Coal-Based Ammonia Plant Operation

Useful experience in startup and initial operations on a new facility in South Africa, especially in terms of plant safety

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Experience during the commissioning and initial operation of a South African ammonia plant included a number of safety problems that provided useful knowledge for improved plant operations.

Among the problem areas and situations were the following: a dust bunker explosions; failure of gasifier oxygen isolation valves; erosion from ash particles impinging on boiler tubes; leaks due to failures at joints between piping and vessels; dangers of toxic gases. This article describes these and other experiences.

At the end of 1974, the 1,100-short ton/day coal-based ammonia plant was brought on stream at the AE & CI Modderfontein plant near Johannesburg, South Africa. It is based on the Koppers-Totzek, low-pressure, high-temperature, coal gasification process. The feedstock is a semi-bituminous coal containing about 14% ash, 36% volatiles, and 1% sulfur.

A simplified process scheme is shown in Figure 1. Oxygen for the gasifiers is supplied from a single-stream air separation unit. Coal dust, produced in two large ring and ball mills, is gasified in six gasifiers. Figures 2 and 3 show air separation and gasification units.

The gas is compressed and desulfurized by washing with methanol at −36°F at a pressure of about 30 atm. Desulfurized gas containing about 58% CO is reacted with steam over conventional iron high-temperature shift catalyst to produce hydrogen. Carbon dioxide is removed from the gas by washing with methanol at −72°F at a pressure of about 51 atm.

Final gas purification to remove residual carbon monoxide, argon, and methane is by washing with liquid nitrogen at −310°F. Ammonia synthesis is at about 220 atm. in a conventional synthesis loop with ammonia refrigeration.

The synthesis gas compressor, refrigeration compressor, and the nitrogen compressor are single-stream centrifugal machines, while two centrifugal raw gas compressors and two centrifugal air compressors are provided in parallel. Except for one of the air compressors, all these major machines are driven by steam turbines. Steam for these machines is raised at 100 atm. and 950°F in two coal-fired spreader-stoker boilers.

The process units cover an area of about 14 acres, and are all controlled from a central control room equipped

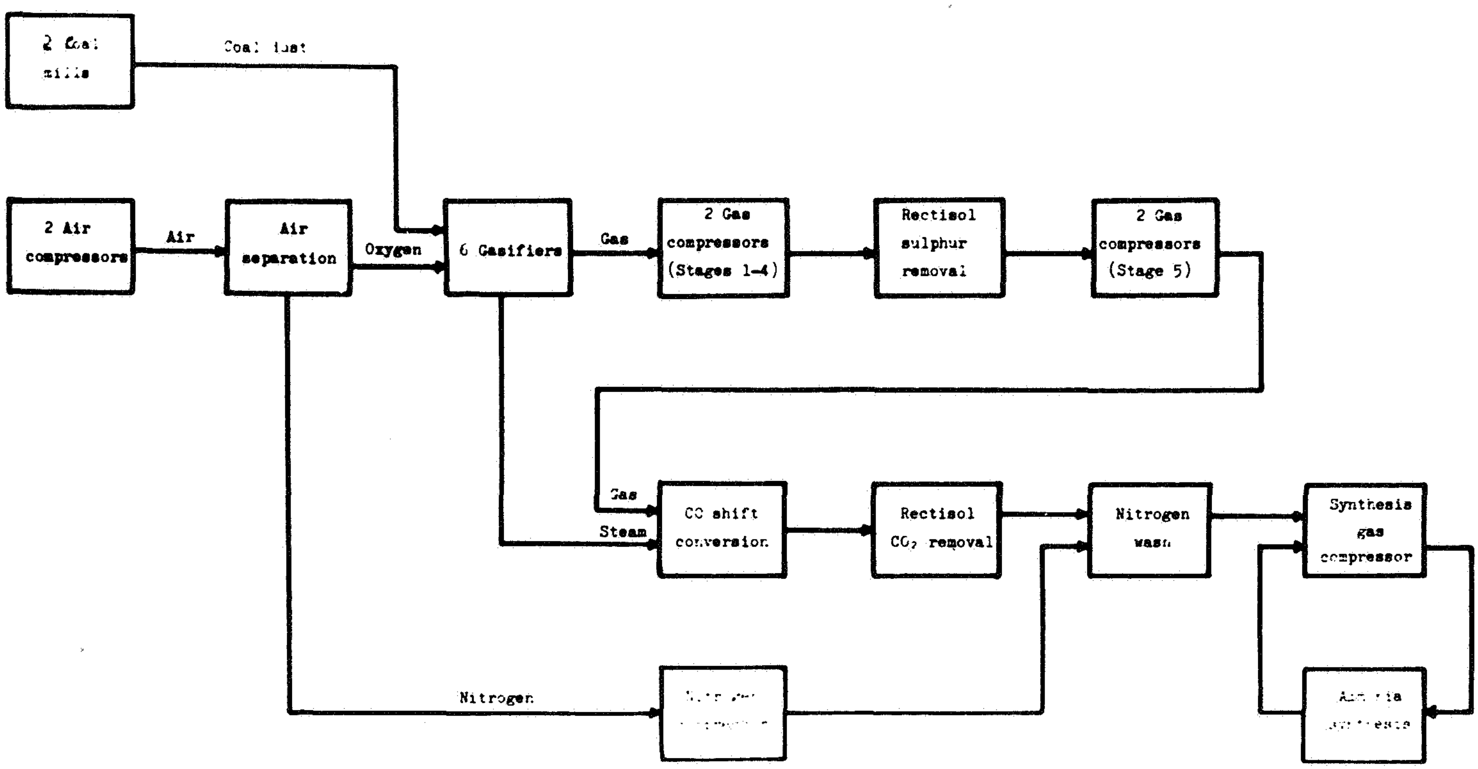


Figure 1. Simplified process scheme.

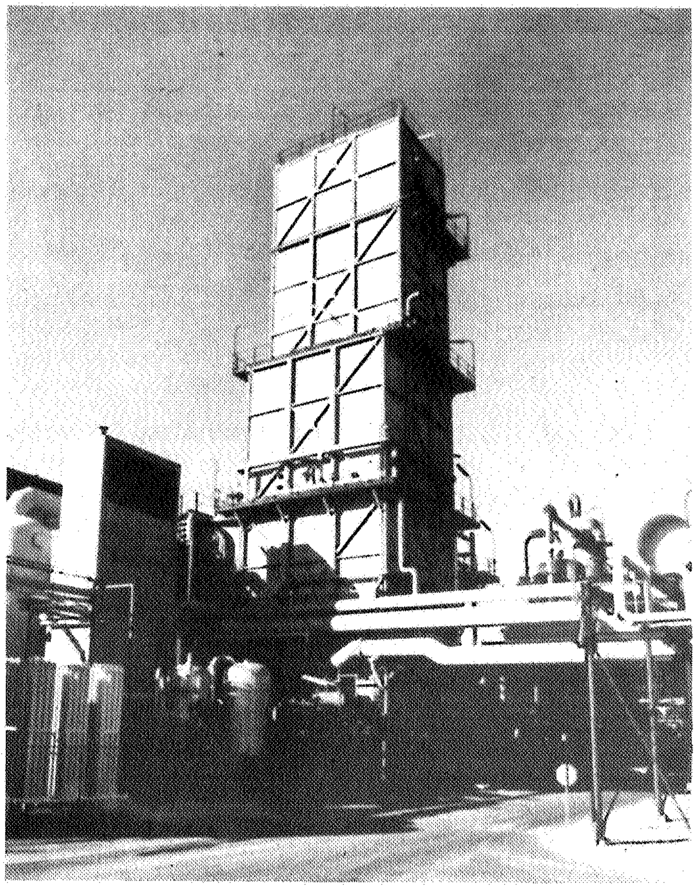


Figure 2. Air separation unit.

with electronic instrumentation. It is illustrated in Figure 4.

Coal is screw fed to gasifier

A simplified arrangement of a gasifier and its waste heat boilers is shown in Figure 5. Coal dust is fed by four screw feeders into blow-pipes. An oxygen/steam mixture introduced at the end of the screw feeders conveys the coal dust at high velocity through the blow-pipes into the gasifier, where the mixture ignites, and the partial oxidation reactions take place.

The coal dust used in the gasification process is very finely milled, 90% of the particles being smaller than 90 microns.

The gasifiers operate at slightly above atmospheric pressure and about 2,900°F. The ash in the coal melts, and part of it flows downwards as a molten slag into a water bath beneath the gasifier. Most of the ash passes up with the gas through a top outlet, where quench water is injected to reduce the temperature, causing the ash to re-solidify. The gas then passes through a radiant boiler and two tubular boilers in parallel, which generate steam at 54 atm. Ash is then removed from the gas in a water wash tower.

A gasifier will operate safely provided:

1. The coal/oxygen ratio is such that reducing conditions are maintained. This implies a steady flow of coal dust from the feeders and a steady flow of oxygen to the blowpipes.
2. The velocity of oxygen/dust mixture in the blowpipe is sufficient to prevent "burn back."
3. Screw feeders are kept supplied with coal dust, enabling a plug of pulverized coal to be maintained at the end of the screw feeder, preventing back flow of oxygen into the coal dust feed bunker.

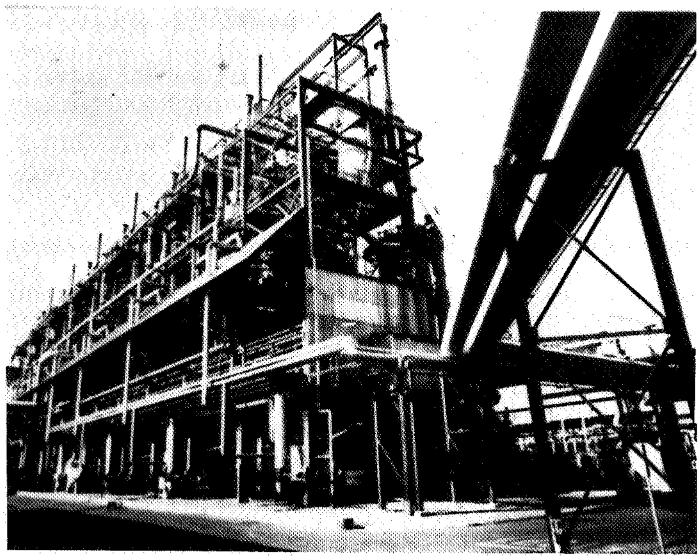


Figure 3. Gasification unit.

Figure 4. Ammonia plant central control room.

During operation, the blowpipe pressures, screw feeder speeds, oxygen flow rates, and dust bunker levels are monitored. If any of these parameters deviate from prescribed limits, the gasifier is automatically shut down. Altogether, there are 28 parameters which can cause a gasifier to trip. We have had many spurious shutdowns of gasifiers, the most common cause being failure of the dust bunker level detectors.

Dust bunker explosion

Failure of low-level probes to operate on demand also caused a dust bunker explosion on one occasion, when it was decided to lower the level in the service bunker on an operating gasifier before taking the gasifier off line for maintenance work. Two low-level detection probes and a mechanical low-level detection probe failed to activate. Dust supply to the screw feeders was lost, and oxygen flowed back into the dust feed bunker, where there was sufficient residual dust to cause an explosion. Fortunately, damage was slight.

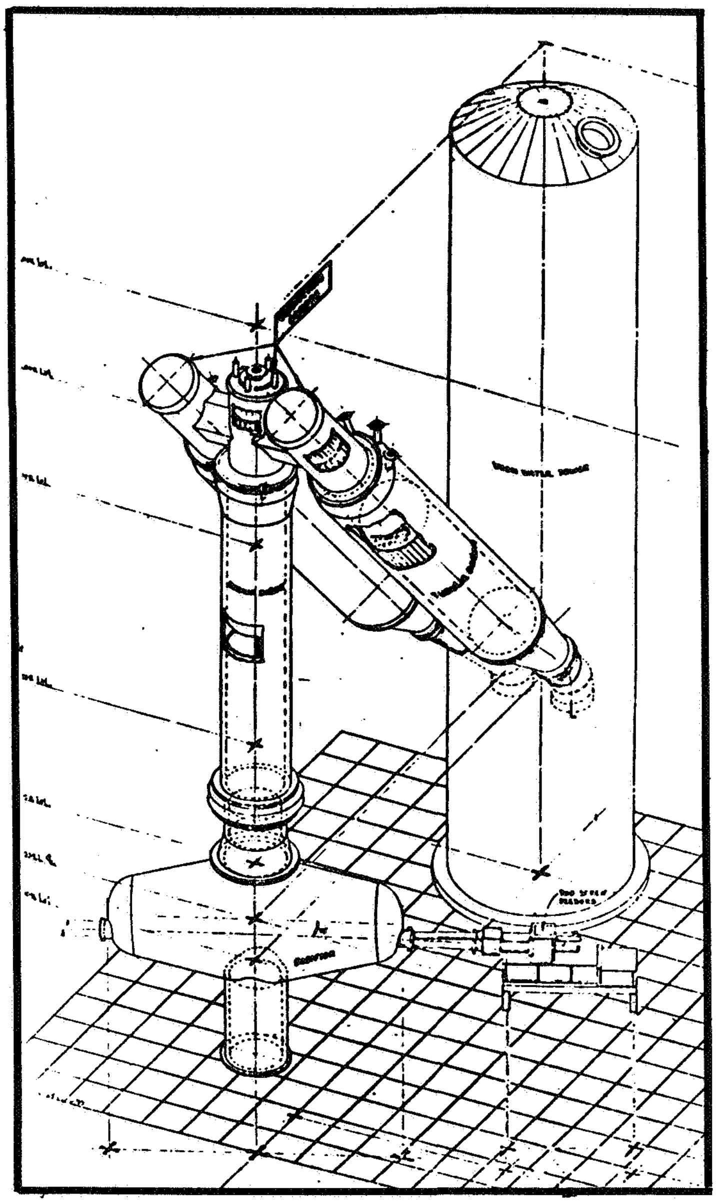


Figure 5. Gasifier and waste heat boilers.

The dust bunker level probes supplied with the plant were of the "capacitance" type. These operate on the principle that dust surrounding the probe will have a higher dielectric constant than the nitrogen in the bunker. The resultant change in capacitance of the system can be detected electronically. These probes have been employed on plants using lignite dust successfully, but we have found they do not operate reliably on coal dust.

An alternative level detecting device is the "tuning fork" probe, in which a fork vibrating at about 80 cycles/sec. is suspended in the dust bunker. Damping of the vibration by the dust is detected electronically. Tests with these probes in our coal dust bunkers have been encouraging and may provide a solution to the problem of detecting dust bunker levels.

Failure of oxygen isolation valves

When a gasifier is shut down or tripped, oxygen to the blowpipes is shut off, the screw feeders are stopped, and the blowpipes are automatically flushed with nitrogen.

On one occasion, an explosion occurred immediately after a gasifer had been tripped. Fortunately, damage was confined to the wash tower and a gas shut-off valve downstream of the wash tower. It was established that the explosion was caused by failure of the oxygen trip valves to stop completely the flow of oxygen into the gasifier. This occurred even though two quick-closing oxygen isolation valves in series, with a trip open vent valve between them, had been provided.

The oxygen isolation valves supplied were butterfly valves with a rubber sealing ring mounted in the disc. Tests showed that these valves could not be relied upon to isolate completely, because the rubber sealing ring near the butterfly shaft tended to jam, preventing full travel of the butterfly. This problem was aggravated by the fact that materials suitable for oxygen at 215°F are generally not true elastomers and tend to deform permanently under stress.

The two basic requirements for an oxygen isolation valve in this service are that it must close quickly and that it must not leak through. We have found these requirements are met by valves employing eccentrically rotating spherical plugs, with flexible arms connecting the plug to the rotating shaft. Positive seal between plug and seat is achieved by elastic deformation of arms.

Three oxygen isolation valves are now installed in series with vent valves between the isolation valves.

Erosion from ash impingement

The radiant and tubular boilers are connected together by three tangent tube boilers, which also raise steam at 54 atm. The gas passing through this system undergoes a change in direction, causing the ash particles to impinge on boiler tubes. The ash, consisting mainly of SiO_2 and Al_2O_3, is abrasive and has caused tube failures in the tangent tube boilers as a result of thinning. Failure of a 54-atm. boiler tube in the gasifier is hazardous because it can cause large quantities of gas to be blown from the water seals beneath the gasifier and water wash tower.

The worst affected boiler tube areas were being eroded at the rate of about 3/16 in. of tube thickness per 1,000 hr. of operation. Fortunately, the erosion is localized and has been arrested by installation of protection plates made of 310 stainless steel. As a trial, we have coated the entire tangent tube surfaces on one set of boilers with an abrasion-resistant alumina material.

Meanwhile, we are monitoring tube thicknesses on the remaining gasifiers to assess whether general erosion might present long term problems.

Leaks due to joint failures

In the first months of operation there have been numerous shutdowns for a variety of reasons. Resultant thermal cycling has given rise to many leaks from failures of pipe and vessel joints. These failures were particularly troublesome on boiler feed water and steam systems, and on process piping and vessels in the carbon monoxide shift unit.

After many forced shutdowns, a team of experts in on-line leak repairs was established on site. This team has undertaken a variety of on-line leak repairs, including a 6-ft. diameter heat exchanger joint which was leaking gas strongly from the tube sheet/end cover joint. The leak was sealed by injecting thermo-setting compound into the area behind the damaged gasket through 60 nozzles which had been fitted into the flange.

Toxic gas hazards

To avoid high concentrations of explosive or toxic gases near ground level, the startup vents, which all release gases at near ambient temperature, discharge to high level flares. The gas produced from the gasifiers contains about 58% CO, and even minor leaks on the plant have led to personnel being affected by carbon monoxide.

The gas compressors have been prone to leakage from casing joints, seals, and lute vessels. Modifications have been made to the sealing system and the lutes and, to further reduce danger to personnel in this area, a carbon monoxide infra-red analyzer will be installed, which will monitor at 12 locations in the area.

The electrostatic precipitators for removal of ash from raw gas were provided with low-level atmospheric vents. These vents had been used on several occasions without incident, for purging the precipitators with gas prior to start-up. When these vents were used on a still, cold night, with severe temperature inversion conditions, gas released did not rise or disperse. Under these extremely unusual weather conditions, a laboratory assistant taking a sample from the top of the precipitator was overcome by carbon monoxide and fatally gassed.

This unfortunate incident led to a complete review of all vents on the plant, and modifications have been made to avoid venting any significant quantities of gas without flaring or dispersing. This applies particularly to gases which are at ambient temperature or colder.

Oil fire due to relief valve failure

One one occasion an oil fire broke out at the synthesis gas compressor oil console. It rapidly spread to the nearby refrigeration compressor console. The fire was extinguished after approximately eight minutes using portable foam generators and fire extinguishers.

A screwed connection on an instrument impulse line on the seal oil system had failed, spraying oil onto a small steam pipe which had not been covered with insulation. Shortly before the incident, difficulty had been experienced in starting seal-oil pumps. When a fault was cleared in an electrical substation, one of the pumps started automatically with the control valves on the seal-oil system blocked in. The relief valve on this pump failed to operate because of an internal fault, resulting in over-pressure and failure of the instrument pipe connection.

The basic cause of the fire was the relief valve failure. It should be mentioned, however, that screwed fittings employing compression ferrules depend on the correct degree of compression of the ferrule being achieved during assembly. Since it is not easy to ensure this, we are trying to elminate such fittings on systems carrying flammable materials at high pressure.

The fire caused severe damage to instrument cables on nearby overhead racks. This demonstrated to us the vulnerability of these cables to fires and we are considering possible ways of protecting them.

Shutdown voting for better control

Where large sections of the plant or critical plant items are required to be shut down on detection of a parameter outside safe limits, a two-out-of-three voting arrangement of sensors have been used. For example, the oxygen concentration of the combined gas stream from the gasifiers is monitored by three oxygen analyzers. Any two of these measuring greater than 0.5% O_2 will cause all gasifiers to be shut down.

Voting systems have also been used in the automatic shutdown of centrifugal compressors on rotor axial movement. In the past, there has been a reluctance on the part of compressor users to connect axial displacement monitors to shut down automatically, mainly because of the high spurious failure rate of the instrumentation.

By use of a two-out-of-three voting arrangement of two axial displacement monitors and one thermocouple, embedded behind the thrust pad babbit layer, the following improvements are predicted:

1. The virtual complete elimination of spurious trips due to instrument failure.

2. A tenfold reduction in the probability of failure on demand.

A mixture of axial displacement monitoring and bearing temperature rise is used because measurement of different parameters avoids trips arising from a common source of failure and increases confidence that actual failure has been detected. Our experience with this arrangement has been entirely satisfactory to date.

Prior to commissioning, dynamic model simulations were used to predict the process response to upsets, such as a trip of the synthesis gas compressor. It was forecast that no difficulty would be experienced in tuning instruments to react to these upsets in a stable manner. These forecasts have been confirmed. The gas purification and CO shift units have a number of large capacity vessels operating at high pressure, which provide inherent stability. Thus, events such as synthesis gas compressor trips have a relatively mild effect on the gas purification and CO shift units.

Heat is recovered from the CO shift and ammonia synthesis by preheating boiler feed water, and from gasifiers by raising process steam. The two coal-fired boilers provide all the steam required for driving the turbines. There is thus less interaction between the process and the steam system than on a conventional gas or naphtha-based ammonia plant.

This advantage is nullified by the relatively slow response of the spreader-stoker, coal-fired steam boilers. With a spreader-stoker boiler, the response to increased steam demand is to increase first the combustion air, then the coal feed rate. This causes increased rate of combustion of coal already on the grate. With a well tuned control system steam, production can at best be increased at about 10%/min., compared with about 20%/min. for a typical gas-fired boiler.

Owing to better than design heat transfer performance of the boiler superheater, the automatic combustion air control system has not been commissioned in order to avoid high temperature excursions on the superheater. With manual control of combustion air, we have experienced some difficulty in preventing loss of 100-atm.

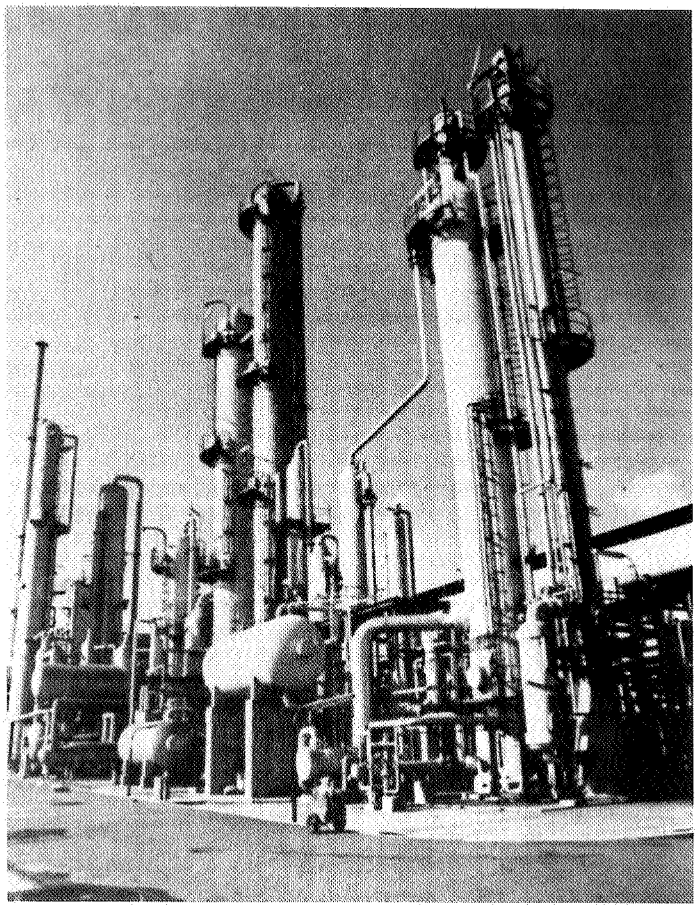


Figure 6. Rectisol gas purification unit.

steam pressure during short term increases in steam demand. Superheater modifications are planned, and once the combustion air automatic control system has been commissioned we expect a faster response from the boilers.

Environmental aspects of the plant

The high operating temperature of the Koppers gasifiers results in gas containing only about 0.1% methane and no detectable amounts of higher hydrocarbons or coal distillation products. This is an advantage in view of the strict effluent controls in force at Modderfontein.

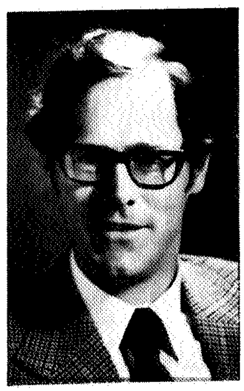
Hydrogen cyanide is present in the gas stream in small amounts, said to be dependent on the ash composition. For the coal in use at Modderfontein, we find 6-17 ppm.v/v of HCN in the gas produced. The coal ash contains about 17% Fe_2O_3, and analyses show that HCN reacts with this iron so that the water from ash settling dams contains only 0.2-0.5 ppm. of HCN.

Combustible sulfur in the coal appears as H_2S and COS in the raw gas. A by-product gas containing about 60% H_2S and COS is produced from the Rectisol desulfurization unit, seen in Figure 6. This gas is usefully burnt in a nearby sulfuric acid plant pyrite roaster.

The ash content of the boiler flue gas is reduced to about 100 mg./cu.m. (normal) in electrostatic precipitators, at which concentration no emission can be seen. Unfortunately, the operation of the precipitators on the coal milling plant is not entirely satisfactory, and work is in progress to try and reduce the coal dust emission to the desired concentration of 150 mg./cu.m. (normal).

Conclusion

The first few months of operation of the plant have not revealed any fundamental safety, control or environmental problems associated with the coal-based process. #



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