Summary
All commercially produced nitric acid is now prepared by the oxidation of ammonia. The requirement for a nitric acid product of 60 % (wt) immediately restricts the choice of a recommended production process. Only two processes are possible, both highly efficient, each offering distinct advantages under different market conditions. The first process is the so-called dual-pressure process. This process features an atmospheric ammonia oxidation stage which takes advantage of the higher reaction yields available at lower pressures. The reaction mixture is subsequently compressed up to approximately 1000 kPa for the absorption stage of the process. The absorption of nitrogen oxide gases is favoured by the higher operating pressures. The second process is the single-pressure process. This process is essentially identical to the dual-pressure technique except that it maintains a pressure of about 1000 kPa throughout the process. The dual-pressure process has slightly lower operating costs due mainly to the higher efficiency in the ammonia oxidation stage. It does however suffer a significant capital cost disadvantage. It is shown that the operating cost advantage would take 21 years to outstrip the initial capital cost difference. This long payback period suggests that the single-pressure process is an economically preferable option, particularly for plant operation in the Western Australian cyclical market. The single-pressure process is also a higher net exporter of medium-pressure steam and has a lower utility requirement, and is therefore selected as the preferred option. The single-pressure ammonia oxidation/absorption process is selected based upon the operating criteria used in the single-pressure process developed by C&I Girdler. It is also anticipated that this plant will be part of a larger chemical complex. Ammonia will be produced by steam reforming of natural gas. The nitric acid plant will take a portion of the ammonia product, and nitric acid and ammonia will then be used to produce ammonium nitrate.

Introduction
The nitric acid processes i.e. the dual pressure process and single-pressure process described in the feasibility studies have become globally accepted, hence, process designers on nitric acid plants have focused more on optimizing the design within the bounds of available equipment, materials of construction, and economics. Both processes have the same potential in terms of production efficiency, product quality, and environmental friendliness. The dual-pressure process was developed and used mainly in Europe, whereas the single-pressure process (developed by Du Pont) is common in America. Figures 1 and 2 are process flow diagrams for the dual-pressure process and the single-pressure process respectively.

Figure 1: Single pressure process
The following sections compare these leading process technologies in order to select the most applicable method of weak nitric acid production.

The Single-Pressure Process shown in Figure 1 was developed to take full advantage of operating pressure in enabling equipment sizes to be reduced throughout the process. A single compression step is used to raise the pressure through the entire process sufficiently to favour absorption. Operating pressures range from 800 kPa to 1100 kPa. Increased consumption of ammonia due to the higher pressure operation can be minimized by increased ammonia oxidation and complete ammonia/air mixing. The higher oxidation temperature results in an increased consumption of platinum and rhodium and the need to rework the gauze every five to seven weeks. The higher temperature and the favourable pressure effect make possible a greater recovery of energy from the process. The process begins with the vaporization of ammonia at 1240 kPa and 35°C using process heat. Steam is then used to superheat the ammonia to 180°C. Filtered air is compressed by an axial compressor to an interstage level and then, following cooling, by a centrifugal compressor to a discharge pressure of 1090 kPa. A portion of the air is diverted for acid bleaching; the remainder is circulated through a jacket surrounding the tail-gas preheater and then used for ammonia oxidation. The heated air and the ammonia vapour (10.3% ammonia by volume) are then mixed and passed through the platinum/rhodium gauze, where the heat of reaction (producing nitric oxide) raises the temperature to between 927°C and 937°C. The heated air and the ammonia vapour (10.3% ammonia by volume) are then mixed and passed through the platinum/rhodium gauze, where the heat of reaction (producing nitric oxide) raises the temperature to between 927°C and 937°C. The reaction gas flows through a series of heat exchangers, energy is recovered either as high-pressure superheated steam or as shaft horsepower from the expansion of hot tail gas. Approximately 70% of the oxidation to nitrogen dioxide occurs as the gas passes through the energy recovery train and is cooled to 185°C. After further cooling to 63°C in the primary cooler/condenser, separation of approximately one third acid product as 42% strength nitric acid is achieved. The remaining gas reaches a 43% oxidation conversion to nitrogen dioxide, with approximately 20% dimerization. The gas is combined with bleached air containing additional nitrogen peroxide; it then passes through an empty oxidation vessel and the secondary cooler. In cooling to 66°C, the gas provides heat to a recirculating hot water system used for vaporizing the ammonia. The gas entering the absorber is 95% oxidized to nitrogen peroxide, and 27% dimerized. In the absorber deionized water is added to the top tray, and weak acid from the low-pressure condenser is added to a tray corresponding to its strength. Down-flowing acid and up-flowing acid alternately mix as the chemical steps of action formation and nitric oxide oxidation take place with the liberation of heat. There are three operational zones in the absorber, these are the lower zone cooled with plant cooling water, the middle zone cooled with chilled water, and the upper zone which is essentially adiabatic. High efficiency of heat removal in the middle and lower zones is particularly important due to its effect on the oxidation and
dimerization reactions. For this design project, chilled water at 7°C is used and the tail-gas exit temperature is approximately 10°C. Acid from the bottom of the absorber is bleached at 1010 kPa with partially cooled compressed air. The bleach air, containing nitrogen peroxide stripped from the acid, is then added to the main gas stream before entering the oxidation vessel. The cold gas is warmed by heat exchange with the hot compressed bleached air, and then heated to the expander inlet temperature of 620°C by two exchangers in the recovery train. The expander recovers 80% of the required compressor power. Expanded tail gas at 300°C flows through an economizer, providing heat to high-pressure boiler feed water and to low-pressure deionized deaerator make-up water. Subsequently tail gas is exhausted to the atmosphere at 66°C and less than 1000 ppm of nitrogen oxides. The chilled water (7°C) for the absorber is supplied by an absorption refrigeration unit, using heat recovered from the compressor intercooler as the energy source. Heat for ammonia vaporization, as previously noted, is available at 35°C and is recovered from the secondary gas cooler. The system uses circulating condensate as the energy transfer medium.

The Dual-Pressure Process shown in Figure 2 was developed to take advantage of two factors:

a) Low-pressure ammonia oxidation;

b) High-pressure absorption or acid formation. In addition to the higher conversion, the lower catalyst gauze temperature (associated with the low-pressure ammonia oxidation) results in a much lower rate of platinum deterioration. Both advantages are maximized at the lowest pressure. In contrast, however, absorption is best performed at the highest pressure. The low-pressure ammonia oxidation is usually performed in the pressure range of 101.3 kPa to 344 kPa. High-pressure absorption is usually performed in the operating range of 800 kPa up to 1010 kPa. The process begins with the vaporization of ammonia at 550 kPa and 7°C, followed by superheating to 76°C using heat from the compressed bleached air. Filtered air is compressed in an axial compressor to 350 kPa and is mixed with the superheated ammonia vapour (10-11% ammonia by volume) prior to entering the converter/reactor. In the converter, the gases react over the platinum/rhodium gauze catalyst. The gases leaving the gauze at 330 kPa and 865°C flow through a series of heat exchangers for recovery of energy, either as high-pressure superheated steam or shaft horsepower from expansion of hot tail gas. Approximately 40% of the oxidation to nitrogen dioxide occurs in the gas as it passes through the energy recovery train and is cooled to 135°C (exit from the tail-gas preheater). After further cooling to 45°C in the medium-pressure condenser, and separation of 20% of the acid product as 30% strength nitric acid, the gas reaches 50% oxidation to nitrogen peroxide with approximately 20% dimerization. The gas is combined with bleach air containing additional nitrogen peroxide and is compressed in a centrifugal nitrous-gas compressor to 1025 kPa. The exit temperature of 224°C is achieved due to the combined heat effects of the compression, the further oxidation to 80% nitrogen peroxide, and the virtual disappearance of the dimer. The compressed gas flows through an empty oxidation chamber, a high-pressure boiler feed water economizer, and a low-pressure deionized water economizer, and thus is cooled to 95°C. Residence time in the system and the effect of increased pressure result in at least 95% oxidation to nitrogen peroxide, but the dimerization is low due to the temperature level. The gas is then cooled to the dew point (50°C) for entry into the absorber. The dimerization increases to 48%, adding significantly to the heat removed prior to the absorber. The system uses circulating condensate as the energy transfer medium. The absorber is essentially the same as that described for the single-pressure process. Tower size and specific design details can be optimized to the particular process conditions and may vary considerably with the temperature of the chilled water. Chilled water at 15°C is used and the outlet gas temperature is 18°C. Refrigeration for the chilled water is provided by the ammonia vaporizer which operates at 7°C. Weak acid from the bottom of the absorber is let down to 330 kPa for bleaching with air from the axial compressor. This air, with nitrogen peroxide stripped from the acid, flows to the suction of the nitrous-gas compressor together with the main nitrous gas stream from the condenser.

3.2.2 Process Comparison

Both processes follow the basic catalytic oxidation of ammonia whereby ammonia is reacted with air in a catalytic converter at temperatures in the range of 850-950°C. Reaction gases pass through a series of energy
recovery stages before entering an absorption column. The bottoms from the column are bleached of dissolved nitrogen peroxide using air, and the resulting solution is the weak nitric acid product. The major difference between the two processes lies in the initial conversion stage. The dual-pressure process employs a conversion stage operating in the range 100-350 kPa, and a reactor temperature of about 865°C. The single-pressure process however operates the converter at 800-1100 kPa, with a reactor temperature closer to 940°C.

**Factors Favouring the Dual-Pressure Process**

In the single-pressure and dual-pressure processes, the catalyst volatilizes at a rate determined by the converter exit-gas temperature. Experimental work indicates that the rate loss of catalyst (without a catalyst recovery system) is approximately three times more rapid at 973°C than at 866°C. From plant operation data, the loss from a dual-pressure converter (operating at 866°C) is estimated at about 0.10 g/tonne of 100% acid, and from a single-pressure converter (operating at 937°C) it is estimated at about 0.38 g/tonne of 100% acid. In the single-pressure process, the ammonia content of the mixture should not exceed 10.5% because of the lower explosive limit. In the dual-pressure process with lower converter pressures, the explosive limit is higher providing additional operating flexibility. Total production cost for a 1500 tonne/day plant built in the USA in 1979 has a $2.15/tonne acid advantage in favour of the dual-pressure process. This advantage is directly attributable to a higher ammonia yield and a smaller indirect cost structure (due mainly to a 20% lower catalyst inventory requirement and less frequent catalyst changes). This production cost advantage also prevails despite inferior steam production capacity. Production cost estimates for a similar sized plant in Europe confirm the dual pressure process advantage of $2.00/tonne of acid produced. Although the plant data relate to overseas operations where cost structures may be different, the figures do illustrate an important and valid trend.

**Factors Favouring the Single-Pressure Process**

The single-pressure process uses a higher ammonia conversion pressure. This higher pressure provides advantages in terms of equipment design, e.g. smaller converter dimensions and a single heat-exchanger-train layout. The higher temperature and the favourable pressure both increase the energy recovery from the process. The single-pressure process provides an extra 10% high-level recoverable heat energy. Plant capital costs in the USA have been estimated at $5.1 million for the single-pressure process and $5.8 million for the dual-pressure process. $0.7 million higher cost of the dual-pressure process is accounted for by the larger vessels required at lower operating pressures. Estimates made for the two plants in European locations show a differential of $0.8 million, also in favour of the single-pressure process. A discounted cash flow (DCF) analysis based on these US figures was performed by matching the capital cost advantage of the single pressure process against the production cost advantage of the dual pressure process. The figures indicate that it would take 21 years for the lower operating cost of the dual-pressure process to finally overcome its initial capital cost disadvantage. Although this plant should be aiming to establish itself as a long term supplier (>20 years), a pay-back period of 21 years is far too long particularly in the fluctuating local nitric acid market. For this reason, the single-pressure process is considered to be an economically superior proposition.

**Process Selection Conclusions**

The single-pressure process appears to be preferred for a plant producing 280 tonne/day of 60% nitric acid. The capital cost advantage of this process surpasses the benefits of the superior operating cost structure of the dual-pressure process. Furthermore, the higher temperature and the favourable effect of pressure enable a greater recovery of energy from the process.