine gas is a respiratory irritant. The TLV is 1 ppm and the gas will produce symptoms of exposure at levels above 3 ppm. Concentrations of 40-60 ppm are dangerous for short-term exposure.



HYDROGEN

Reference: Chemical Hazard Response Information System - U.S. Coast Guard.

6. CARBON MONOXIDE

Molecular Weight 28.0 Boiling Point (at 101.3 kPa) -191.5° C Freezing Point -199° C Density at -191.5° C 791 kg/m^{3} Vapour Specific Gravity Data not available Flammable Limits in Air 12% - 75% TLV 50 ppm

Reference: Chemical Hazard Response Information System - U.S. Coast Guard.

7. UREA-FORMALDEHYDE SOLUTION

(UFC 80) will contain 20% free formaldehyde

Molecular Weight 18.30 = 100°C Boiling Point (at 101.3 kPa) $-20 - 30^{\circ}C$ Freezing Point Density 1290 - 1330 kg/m³ Vapour Specific Gravity 1.03 Flammable Limits in Air 7.0% - 73% (dependant on the content of methanol.) TLV (formaldehyde) 2 ppm IDLH " 100 ppm Odour " " Pungent, irritating

Note: A 37% solution of formaldehyde in urea will be used in this process.

Reference: 1) Chemical Hazard Response Information System - U.S. Coast Guard - for Formaldehyde.

2) Dyno Industries Safety Sheet (1987) - Urea - Formaldehyde Solution (UFC 80)

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8. MDEA (n-MethyldiEthanolAmine)

Physical Description: Colourless Liquid

Molecular Weight 119 247°C Boiling Point (at 101.3) kPa) -21°C Freezing Point 1.0377 Density at 20°C TLV Not regulated 0dour Amine-like 135°C Flash Point ${\tt Flammability}$ Combustible Vapour Pressure at 20°C <0.01 mm Hg 150°C 25 Solubility Miscible with water

Reference: Safety Data Sheet supplied by Foster Wheeler.

SAFETY DATA SHEET

UREA

CHEMICAL NAME:

Carbonyl Diamide

SYNONYMS:

Carbamate

MOLECULAR FORMULA: CO(NH2)2

GENERAL HAZARD STATEMENT:

Practically non harmful. Non flammable. Avoid Generating dust. Use good industrial hygiene.

PHYSICAL PROPERTIES: White crystalline material

Highly soluble in water pH of 10% soln 7.5 min.

HEALTH CONSIDERATIONS:

Considered to be practically non harmful by all exposure routes. Nevertheless as with any industrial chemical ingestion, inhalation of dust/vapours, prolonged or repeated skin contact should be avoided by good standards of industrial hygiene. Contact with skin may result in irritation. Prolonged or repeated skin contact to be avoided. Inhalation of dust may result in respiratory irritation.

THR = MOD via skin, iv and oral routes.

PERSONAL PROTECTION RECOMMENDATIONS:

Use good industrial hygiene. Avoid skin and eye contact. Wear appropriate protective clothing; long sleeve shirt, trousers, glasses and gloves. Use with adequate ventilation. Avoid inhalation of dust. If inhalation risk exists wear dust respirator.

FIRST AID:

Skin:

Wash skin thoroughly with water. Remove contaminated clothing. Wash contaminated clothing before re-use.

Eyes:

Immediately hold eyes open and flood with large quantities of

water. In all cases of eye contamination it is a sensible precaution

to seek medical advice.

Mouth:

If ingested give Syrup of Ipecac (APF) and seek medical advice.

HANDLING:

Avoid generating dust. It is recommended that running water be available in any area where urea is handled.

STORAGE:

Store in a cool, dry shaded place away from combustible materials and foodstuffs.

EXPLOSION HAZARDS:

Not considered to be a significant fire risk. Will decompose if involved in a fire omiting noxious fumes.

EXTINGUISHING MEDIA:

Water spray, foam, carbon dioxide or dry chemical.

SPILLS:

Sweep up spillage and store.

TOXICITY:

Acute ORAL LD_{LO} (domestic animals) = 511mg/kg

July 1984

PRODUCT SAFETY DATA SHEET

CATALYST 50-2

ALTERNATIVE NAME GENERAL PROPERTIES

MATERIAL HAZARDS
PERSONNEL HAZARDS

Skin Contact
Eye Contact
Ingestion

Inhalation

PRECAUTIONARY MEASURES

FIRST AID

Inhalation

Skin Contact Eye Contact Ingestion

STORAGE SPILLAGE Hydrodesulphurisation Catalyst.

Green solid in extrudate form Typical charged density 0.7 kg/l Contains nickel and molybdenum oxides insoluble in water.

Non-flammable but may be pyrophoric in the freshly reduced state.

Of relatively low oral toxicity but can be irritating to the skin, eyes and mucous membranes.

Prolonged contact may produce dermatitis.

May result in irritation and conjunctivitis.

Large quantities may cause Irritation.

Dust may cause upper respiratory irritation.

Ni compounds are classified in certain countries as potential carcinogene. However Ni-containing catalysts have been in use for a long period of time and there is no evidence that they present a carcinogenic risk. Nevertheless inhalation of the dust should be minimised and appropriate occupational exposure limits should be strictly observed.

The catalyst should be manhandled in a manner that minimises the generation of dust. Advice on procedures for charging and discharging of catalysts are given in the ICI publication 'Catalyst Handling'.

Gloves, goggles and approved dust masks should be worn during charging or discharging operations.

All personnel should be acquainted with the hazards associated with the material.

Remove the patient to fresh air. Keep warm and at rest. Gargle with water. If necessary, obtain medical attention.

Wash affected areas with copious quantities of water.

Irrigate immediately with copious amounts of water for at least 15 minutes.

Do not induce vomiting. Give milk or water to drink. Obtain medical attention if more than small quantities have been swallowed.

Keep containers dry and tightly closed during storage.

Collect all spilt material by mechanical means and place in a clean container. Avoid generation of dust.

Label the container.

Do not wash into any public water supply.



PRODUCT SAFETY DATA SHEET

CATALYST 32-4

ALTERNATIVE NAME

Sulphur Removal Catalyst

GENERAL PROPERTIES

White solid spherical granules Charged bulk density 1.1 kg/l

Contains zinc oxide with a small amount of cement

insoluble in water.

MATERIAL HAZARDS

Non-flammable.

PERSONNEL HAZARDS

The material may be irritating to the eyes, mucous membranes and gastro-intestinal tract.

Skin Contact

Physical irritation only.

Eye Contact

May result in physical irritation.

Ingestion

Large quantities may cause irritation in the gastro-Intestinal tract.

Inhalation

High concentrations of very finely divided dust may produce symptoms of 'metal fume fever' — irritation of the upper respiratory system, coughing,

fatigue and fever. Symptoms disappear after 24-48 hours.

PRECAUTIONARY MEASURES

The catalyst should be manhandled in a manner that minimises the generation of dust. Advice on procedures for charging and discharging of catalysts are given in the ICI publication 'Catalyst Handling'.

Gloves, goggles and approved dust masks should be worn during the charging and discharging operations

All personnel should be acquainted with the hazards associated with the material.

FIRST AID

Inhalation

Remove the patient to fresh air, keep warm and at rest. Gargle with water.

Seek medical attention if the symptoms persist.

Skin Contact

Wash the affected areas with water

Eye Contact

Irrigate immediately with water for 15 minutes.

Ingestion

Do not induce vomiting. Give milk or water to drink.

STORAGE

Keep the containers dry and tightly closed during storage.

SPILLAGE

Transfer to another container. Wash away the remainder with water.



PRODUCT SAFETY DATA SHEET

CATALYST 57-3

ALTERNATIVE NAME
GENERAL PROPERTIES

Natural gas steam reforming catalyst.

Light grey ring pellets

Typical charged density 1.0 kg/l

Contains nickel oxide dispersed on a ceramic support

Insoluble in water

Melting point in excess of 1000°C.

MATERIAL HAZARDS

Non-combustible Non-corrosive

Avoid cooling the reduced catalyst to less than 150°C in the presence of CO because of the danger of formation of nickel carbonyl under these conditions.

PERSONNEL HAZARDS

Of relatively low oral toxicity but can be irritating to the skin, eyes and mucous membranes.

Skin Contact Eye Contact Ingestion Inhalation

Prolonged contact may produce dermatitis.

May result in irritation and conjunctivitis,

Large quantities may cause irritation.

Dust may cause upper respiratory irritation.

Ni compounds are classified in certain countries as potential carcinogens. However Ni-containing catalysts have been in use for a long period of time and there is no evidence that they present a carcinogenic risk. Nevertheless inhalation of the dust should be avoided and appropriate occupational exposure limits should be strictly observed.

PRECAUTIONARY MEASURES

This material should be handled in a manner that minimises the generation of dust. Advice on procedures for charging and discharging of catalysts is given in the ICI publication 'Catalyst Handling'.

Gloves, goggles and approved dust masks should be worn during charging or discharging operations.

All personnel should be acquainted with the hazards associated with the material.

FIRST AID

Inhalation

8kin Contact Eye Contact

Ingestion

Remove the patient to fresh air. Keep warm and at rest. Gargle with water. Seek medical attention if symptoms persist.

Wash the afected areas thoroughly with water.

Irrigate immediately with water for 15 minutes. Obtain medical attention.

Do not induce vomiting. Give milk or water to drink.

Obtain medical attention if more than small quantities have been

swallowed.

Keep containers dry and tightly closed during storage.

Collect all split material by mechanical means and place in a clean container. Avoid generation of dust.

Label the container.

Do not wash into any public water supply.

STORAGE SPILLAGE



PRODUCT SAFETY DATA SHEET

CATALYST 54-3

ALTERNATIVE NAME GENERAL PROPERTIES Secondary steam reforming catalyst.

Light grey ring pellets

Typical charged density 1.0 kg/l Contains nickel oxide and aluminium oxide

Melting point in excess of 1000°C.

MATERIAL HAZARDS

Non-flammable Non-corrosive

Avoid cooling the reduced catalyst to less than 150°C in the presence of CO because of the danger of formation of nickel carbonyl under these conditions.

Of relatively low oral toxicity but can be irritating to the skin, eyes and

PERSONNEL HAZARDS

mucous membranes. Prolonged contact may cause dermatitis. May result in irritation and conjunctivitis.

Skin Contact **Eye Contact** Ingestion Inhalation

Large quantities may cause irritation. Dust may cause upper respiratory irritation.

NI compounds are classified in certain countries as potential carcinogens. However Ni-containing catalysts have been in use for a long period of time and there is no evidence that they present a carcinogenic risk. Nevertheless inhalation of the dust should be avoided and appropriate occupational exposure limits should be strictly observed.

PRECAUTIONARY MEASURES

The catalyst should be manhandled in a manner that minimises the generation of dust. Advice on procedures for charging and discharging of catalysts is given in the ICI publication 'Catalyst Handling'.

Gloves, goggles and approved dust masks should be worn during charging or discharging operations.

All personnel should be acquainted with the hazards associated with the material.

FIRST AID Inhalation

Remove the patient to fresh air. Keep warm and at rest. Gargle with water. If necessary, obtain medical attention.

Skin Contact Eye Contact

Wash the affected areas with copious quantities of water.

Ingestion

Irrigate immediately with copious amounts of water for at least 15 minutes. Obtain medical attention.

Do not induce vomitting. Give milk or water to drink. Obtain medical attention if more than small quantities have been swallowed.

STORAGE

Keep containers dry and tightly closed when not in use.

SPILLAGE

Collect all spilt material by mechanical means and place in a clean container. Avoid generation of dust.

Label the container.

Do not wash into any public water supply.



PRODUCT SAFETY DATA SHEET

CATALYST 54-4

ALTERNATIVE NAME GENERAL PROPERTIES

MATERIAL HAZARDS

PERSONNEL HAZARDS

\$kin Contact Eye Contact Ingestion Inhalation

PRECAUTIONARY MEASURES

FIRST AID

Inhalation

8kin Contact Eye Contact

Ingestion

STORAGE SPILLAGE Secondary steam reforming catalyst.

Light grey ring peliets Typical charged density 1.0 kg/l Contains nickel oxide as a ceramic support Melting point in excess of 1000°C.

Non-flammable Non-corrosive

Avoid cooling the reduced catalyst to less than 150°C in the presence of CO because of the danger of formation of nickel carbonyl under these

Of relatively low oral toxicity but can be irritating to the skin, eyes and mucous membranes.

Prolonged contact may cause dermatitis. May result in irritation and conjunctivitis. Large quantities may cause irritation. Dust may cause upper respiratory irritation

Ni compounds are classified in certain countries as potential carcinogens. However Ni-containing catalysts have been in use for a long period of time and there is no evidence that they present a carcinogenic risk. Nevertheless inhalation of the dust should be avoided and appropriate occupational exposure limits should be strictly observed.

The catalyst should be manhandled in a manner that minimises the generation of dust. Advice on procedures for charging and discharging of catalysts is given in the ICI publication 'Catalyst Handling'.

Gloves, goggles and approved dust masks should be worn during charging or discharging operations.

All personnel should be acquainted with the hazards associated with the material.

Remove the patient to fresh air. Keep warm and at rest. Gargle with water. If necessary, obtain medical attention.

Wash affected areas with copious quantities of water.

Irrigate Immediately with copious amounts of water for at least 15 minutes. Obtain medical attention.

Do not induce vomiting. Give milk or water to drink. Obtain medical attention if more than small quantities have been swallowed.

Keep containers dry and tightly closed when not in use.

Collect all spilt material by mechanical means and place in a clean container. Avoid generation of dust.

Label the container.

Do not wash into any public water supply.



PRODUCT SAFETY DATA SHEET

CATALYST 15-4, 15-5

ALTERNATIVE NAME

GENERAL PROPERTIES

MATERIAL HAZARDS

PERSONNEL HAZARDS

Skin Contact Eye Contact

Ingestion

Inhalation

PRECAUTIONARY MEASURES

High Temperature Shift Catalyst

Brown pellets

Charged bulk density 1.0 kg/l

Contains oxides of iron and chromium Melting point in excess of 1,000°C.

None

Non-flammable Non-corrosive

Contains small quantities of hexavalent chromium compounds and may be irritating to the eyes, mucous membranes and gastro-intestinal tract.

Frequent contact with the dust may result in dermatitis and ulceration.

May result in irritation and conjunctivitis.

Absorption of large quantities can produce irritation, nausea, vomiting

and diarrhoea.

material.

Dust may cause upper respiratory irritation. Prolonged exposure to the

dust may cause ulceration of the nasal passages.

The catalyst should be manhandled in a manner that minimises the generation of dust. Advice on procedures for charging and discharging of catalysts are given in the ICI publication 'Catalyst Handling'.

Gloves, goggles and approved dust masks should be worn during charging or discharging operations.

All personnel should be acquainted with the hazards associated with the

FIRST AID

Inhalation

Remove the patient to fresh air, keep warm and at rest. Gargle with water. If necessary seek medical attention.

Skin Contact

Wash the affected areas with soap and water.

Eye Contact

Irrigate immediately with copious quantities of water for at least 15 minutes. Obtain medical attention.

Ingestion Do not ind

Do not induce vomiting. Give milk or water to drink. Obtain medical attention if more than small quantities have been swallowed.

8TORAGEKeep containers dry and tightly closed during storage.

SPILLAGE Transfer to another container. Wash away the remainder with water.



PRODUCT SAFETY DATA SHEET

CATALYST 53-1

ALTERNATIVE NAME

GENERAL PROPERTIES

MATERIAL HAZARDS

PERSONNEL HAZARDS

Skin Contact

Eye Contact

Ingestion

Inhalation

PRECAUTIONARY MEASURES

FIRST AID

Inhalation

Skin Contact

Eye Contact

Ingestion

STORAGE

SPILLAGE

Low Temperature Shift Catalyst

Grey solid in pellet form

Density 0.95 kg/l

Contains oxides of copper and zinc

Insoluble in water

Melting point in excess of 1,000°C. Partially soluble in mineral acids.

May be pyrophoric when freshly reduced otherwise non-flammable.

The material may be irritating to the eyes, mucous membranes and gastrointestinal tract.

Physical Irritation only.

May result in irritation and conjunctivitis.

Absorption of large quantities can produce irritation, nausea, vomiting

and diarrhoea.

High concentrations of very finely divided dust may produce symptoms of 'metal fume fever' — irritation of the upper respiratory system, coughing,

fatigue and fever. Symptoms disappear after 24-48 hours.

The catalyst should be manhandled in a manner that minimises the generation of dust. Advice on procedures for charging and discharging of catalysts are given in the ICI publication 'Catalyst Handling'.

Clover goods and arrowed due made about the

Gloves, goggles and approved dust masks should be worn during charging or discharging operations.

All personnel should be acquainted with the hazards associated with the

material.

Remove the patient to fresh air. Keep warm and at rest. Gargle with water. If necessary, obtain medical attention.

Wash affected areas with copious quantities of water.

Irrigate immediately with copious amounts of water for at least 15 minutes.

obtain medical attention.

Do not induce vomiting. Give milk or water to drink. Obtain medical attention if more than small quantities have been swallowed.

Keep containers dry and tightly closed during storage.

Colloot all spilt material by mechanical means and place in a clean

container. Avoid generation of dust.

Label the container.

Do not wash into any public water supply.



PRODUCT SAFETY DATA SHEET

CATALYST 11-3

ALTERNATIVE NAME
GENERAL PROPERTIES

MATERIAL HAZARDS

PERSONNEL HAZARDS

Skin Contact Eye Contact Ingestion Inhalation

PRECAUTIONARY MEASURES

FIRST AID Inhalation

Skin Contact Eye Contact Ingestion

STORAGE SPILLAGE Methanation Catalyst

Grey pellets

Typical charged density 1.12 kg/l

Contains nickel oxide on a ceramic support.

Insoluble in water.

Melting point in excess of 1000°C.

Non-flammable but may be pyrophoric in the freshly reduced state.

Non corrosive.

Avoid cooling the reduced catalyst to less than 150°C in the presence of CO because of the danger of formation of nickel carbonyl under these

Of relatively low oral toxicity but can be irritating to the skin, eyes and mucous membranes.

Prolonged contact may produce dermatitis.

May result in Irritation and conjunctivitis.

Large quantities may cause irritation.

Dust may cause upper respiratory irritation.

Ni compounds are classified in certain countries as potential carcinogens. However Ni-containing catalysts have been in use for a long period of time and there is no evidence that they present a carcinogenic risk. Nevertheless inhalation of the dust should be avoided and appropriate occupational exposure limits should be strictly observed.

The catalyst should be manhandled in a manner that minimises the generation of dust. Advice on procedures for charging and discharging of catalysts are given in the ICI publication 'Catalyst Handling'.

Gloves, goggles and approved dust masks should be worn during charging or discharging operations.

All personnel should be acquainted with the hazards associated with the material.

Remove the patient to fresh air. Keep warm and at rest. Gargle with water. If necessary, obtain medical attention.

Wash affected areas with coplous quantities of water.

Irrigate immediately with copious amounts of water for at least 15 minutes.

Do not Induce vomiting. Give milk or water to drink. Obtain medical attention if more than small quantities have been swallowed.

Keep containers dry and tightly closed during storage.

Collect all spilt material by mechanical means and place in a clean container. Avoid generation of dust.

Label the container.

Do not wash into any public water supply.



PRODUCT SAFETY DATA SHEET

CATALYST 35-4

ALTERNATIVE NAME

GENERAL PROPERTIES

Ammonia Synthesis Catalyst.

Black irregular lumps

Contains Magnetite with small quantites of oxides of

Aluminium, Potassium and Calcium Charged bulk density 2.5 - 3.0 kg/l

Soluble in Concentrated Acids

Melting point in excess of 1,000°C.

MATERIAL HAZARDS

PERSONNEL HAZARDS

Inhalation

Skin Contact **Eye Contact**

Ingostion

PRECAUTIONARY MEASURES

Insoluble in water

Non-flammable but the catalyst is pyrophoric in the reduced form.

A relatively harmless material.

Magnetite is generally regarded as a nuisance particulate with a Threshold Limit Value of 5 mg/m3 for the fume, and with a value of 10 mg/m3

recommended for the dust (8-hour time weighted average)

Continued exposure to high concentrations of iron oxide fume leads to accumulation in the lung. Such accumulation is visible on an X-ray plate,

but is considered to be benign (siderosis).

Non-irritant

Dust may give rise to physical irritation.

Practically non-harmful. Listed as a food additive:

The catalyst should be manhandled in a manner that minimises the gonoration of dust. Advice procedures for charging and discharging of catalysts are given in the ICI publication 'Catalyst Handling'.

Gloves, goggles and approved dust masks should be worn during charging and discharging operations

All personnel should be acquainted with the hazards associated with the material.

FIRST AID

Inhalation

Skin Contact

Eye Contact

Ingestion

STORAGE

SPILLAGE

Remove the patient to fresh air. Keep warm and at rest. Gargle with water. If necessary, obtain medical attention.

Wash thoroughly with water.

Irrigate with water for 15 minutes.

Do not induce vomiting. Give milk or water to drink.

Keep containers dry and tightly closed during storage.

Transfer to another container. Wash away remainder with a large amount

of water.



Appendix B

Ammonia: Historical Review Of Incidents



The following has been obtained from reviewing published ammonia incidents:

Location	Date	Cause/Consequence	*K/I
Liverpool UK	19 Apr 1963	Road tanker jammed under bridge puncturing the tanker. Two tonnes of ammonia released.	-/20
Cincinnati USA	23 Jan 1968	Ammonia tanks exploded at a plant.	
Kelley Iowa USA	21 Apr 1968	Freight train derailed. Ammonia tank car ruptured. Local residents fled from homes.	-/-
Lieven France	21 Aug 1968	Tank collapsed due to corrosic stress fatigue. Release of tank coto form cloud.	
Glasgow Scotland UK	5 Dec 1968	Explosion at cold storage warehouse led to release of ammonia. Workmen evacuated.	-/- ·
Crete Nebraska USA	18 Feb 1969	Freight train derailed and rammed into a tank car filled with 116m ³ of liquified anhydrous ammonia.	8/35
Early Iowa USA	19 Mar 1969	Spur of pipeline was cracked open by workmen attaching an extension to the mainline. Favourable winds prevented ammonia fumes from spreading to nearby homes.	
Upland Indiana USA	25 Mar 1969	Freight train with ammonia cars jumped the tracks. Tanks did not rupture. No injuries.	
Cumming Iowa USA	1 May 1969	125m ³ anhydrous ammonia tank car exploded 2 days after being damaged in a derailment. It had been examined and declared safe by experts.	-/-
Rockwell Texas USA	27 Nov 1969	Anhydrous ammonia gas leaked from 5 tank cars which had overturned. 200 persons evacuated.	<u>-/-</u>
Munday Texas USA	Dec 1968	Tank carrying anhydrous ammonia crashed into building forcing evacuation of residents.	-/-



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Location	Date	Cause/Consequence	*K/I
Dickinson W. Virginia USA	21 Jan 1970	Tank car leaked ammonia type gas fumes.	-/9
Clinton Iowa USA	30 Mar 1970	Incident at ammonia processing plant. Extensive damage.	-/7
Callao Missouri USA	8 Jan 1971	Derailed tank car carrying liquid ammonia burst open on railroad bridge causing evacuation of homes near Callao.	-/
London England UK	15 Mar 1971	Explosion at cold storage warehouse. Ammonia Cylinders exploded in fire.	-/11
Tunis N. Carolina USA	11 Oct 1972	Concentration of ammonia in nitric acid plant reached explosive range. Ignited explosively by its reaction with the catalyst.	-/-
Potchefstroom S. Africa	13 Jul 1973	Sudden failure of dished end of 50 tonne storage vessel due to embrittlement associated with failure of non stress-relieved vessel after a major repair.	18/65
Blair Nebraska USA	9 May 1974	Storage tank overfilled. Liquid ammonia entered compressors. Relief valve operated. Explosion following ignition by a gas-fired water heater. Extensive structural damage.	
Arklow Eire	18 Aug 1974	Pressure vessel at 30.4 bars ruptured. Slight damage to rest of plant.	
Busan	1 Dec 1975	Large tank of ammonia gas exploded at a fish factory.	5/85
Sittard Zuid-Limburg	12 Mar 1976	Minor explosion and fire at ammonia unit of plant. Minor injuries.	-/20



Location	Date	Cause/Consequence	*K/I
Houston Texas USA	11 May 1976	Tractor and trailer crashed on to a highway. Tank ruptured and exploded. Extensive property damage. Buildings in area evacuated.	5/15
Deer Park Texas USA	12 May 1976	Tank truck carrying anhydrous Ammonia crashed through a guard- rail at a freeway inter-change and plunged to the ground. Tank burst on impact, releasing clo of anhydrous ammonia fumes.	6/20 ouds
Cartagena Columbia S. America	9 Dec 1976	Explosion at fertiliser plant manufacturing anhydrous ammonia Fertilizer Ammonia fumes spread over large area reaching the nearby town.	21/30
Glen Ellyn and Glendale Heights Illinois USA	1976	Rail car containing 78 tonnes of anhydrous ammonia was derailed and punctured. At least 700 people evacuated.	-/7
Landskrona Sweden	16 Jan 1977	Hose from ship to shore tank burst. Large cloud of ammonia gas formed.	2/2
Cueranveca Mexico	7 Mar 1977	Ammonia escaped from pipeline. Gas spread through sewer system. Local residents evacuated.	2/80
Llandarcy UK	18 Jun 1977	Fire at oil refinery led to ammonia leakage.	-/-
Pensacola Florida USA	9 Nov 1977	Freight train derailed. 2 rail cars punctured and anhydrous ammonia released. 1,000 people evacuated.	2/46
Thorganby Nr. York UK	1977	Pipe fractured in food-processing factory releasing up to 3 tonnes of liquid ammonia.	1/18
Crewe UK	30 Jul 1978	Ammonia gas road tanker found leaking.	/
•			



Location	Date	Cause/Consequence	*K/I
Manfredonia Italy	9 Aug 1978	Valve in pump delivering ammonia from a tank car to the plant ruptured under pressure and released 31-41 kg of ammonia. 5,000-10,000 people evacuated from their homes.	
Halsa Norway	8 Nov 1978	Ammonia tank exploded following a fire causing extensive damage.	-/-
Paddington London UK	12 Dec 1978	Ammonia leaked from an ice-cream factory.	-/-
Crestview Florida USA	8 Apr 1979	Derailment of goods train. 5,000 people evacuated.	-/1
Barnesville Minnesota, USA	10 Jun 1981	40-50 tons anhydrous ammonia escaped from storage terminal over 25 minutes. Heating system failure allowed pressure to build up, relief valve blew.	-/30
Czechoslovkia	Oct 1981	Hydrogen leak in ammonia synthesis H.P. section, explosion, fire.	6/29
Portland, Oregon, USA	5 Feb 1982	25,000 tank with malfunctioning valve spilled 3-5 tons anhydrous ammonia. Area 3 miles downwind evacuated.	-/-
Sluiskil Netherlands	9 Dec 1984	Hydrogen embittlement in a pipe in the ammonia synthesis H.P. section leading to explosion and f	1/- ire.

NOTE: * This column refers to the number of people reported killed and injured respectively.



Appendix C

Proposed Ammonia/Urea Plant EPA Guidelines For The Preliminary Risk analysis



1. SUMMARY

The document should contain a clear and concise summary of the preliminary risk analysis.

2. INTRODUCTION

- Background to this study
- Study aims and objectives
- General nature of the project
- Philosophy of approach risk assessment
- Risk standards and guidelines

3. PROJECT DESCRIPTION

- Site location and environment of the project site
- Meteorology including wind direction, atmospheric stability, temperature and surface roughness length
- Process description
- Other parameters in the surrounds of the chosen site which need to be considered in the risk analysis

4. FACTORS AFFECTING SITE SELECTION AND RISK TO PUBLIC AND NEARBY FACILITIES

- Hazardous material properties
- Hazards associated with Urea-Ammonia plants and Ammonia
- Hazards of process, storage and Operations proposed
- Review of Safety Record of Similar Facilities
- Review of Engineering Codes and Standards
- Review of Safety Engineering Design
- Review of other factors ie Domino Effect, Export Loading, Shipping etc.

5. RISK ASSESSMENT

- Methodology
 - Identification of potential major unwanted events ie checklist of hazards

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- Estimation of likelihood of failure
- Calculation of consequences of failure including diffusion characteristics
- Development of risk levels ie relationship between likelihood and consequences of failure
- Discussion of "acceptability" of risk levels in WA

6. CONCLUSION AND RECOMMENDATIONS

- Results of risk assessment and conclusions as to site acceptability
- Discussion of safety assumptions taken into account including safety engineering design, management and operational aspects, safety auditing etc.
- Recommendations of additional safety factors which need to be considered by the proponent

APPENDICES

- Failure rate data
- Meteorology of the site including wind rose
- Risk Assessment calculation methods
- Summary of major Ammonia release incidents



APPENDIX D SIMPLIFIED PROCESS FLOW SCHEMES



