Complete 32,000 ton/yr Sodium Cyanide (NaCN) Plant

with Super High Quality Liquor production

The Sodium Cyanide (NaCN) plant produces HCN from methane, ammonia and air. The HCN is then reacted with caustic soda (50% NaOH) to produce a sodium cyanide liquor of approximately 30 - 32% NaCN. The liquor is purified and diluted to 30% for sale.

The plant is capable of producing approximately 18,000 tonnes per annum of HCN which is converted directly to 32,600 tonnes per annum of NaCN.

Process Chemistry

In the HCN converter stage a gaseous mixture of ammonia, natural gas and air is passed over the noble metal catalyst where the ammonia and natural gas react exothermically to form HCN:

$$NH_3 + CH_4 \rightarrow HCN + 3H_2$$

Approximately 60 – 65% of the reagent gasses react as above. Of the remaining ammonia, approximately 50% passes through unreacted and the other 50% breaks down to nitrogen and hydrogen.

Virtually all of the natural gas not converted to HCN is partially or completely combusted in air to produce CO_2, H_2O and CO. All unreacted gasses, along with the side reaction products, are sent to the main plant stack for flaring.

The HCN is removed from the gas stream by passing through NaCN liquor containing excess NaOH. Some CO_2 is absorbed at this stage producing sodium carbonate (Na_2CO_3).

$$HCN + NaOH \rightarrow NaCN + H_20$$
$$C0_2 + 2NaOH \rightarrow Na_2C0_3 + H_20$$

At this point in the process some of the unlimed NaCN liquor is fed to the No.2,3 and 4 Stock Tanks, this is known as standard grade liquor.

The liming process is used to convert soluble Na_2CO_3 to insoluble calcium carbonate ($CaCO_3$). This is removed by filtration.

$$Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2NaOH$$

The filtered liquor is known a high quality liquor. A higher grade of sodium cyanide known as Super High Quality Liquor (SHQL) is also produced in the sodium cyanide plant by reacting liquid HCN from HCN6 with 50% sodium hydroxide solution.

<u>Process Flow Diagram</u>

A simplified flow diagram of the NaCN plant is shown in fig 2.3.1.

<u>Process Inputs</u>

Natural Gas

Natural gas is supplied to the NaCN plant by pipeline from site distribution system.

Hydrocyanic Acid (HCN)

HCN used for Super High Quality Liquor production is manufactured in the HCN6 plant. It is imported to the NaCN plant by pipeline to the evaporator section via the ACH3 plant.

Note: The manufacture, import and central storage of HCN is covered in the HCN6 document which forms part of this application.

Ammonia

Gaseous ammonia is imported by pipeline.

50% NaOH Solution

Caustic Soda is delivered by road tanker and is stored on the NaCN Plant.

Sodium Hypochlorite Solution

Sodium hypochlorite is delivered by road tanker and stored to the South side of the NaCN plant.

Catalyst

The noble metal catalyst bed, for the conversion of natural gas and ammonia to HCN, is replaced approximately every 6 months.

Lime

Lime (calcium hydroxide) is imported by road tanker and stored on the NaCN plant.

Water

There are several sources of water used on the NaCN plant:

Demineralised water is used for the dilution of NaCN liquor to the correct strength and to feed the waster heat boiler.

<u>Process Description</u>

Overview (see fig. 2.3.1)

The plant produces HCN by the catalytic conversion of ammonia and natural gas in an air stream. The HCN, combined with liquid HCN receipts by pipeline, is reacted with 50% sodium hydroxide solution to produce sodium cyanide liquor of approximately 30% NaCN.

Conversion and Waste Heat Recovery

In the converter, the mixed gases react exothermically to produce HCN (and hydrogen) on a platinum-rhodium gauze catalyst that operates at a pressure of 1.3 barg and a temperature of 950 –1050^{o}C. Side reactions produce carbon monoxide and carbon dioxide. The hot gases exit the converter and are used to generate steam at a pressure of 21.7 barg in a waste heat boiler. Further cooling occurs with heat exchange with the boiler feed water in an economiser. The process gas, containing about 8% by volume of HCN and 2% of unreacted ammonia is passed to the HCN absorber at a temperature of at least 100^{o}C and a pressure of about 70mbarg.

HCN Absorption

The HCN produced in the converter is absorbed in the HCN absorber, using 50% NaOH, to produce NaCN liquor. An excess of NaOH in the liquor is necessary to prevent localised HCN polymerisation. The absorption process also produces sodium carbonate (Na_2CO_3) by the reaction of carbon dioxide by-product with NaOH. The Na_2CO_3 is removed in the liming and filtration stage. The HCN absorber exit gases, now depleted in HCN, pass to the main plant stack where they are burnt.

Liming and Filtration

The 30 % w/w sodium cyanide liquor made in the HCN absorber contains between 0.6 and 1.15% w/w sodium carbonate. This is removed from the liquor by the addition of 60-175 kg/h calcium hydroxide (lime). The lime addition rate depends on the liquor rate and on the sodium carbonate concentration. Calcium carbonate is precipitated and is removed from the liquor by a rotary vacuum filter (Rovac). The sodium carbonate level is reduced to between 0.1 and 0.3% w/w. The filter cake is washed with water to remove the bulk of the cyanide liquor before being discharged to the toxic effluent treatment section for neutralisation.

The vacuum driving force for the Rovac is applied to the metafilter feed tank using the Nash Vacuum pump that exhausts directly to atmosphere. The liquor is then pumped to one of two polishing filters (metafilters) in order to reduce colour and remove any fines that passed through the Rovac. The sodium cyanide liquor, now substantially free of carbonate, is pumped to cyanide liquor storage via a cooler to minimise hydrolysis of the cyanide to formate.

Evaporation

No.2 Evaporator, the smaller of the two at about 60te capacity, is used to produce Super High Quality liquor, a purer sodium cyanide liquor using liquid HCN imported from the ACH3 HCN storage. This is a batch process using a vessel previously used to produce solid sodium cyanide. Due to the high offtake of the recirculation loop on the vessel, it must be first filled with demineralised water and a heel of caustic to establish a working level. HCN and 50% caustic are then fed to form sodium cyanide liquor.

Steam is applied to the circulation loop to evaporate water purely to control the level in the vessel.

Vacuum is applied to the vessel, using steam ejectors, to minimise hydrolysis of the cyanide to formate and ammonia. The circulation loop must be maintained to ensure correct control over the HCN/caustic reaction. Loss of vacuum, caustic flow, high level low level or recirculation flow trips the HCN feed.

The evaporator overheads (water and a low levels of HCN) are condensed and fed straight to the effluent treatment system.

The product liquor is pumped directly to stock tanks in the liquor storage area.

NaCN Liquor Storage

There are 9 storage tanks in this area, each one set aside for storage of a particular grade of liquor. The maximum liquor storage capacity is 1615 tonnes. Each storage tank is fitted with a level indicator and an independent high level alarm.

Tank No.	Contents
2, 3 & 4	These tanks are used to store Standard grade liquor. (unlimed)
5	Used for the storage of limed, low carbonate liquor for recycle to the HCN Absorber
6 & 7	Used for super high quality grade liquor storage.
8 & 9	Storage of high quality liquor. Like evaporator feed liquor. This liquor has been passed through the liming section and contains less impurities than standard liquor.
Shutdown Tank	This tank is kept empty and is used to drop the contents of either evaporator if a leak of NaCN develops. The tank is sized to take the full contents of either evaporator.

From here all grades of liquor are loaded to road tankers at the NaCN liquor tanker filling depot.

NaCN Liquor Tanker Filling

NaCN liquor is exported as a product in road tankers. Which are filled by selecting a tank and pumping liquor into the top of the barrel. The total flow of liquor is automatically controlled by means of a batchmeter. The area is continuously manned during tanker filling operations.

Effluent Treatment

The effluent treatment facility receives and treats the continuous purges referred to in previous above, and any washings, leaks and spillages which may arise on the NaCN plant and liquor storage and tanker loading area. Additionally, the facility also receives batches of effluent arising from other process areas, these are

- ACH3 and ACH4 cubicle secondary containment sumps
- Purge from the HCN still at HCN6, if too high in HCN to be discharged to BB06

All effluent from the above areas remote from the sodium cyanide plant itself is pumped slowly to the effluent treatment system. If there is a problem with the effluent treatment system, e.g. due to increased load from the sodium cyanide plant, the transfers are stopped immediately.

The alkaline cyanide effluent is treated with 10-15% sodium hypochlorite solution in four stirred vessels in series. The sodium hypochlorite solution reacts with cyanide to form the less toxic cyanate. The treated effluent, containing less than 10 ppm of cyanide, flows to drain where, after mixing with other effluents, it is discharged via a consented outfall, BB03, to Billingham Beck.

The hypochlorite storage consists of 3 tanks, with a total storage capacity of 250 tonnes, filled from road tankers, from which sodium hypochlorite flows to the treatment vessels by gravity. The flows are continuously measured, a high flow being indicative of an abnormally high loss of cyanide.

If the treatment facility is in danger of being overwhelmed by a sudden large increase in cyanide load or if the treatment process fails to function, then the operator may divert the effluent leaving the fourth (final sump) into a large (300 m3) secondary containment pit whilst the problem is being attended to. Later, the contents of the pit can be pumped back into the effluent treatment system for re-treatment. As there are eH analysers in each sump, if there is a spillage the operator will have many warnings before the effluent reaches BB03. The first sump will have high cyanide and then the second, third and finally the fourth. When this sequence starts to happen the operator will divert the effluent stream to the secondary containment pit.

The secondary containment pit has sufficient capacity to contain all of the liquor released from a catastrophic failure of the largest vessel on the sodium cyanide plant.

Caustic Storage and Dilution.

The 50% w/w sodium hydroxide solution used in the absorber and evaporators on the sodium cyanide plant is stored in a series of tanks on the sodium cyanide plant.

The 50% w/w caustic is imported in road tankers and offloaded directly into 3 linked tanks with a 225te capacity. From these tanks the 50% caustic is pumped into a 20te capacity dilution tank located in the storage area where the caustic is diluted to give a 25% w/w solution by the addition of softened water. This 25% caustic solution is used on the effluent treatment sections of the Monomer 7 and Monomer 8 complexes.

An operator from the sodium cyanide plant is always present during off-loading operations.

Drainage Systems

All effluent from the sodium cyanide plant, liquor storage and tanker loading area passes first through the effluent treatment system before being discharged via outfall BBO3. All additional effluent streams which are pumped to the sodium cyanide plant effluent treatment system will also discharge to BBO3

Any effluents arising from the caustic import depot will be discharged to BBO3 via the effluent treatment system.

Process Outputs

NaCN Liquor

Liquor is exported as 30% NaCN in three forms, standard (unlimed), high quality and super high quality which has a lower concentration of contaminants.

NaCN Plant Control Philosophy

The NaCN plant is operated on a continuous basis and controlled and monitored from a Distributed Control System (DCS). Minimum operator intervention is required under normal operation.

Absorption of HCN into caustic soda is the critical step which determines the efficiency of HCN recovery and avoids HCN being burnt. Consequently it is essential that the HCN absorber liquor is always circulating and is always alkaline. The flow of fresh caustic soda solution to the Centre of the tower is ratioed to the converter load. pH control of the circulating liquor adjusts the flow of trim caustic to the recirculation line. The recirculation flow is set at 200 m3/hr.

If either the absorber circulation pump or caustic feed pump fails, an alarm is generated and the operator shuts the plant down immediately. If there is any delay in this action, the liquor inside the vessel will turn black within 3 minutes from HCN polymerisation and the gases from he converter will be burnt in the stack. A runaway HCN reaction could not occur as the solubility of HCN in aqueous solutions containing ammonia is very low (<1% W/W) and the water would remove the heat of reaction. Therefore, the loss of caustic supply to the HCN Absorber is considered to be a product quality issue and not a safety issue.

Ancillaries

HCN Pipeline and Plant Cubicles

The HCN pipeline enables liquid HCN to be transferred from HCN storage at the ACH3 plant, directly into the evaporation section for use in SHQL production. There is no HCN storage on the NaCN plant. All flanges, joints, valves, etc. in this pipeline are located in HCN cubicles.

On shutdown, the pipework local to the evaporators is washed out by an automatic washing system sequence using hot water. The hot water flushes the HCN flow control system through to the evaporators. If the shutdown is prolonged then the entire pipeline from ACH3 to the evaporators is flushed through.

An HCN cubicle comprises of an enclosure whose purpose is to confine any conceivable spillage or leak. Any volatile material spilled or otherwise released within a cubicle is extracted by a fan and discharged via a stack at height where its release into the atmosphere is designed to avoid a significant hazard to individuals, either inside or outside the site boundaries.

The cubicle vent fan is operated continuously and it is treated as local exhaust ventilation in terms of operational checks. The cubicle vent stacks are continuously monitored for the presence of HCN. The cubicles are provided with sumps to contain any liquid spillages.

Decontamination Area

The courtyard of the NaCN plant is used for decontaminating all materials/equipment that leaves the works. All washings drain to the effluent treatment section.

2.3.1 Control of Point Source emissions to Air

To ensure that the emissions to air remain insignificant, besides applying the BAT for Management Techniques, the following are specific to the plant:

1. The major emissions to air are to the plant stack, which is lit continuously to burn any ammonia or HCN that may slip through the conversion and absorption process. The plant flare has been demonstrated to have a combustion efficiency of 99.17%. If the flare cannot be lit within an hour the plant is shutdown.

2. Monitoring and control of various temperatures in the main process equipment helps minimise emissions, by ensuring the process operates efficiently. Key process efficiency measurements are continually monitored.

3. Two cooling water condensers minimise discharges via the evaporator ejector vent.

4. The flanges and valves for the HCN pipeline are contained within ventilated cubicles which discharge via vents at height, which reduces the ground level concentration of components. The cubicle vents are constantly monitored for HCN and have high concentration alarms and trips.

2.3.2 Abatement of Point Source emissions to surface water and sewer

All liquid flows and the slurry from the filtration section of the plant are channelled to the cyanide effluent treatment section via a series of drains and gulleys on each floor of the plant. Any cyanide present is destroyed by reaction with sodium hypochlorite to produce sodium cyanate, in four stirred treatment pits in series.

The addition of sodium hypochlorite to each sump is automatically controlled using an analyser that measures the extent of the cyanide destruction reaction by means of eH measurement of the redox potential.

Emissions reaching the drain then flow to BB03 outfall. The Plant operation complies with its permit to operate, and there are no emissions to public sewers. BB03 is the outfall route for the cyanide effluent treatment plant as well as stormwater run-off from site roads, the site laboratories and the site restaurant. In addition ‘scour water’ is added to ensure that there is sufficient velocity in the drain to ensure that the suspended solids do not settle out, which could ultimately lead to blockages. When the plant is not operational the ‘scour water’ is isolated.

If the treatment facility is in danger of being overwhelmed by a sudden large increase in cyanide load or if the treatment process fails to function the operator can divert the effluent. The flow leaving the fourth (and final) sump can be directed into a large (300 m^3) secondary containment pit, whilst the problem is rectified. The contents of the pit can then be pumped back into the effluent treatment system.

The effluent is diverted by means of a large valve, remotely operated from the sodium cyanide control room, which when closed blocks the drain. The effluent then overflows via a weir into the secondary containment pit. It takes three minutes for the diversion valve to move from fully open to the fully closed position. If the diversion valve fails to close, identified from the valve position indicator in the control room, the operator is required to operate the valve manually. The operation of this valve is tested on a regular basis by the plant operating team.

The secondary containment pit has sufficient capacity to contain all the liquor released from the catastrophic failure of the largest vessel on the sodium cyanide plant. Continuous monitoring of the outfall for consented analytes and alarm values at warning limits ensures that the diversion valve is closed soon enough to prevent consents being breached.

Improvement programme

To ensure that the emissions to water remain insignificant, besides applying the BAT for Management Techniques, the following are specific to the plant

1. All storage tanks are located within bunds. The tanks are equipped with high level alarms and independent high level trips which stop the feed into the tanks.

2. HCN liquor is not stored on the NaCN Plant but is imported as required from the HCN Plants.

2.3.5 Odour Control

Ammonia, Nitrogen Dioxide and Chlorine are the components released from the process that have the potential risk of an odour emission. Ammonia and NO2 are released from the main plant stack which benefits from height and temperature to aid dispersion. Ammonia and Chlorine are present in other intermittent process vents and in the storage tanks where they are present in extremely low concentrations when compared with the odour threshold value. As the compounds are part of a mixture the actual emission concentration should be converted to odour units. This would require the emission to be captured and tested by an odour panel however as the odour risk is believed to be low this characterisation is believed to be unnecessary. The measures taken to limit the releases are described in section 2.3.1.