

Ammonia Recovery from Sodium Cyanide Production Waste Gas

Yesika Suarez Kuzma

School of Oil and Gas Engineering

CSBP Limited

Abstract

CSBP produces Sodium Cyanide which is extensively used by the gold mining industry. Ammonia is one of three raw materials used in its manufacture. Ammonia is not fully converted in the reaction, and, since world ammonia prices have risen, CSBP has decided to revisit the potential benefits of implementing an ammonia recovery system. These recovery systems are used in cyanide plants around the world and it is believed that the technologies have been improved over the last 40 years. This paper describes three different technologies available in the market and shows the advantages and disadvantages of each option being added to the current process.

1.0 Introduction

CSBP is one of the Australia's major suppliers of chemicals, fertilisers and related services to the mining, minerals processing, industrial and agricultural sectors. CSBP's core chemical products include: ammonia, ammonium nitrate, sodium cyanide, chlorine and caustic soda. Sodium cyanide is purchased by the gold-mining industry, both as a solution and as solid, for use in the gold extraction process as a leaching agent.

CSBP operates two Sodium Cyanide plants. Sodium Cyanide plant number 1 (SCP1) commissioned in 1988 with a current capacity of approximately 35,000 tonnes per year and SCP2 commissioned in 1996 with a current capacity of 25,000 tonnes per year.

To produce Sodium Cyanide solution, the raw materials are reacted on a platinum-rhodium gauze catalyst at about 1050 °C to produce hydrogen cyanide (HCN). The HCN is immediately absorbed in caustic soda to produce the final product, a 30% w/w solution of sodium cyanide in water containing about 0.4% free caustic soda. The waste gases from the absorption process, containing approximately 2% of NH₃ and some CO₂, HCN, H₂O, N₂ and H₂, are burned with natural gas and air before discharge to the atmosphere.

Burning the ammonia in the waste gas incinerator generates power which is consumed on site and reduces the import of electricity from the supplier. In September 1993 the NO_x emissions needed to be reduced to meet industry standards. Ammonia recovery, chemical absorption, low NO_x incinerator among other options were evaluated. At that time Ammonia recovery was not financially viable.

As shown in Figure 1 taken from Sodium Cyanide Plant Manual, in the manufacturing process of Hydrogen Cyanide (HCN), ammonia (NH₃), methane (CH₄) and air are used as raw materials. They are introduced into the gas mixer (1) and reacted on (2) a platinum-rhodium gauze catalyst at about 1050 °C to produce hydrogen cyanide (HCN). The HCN is immediately absorbed (3) in caustic soda to produce the final product, a 30% w/w solution of sodium cyanide (NaCN) in water containing about 0.4% free caustic soda. The waste gases from the absorber (3) are drawn into the blowers (4) and delivered to the incinerator (5) where they are burnt with natural gas and air to generate steam and ultimately electricity in (6) before discharging the resulting safe combustion products to the atmosphere (Daniel Ferguson, 2005).

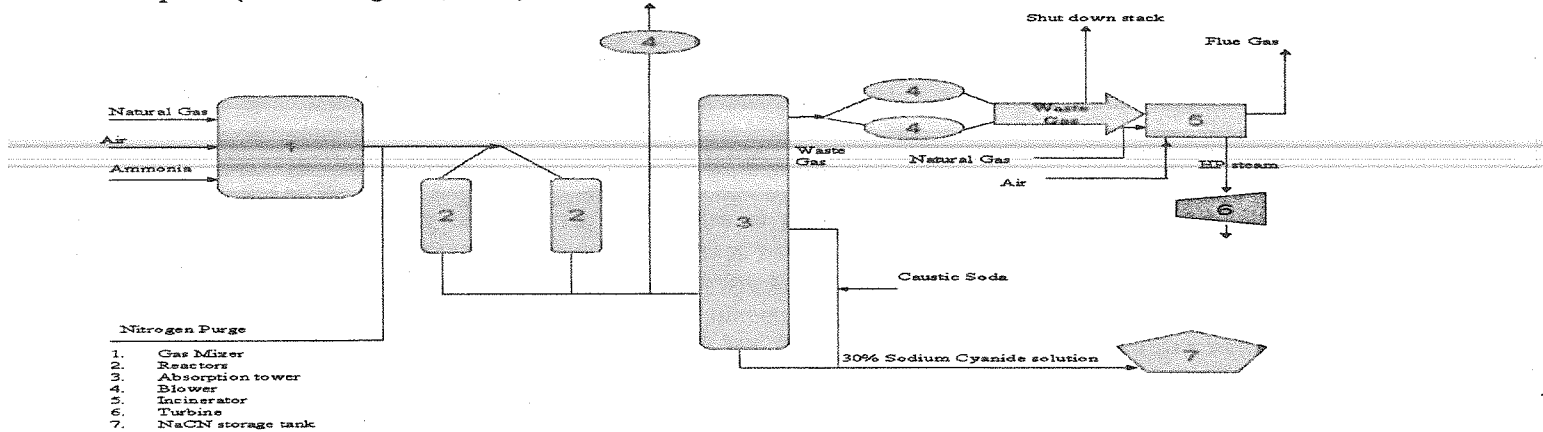


Figure 1 Sodium Cyanide manufacturing process installed at CSBP.

Recently, ammonia prices have been rising sharply and there is a potential for increase return if the full value of the ammonia can be recovered instead of being burned. There are a number of different technologies available in the market. This paper reviews two different options which are shown in Figure 2.

2.0 Review of Alternative Technologies

The proposed Ammonia recovery process must be compatible with the technology already operating on site. The two options considered are shown in Figure 2; Option 1 involves the removal of the ammonia from the waste gas, and then returning it into the Hydrogen Cyanide (HCN) manufacturing process, while option 2 converts it into Sulphate of Ammonia (SOA). In both cases the stream inlet to the new process is the waste gas coming from the top of the absorber (3) shown in Figure 1

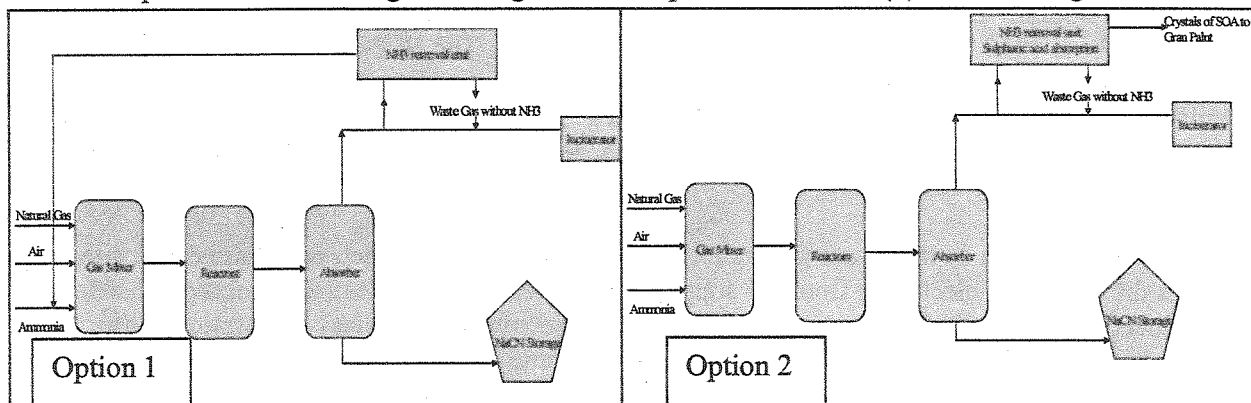


Figure 2: Options considered to improve the existing NaCN process.

For option 1 the technologies reviewed are described below:

2.1 Ammonia absorbed in water

The absorption of NH_3 in water is a very simple process. The gas is fed at the lower part of the absorber (1) where a lean solution is passed counter-current. The absorption tower needs to be operated at least at 1.3 MPa. The rich solution leaving the absorber is heated up to 160 C before entering the distillation column (2). The overhead product from the distillation column (2) contains ammonia vapour and non-condensable gases which are liberated in the ammonia condenser (4). The process is based on a closed loop where the lean solution is depressurized and introduced to the absorber. This process described above is utilized by the CSBP's Ammonia Plant. A general flow diagram of this process is shown below in Figure 3.

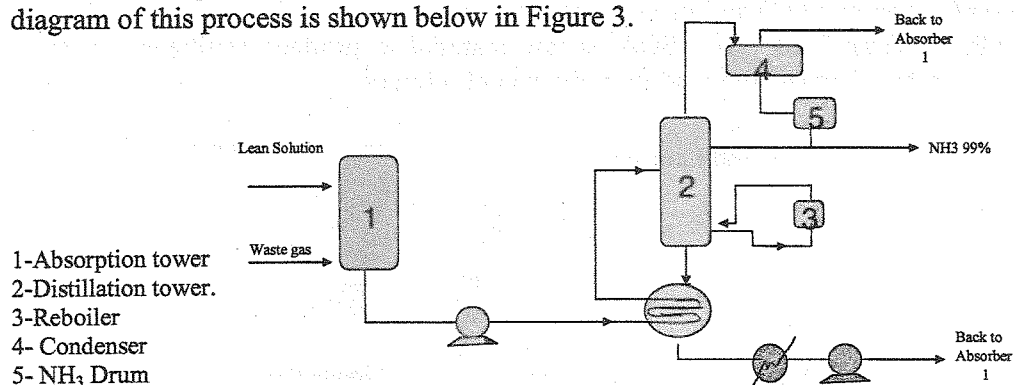


Figure 3: Ammonia absorption in water process used by CSBP Ammonia Plant.

2.2 Ammonia absorption using phosphoric acid

This option has been developed and used by Dupont's Memphis plant for 45 years and it has been continuously improved since then. DuPont's ammonia recovery process which is designed to recover 600 kg/h of ammonia is described as follows (Akerkvaerner, 2005). Cooled ammonia rich off gas is introduced to an ammonia absorber (1) where the ammonia is absorbed in a circulating phosphate solution. Approximately 98% of the NH_3 is recovered and fed to an ammonia stripper (3) to remove traces of volatile compounds. The stripped solution is recycled to the absorber for reuse and the ammonia is passed through an Enricher unit (5) where the overhead product is sent back to the HCN reactor and the bottom product is waste water. The process flow diagram can be seen in Figure 4 (Harrison, 1973).

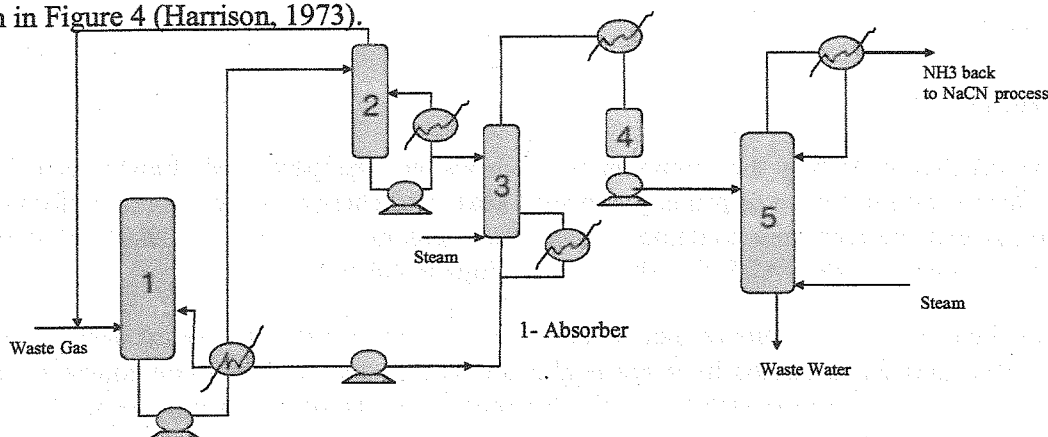


Figure 4: Ammonia recovery using Phosphoric acid according to Harrison's patent.

For option 2 the technology reviewed is described below:

2.3 Ammonia absorption using sulphuric acid

As shown in Figure 5, the waste gas is fed at the bottom of the absorber column (1). Water is introduced at the top of the column and passed counter-current. Sulphuric acid is pumped through the recirculation system to maintain 30% ammonium sulphate solution from the base and also to maintain an acidic pH. The gas from the absorber (1) goes into a blower (5) and to the incinerator (at the NaCN plant), while the sulphate of ammonia is introduced to an HCN stripper (4). The bottom product from the stripper is neutralized with caustic soda, cooled and sent to storage. This process produces a SOA solution of 30-35 wt% which is stored in tank (6). This solution has to be then introduced into a crystallization unit (11) and its associated equipment (7, 8, 9, 10, and 12) to obtain the final product. CSBP's "Gran Plant" uses SOA as raw material to produce fertilizers. At the moment, SOA is being purchased across the road from the nickel refinery.

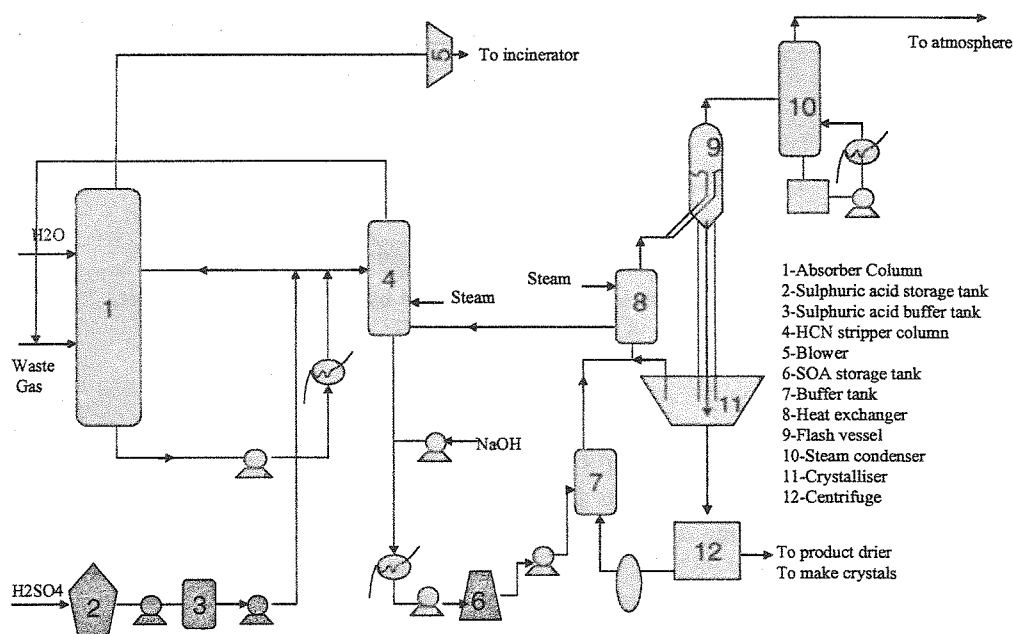


Figure 5: Crystals of Sulphate of Ammonia process proposed by ROHM GMBH Fabrik.

3.0 Discussion

3.1. Current process:

Before the benefits of removing the ammonia were re-visited, the perceived drawbacks of its removal (e.g. flame stability) were of primary concern. Mass and energy balances were performed, and it was found that the ammonia contained in the waste gas raises around 2,500kg/h of steam which translates to approximately AU\$200,000 a year savings in electricity.

Regarding the flame stability, it proved not to be an issue since a previous report showed that "ammonia is a fuel gas characterised by a reasonable calorific value. The key component of the waste gas for ensuring combustion stability is the hydrogen, the stability is supplemented by the

natural gas burnt in the primary section of the burner as a result no impacts will be shown if ammonia is removed" (Worley Engineering PTY Limited, 1994).

3.2. Ammonia Absorbed in Water:

According to the process superintendent-Ammonia Plant, the estimated capital cost of the equipment (not including installation) shown in Figure 3 is summarized in Table 1.

Equipment	Quantity required	Cost AUS
Heat Exchangers	2	200,000
Pumps	4	760,000
Columns	2	400,000
Compressor	1	1,500,000
Total		2,860,000

Table 1: Equipment cost.

Probably this option is the easiest and the one with the lowest capital cost. However, the HCN manufacture process is done under vacuum so that the waste gas pressure is only around 10 kPa. In order to absorb the ammonia pressure at least 100 times of the current operating pressure is required.

A centrifugal compressor to compress the waste gas from 10 KPa to 1300 kPa with 75% adiabatic efficiency was modelled in HYSYS to consume in excess of 5MW of shaft power which means electricity cost around AU\$3,500,000 per year to run the process, making the project not financially viable as savings in recovering the ammonia will only reach up to about AU\$1,600,000 a year.

Apart from this issue, it should be noticed that CSBP's Ammonia Plant Recovery unit operates dry feed gas while CSBP's Sodium Cyanide Plant waste gas contains about 20 mol % water vapour. If this water is condensed in the process, water level will continually build up. Therefore water disposal is required on a continuous basis.

3.2. Ammonia Absorption using phosphoric acid:

When Akerkvaerner personnel were contacted via email an estimated capital cost of US\$8 million was advised. Operating cost involves phosphoric acid usage, medium pressure steam and electricity. These costs are shown in Table 2.

Utilities	Normal consumption per kg NH3 recovered	Consumption per year	Cost AUS/year
Medium Pressure steam (Kg)	16	60,700,000	911,000
Medium voltage (480v) KWh	0.08	304,000	27,000
Phosphoric acid Kg (75 wt%)	0.005	19,000	7,000

Table 2: Costs involved in phosphoric acid absorption.

This option does not require high compression cost since the waste gas pressure needs only a slight boost through a blower to compensate for the 7 kPa pressure drop across the absorption tower before going into the incinerator. However, high quantities of steam are required which seems to exceed the OPEX savings required to obtain a positive NPV.

On the other hand, the introduction of phosphoric acid in the Sodium Cyanide Plant requires training and safety measures to be taken by the operating personnel. Even though insignificant amounts of ammonium phosphate in the waste water stream are expected, special care would need to be taken to ensure CSBP's licence limit for phosphorus would not be exceeded.

3.3. Ammonia Absorption using sulphuric acid:

According to ROHM the capital cost of the plant was AU\$10 million by 1994 (AGR Expansion Feasibility, 1994), using a simple exponential estimate according to the formula (Perry's, 1984):

$$C2 = C1 * (q_2 / q_1)^n$$

Where:

C2: Current cost

C1: Previous cost

q₂: New production capacity

q₁: Previous production capacity

n: 0.7

The new capital cost is \$ 14,600,000 in 1994 dollars. Allowing 4% per annum price inflation over the past 11 years, the estimated 2005 price for this installation would be about \$ 22,500,000.

Operating costs of the utilities involved are shown in Table 3.

Utilities	Normal consumption	Cost AUS/year
Caustic Soda (Kg/h)	2	5,000
Sulphuric Acid (Kg/h)	1380	1,508,000
Power Kwh	41	12,000

Table 3: Operating cost involved in the sulphuric of ammonia manufacturing process.

The capital cost of this option is about doubled that option 2. Crystalliser and drying units are required since mass balance from the recovery plant gives a maximum rate of SOA of 14,700 tonnes as 100%SOA. Now, if 38%SOA is used in order to avoid precipitation in the piping, a total of 38,700 tonnes/annum of solution would be produced. The maximum quantity of water that "Gran Plant" can handle is 12,000 tonnes/annum. The water introduced from the recovered solution would be 24,000 tonnes/annum which exceeds this allowance. Therefore the final product from the recovery plant needs to be SOA crystals which represents the most expensive option. Capital cost is increased considerably when a crystalliser comes into picture. However, perhaps there is the option of pumping SOA solution across the road to the nickel refinery which already produces crystalline SOA for CSBP's use and negotiating a fee for crystallising the SOA solution from this potential recovery process. This will reduce the capital cost because only a 2 km stainless steel 50mm ERW 304 ASTM-A269 pipe line with PRESSFIT joints would need to be installed (quoted by a CSBP Field Engineering Superintendent at \$62/m, not including pipe supports or fittings).

Finally, this option as well as the phosphoric acid option requires acid handling which involves extra safety measures and training.

3.4. Preferred option

NPV calculations were carried on assuming a discount rate of 10% and ten years plant life time. Results are shown in Table 4.

Option	NPV AUS
1	- 16,000,000
2	- 7,600,000
3	- 19,300,000

Table 4: NPV comparison table for alternative options.

None of the above options showed a positive NPV. Therefore, it seems that the retention of the current practice of generating power from the combustion of the ammonia represents the best value for money.

4.0 Conclusion and further work

This paper shows a general overview of alternatives of three different technologies available in the market to recover ammonia from the waste gas. As expected, operational conditions are very important in determining compatibility of different processes. Preliminary evaluations show that water absorption (option 1) is not a financially viable option due to its high operating costs. Absorption using phosphoric acid (option 2) resulted in a negative NPV at current market revenues and engineering construction costs. Absorption using sulphuric acid (option 3) also resulted in a negative NPV. However, it is believed that if the costly installation of a crystallization unit could be avoided by CSBP paying a toll for the crystallisation of the solution by a third party, the sulphuric acid route may prove to be viable. Failing that, it is concluded that the current practice of combusting the ammonia, thereby producing electricity, continues to be the best option.

5.0 References

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