Carry-Over of Absorption Solution in Petrochemical Complex: A case study

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Abstract

A case study was conducted to investigate the reasons behind decline of a CO_2 compressor processing capacity in 1,000 tonne/day urea plant. The suspicious sources and the problem route were investigated. Preliminary investigations revealed that the compressor internals suffers from deposits of white powder. Laboratory analysis showed presence of potassium salts. These deposits are believed to be responsible for this decline in the compressor capacity and consequently, reduction of the urea plant productivity.

In periodic events during turn/around or when the productivity reduced significantly, the plant has to shutdown for cleaning the compressor. Deionised water (during T/A, every tow years) or online LP steam (during normal operation period) is used for washing and cleaning. Forced shutdown for one day can simply result in direct losses of production worth of thousands US dollars (urea price > \$200/m.t.).

 CO_2 feed to urea plant is supplied from acid gas removal section (Benfield section) in ammonia plant that uses hot potassium carbonate solution as absorption solution. The study methodology to identify the main causes of problem is presented along with brief details on process equipment inspection and evaluation, laboratory analysis, and process simulation. Main findings and future plan of work are presented.

Key words: Urea Plant, Benfield Process, Carry-over phenomenon, operational analysis

1. Introduction

 CO_2 removal unit was operating satisfactorily with regard to the CO2 removal capability but was performing unsatisfactorily with respect to present a clean CO_2 gas which is sent to urea plant.

1.1 Ammonia Process

Ammonia is produced from water, oxygen and NG (Fig.1). Ammonia plants are commonly integrated with other plants, particularly with fertilization such as urea plants which make use of the CO_2 produced in ammonia processes as by-product. In the ammonia plants, there are several purification stages and reactions on catalyst reactors that those are the key to successful and economic operation. CO_2 should be removed as it acts as poison to ammonia catalyst.

1.1.1 Benfield Process (CO₂ Removal System)



Fig. 1 Chemistry of Ammonia Process [1,17]

The potassium carbonate to CO_2 absorption has been known for many years. The <u>Ben</u>son and <u>Field</u> have owned a patent of hot potassium carbonate process that called <u>Benfield</u> Process [2]. The absorption and desorption are based on the following reaction:

 $K_2CO_3 + CO_2 + H_2O = 2KHCO_3 + Heat$ ----- (1) The existing Benfield Process consists of a packed absorption column to absorb CO₂ in the lean Benfield solution (Benfield solution contains aqueous potassium carbonate/bicarbonate, vanadium and Diethanolamine; see Fig. 2). The CO₂ rich solution from the absorber is then stripped of its dissolved CO₂ with steam in another packed column (regenerator column) to produce lean solution. The outlet process gas from Benfield section absorber has very low CO₂/CO Concentration (0.1% / 0.3%).



Fig. 2 Benfield Section Schematic with Major Equipments

Desorber has one washing tray at the top, situated above the packed bed, and utilizes part of returned condensate to wash the outlet CO_2 gas from any entrained solution. A mist eliminator is also provided to remove entrained liquids with gas. The CO_2 gas is then passed through heat exchange coolers, then through the condensate separator unit. CO_2 now has high purity and ready to deliver to urea plant.

1.1.2 Operational History of ammonia plant

The plant was commissioned in 1978 with design capacity of 1,000 MTPD and revamped in 1991 to increases the production capacity to 1,200 MTPD. In early 1990s, the company, which carried out the upgrading, claimed in its feasibility study of upgrading that the Benfield section was capable to handle the upgrading without need

for any major modifications. The quality of CO_2 gas was not changed significantly but the total volumetric flow rate was increased by 3.4% (wet basis) of the original flow rate.

Long term of successful operation in ammonia plant revealed that there was no sign or evidence in the plant boundary limits that might indicating there was a problem related to potash carry over. The carry-over phenomenon was not been noticed neither with CO_2 stream from desorber nor from the process gas stream from absorber. On the other hand, the problem was noticed in urea plant which receives the CO_2 from ammonia plant.

2. Urea Process

Urea is produced by combining ammonia and carbon dioxide at high pressure (140 bar) and high temperature (180-190°C) to form ammonium carbamate, which is then dehydrated by heat to form urea and water, according to the following reaction:

 $2NH_3 + CO_2 \rightarrow NH_2COONH_4 \rightarrow CO (NH_2)_2 + H_2O$ ----- (2)

Pressurised CO₂ is critical issue for the urea operation.

2.1 Operational History of urea plant

Urea plant was commissioned in 1981. Since start up, the plant was rarely shutdown due to internal problems. However, during turn-rounds small quantities of potash deposit in CO_2 compressor were noticed but were not causing great concern as these deposits was causing ignorable limitation in the operation load. After upgrading ammonia plant came again to operation (1991), the problem of heavy potash deposits has been experienced since start-up operation significantly leading to shutdown of the plant in some events.

A number of modifications have been implemented to overcome this problem without sign of success. These implementations include modification on the CO_2 supply pipeline such as modified drains and installation of traps to provide better drainage of condensate. Furthermore, an impingement plate was installed in gas inlet nozzle in upstream knock out drum of the CO_2 compressor. Yet, there was no improvement of situation.

During turn-around (planning shutdowns), since 1996 and whenever the CO_2 Compressor is shut down; the low pressure section was cleaned with LP steam as temporary solution as per in-house procedure. This washing avoids opening the compressor for cleaning and assures restoring the compressor performance. This temporary solution improves the performance for a while as the performance was gradually lost within three months from cleaning. Moreover, during every available opportunity, the compressor is cleaned in order to maintain steady performance for compressor as far as possible.

3. Potash Carry-Over: Problem Statement

The potash transfers from CO_2 desorber at ammonia plant up to CO_2 compressor in urea plant. It was reported that the CO_2 compressor experiences deviation from design values with compressor vibration. Its efficiency has deteriorated in relatively short operation time after cleaning and maintenances jobs, roughly within three months. This leads to load limitation for compressor and then resulting in dropping of urea production. Ultimately, it leads to force the plant to shutdown for cleaning purposes. Repetition of this cycle of shutdown, cleaning and start-up is burdening the facility equipments and production. During urea turn-around, the maintenance of the compressor indicated that there were smooth deposits of white scale layer inside the compressor in the low pressure section (first and second stages); see Photo 1.

Photo1: Deposits on the Compressor's Internals

In order to maintain stable operation conditions, reduction of CO_2 flow rate to compressor becomes essential. Moreover, increase of compressor energy load to overcome capacity limitations is applied. As a result, the urea plant productivity is reduced gradually. The

chemical analysis of deposits confirmed presence of potassium carbonate (K_2CO_3) and bicarbonate (KHCO₃) salts which are defined as Potash (Table 1). The chemical composition is similar to the absorption solution used in Benfield section.



Table 1 Analysis of Deposit			
K ₂ CO ₃	87.02 %		
KHCO ₃	12.52 %		
Fe + Water	0.46 %		

4. Potash Presence along CO₂ Path: Indication and Monitoring

The monitoring program is applied for tracing and tracking the potassium ions transfer. It has been found that potash is available in profile along the CO_2 pipeline and scrubbing facilities from ammonia plant upto urea plant. The analysis of potash presence in CO_2 path defined, as presence of potassium ions (K⁺) in water or condensate, has been carried out on regular basis to follow up the problem. Some analysis may be done on hourly basis when the problem starts to affect the compressor. The following illustration in Fig. 3 confirms presence of potash profile in different locations. It covers area of CO_2 transfer line from the Desorber in Benfield section upto the compressor in the urea plant. Clearly, CO_2 passes many scrubbing, separation and washing facilities before enters the compressor. However, potash concentration is presence before the compressor in unexpected concentration.



Fig. 3 Presence of Potash in Condensates and Circulated Water

In normal situation and per design, the potash concentration should be 6 ppm or less in the first scrubbing unit downstream the CO_2 desorber (Fig. 3, it is 2.5 ppm) and should be nil in the last scrubbing unit before the CO_2 compressor directly (Fig. 3, it is 36 ppm). Fig. 3 shows average values and they are usually found in neighbourhood of these values.

5. Analysis of Process and Scrubbing Units along CO₂ Path

Evaluation of the process and scrubbing units along CO_2 path are essential to check whether they are involved in the potash carry over problem or not and to what extent they are. These units handle CO_2 at different stages and conditions from ammonia plant to urea plant. The evaluation was done separately and will be illustrated as follows; CO_2 compressor, Knock-out drum, CO_2 pipeline, CO_2 cooler and finally to the CO_2 desorber.

5.1 CO₂ Compressor

Carbon dioxide compressor is one of the most critical equipments in urea plant as urea production based on a chemical reaction between NH_3 and CO_2 under high pressure. Centrifugal compressor with four stages and intercoolers is used to compress the coming CO_2 from ammonia plant, which is relatively at atmospheric pressure (1.10 kg/cm²a & 39 °C), up-to high pressure (143 kg/cm²a & 125 °C). The output conditions are the feed conditions of urea production process. Because of cooling, a very small amount of water would be condensed as result of variation in operation conditions between stages. Obviously, CO_2 feed stream is saturated

with water. The compressor consumes power through steam turbine. To develop the required gas velocities and head, impellers must rotate at very high speeds which make design of the compressor components (e.g. driver, gear) and its operating conditions extremely critical. The operation data were used in order to calculate the stages' efficiencies (Table 2).

Table 2 Compressor Designed Terrormanee Data					
		Stage 1	Stage 2	Stage 3	Stage 4
	Compression Ratio	4.578	4.876	2.813	2.131
Design	Adiabatic Efficiency	67%	60%	44%	66%
Normal	Adiabatic Efficiency	65.41%	61.1%	46.2%	66.8%
Operation					

Table 2 Compressor Designed Performan	ice Data
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The problem can be noticed from presences of potassium ions in condensates, increase the compressor vibrations and variation of operating conditions as reported (Table 3).

	CO2 Flow Rate	2nd discharge	2nd discharge	Steam Flow to	
		pressure	temperature	Turbine	
Before Cleaning	95 % from normal	107 %	110 %	108 % from normal	
After Cleaning	100% from normal	100% from normal	100% from normal	100% from normal	

Table 3 Operation Condition before and after Cleaning the Compressor

There is no recommendation can be given as the compressor is not the sources of problem but it suffers from it.

5.2 Knock-Out Drum

A knockout drum is provided to eliminate mist entrainments in the CO_2 gas fed to the CO_2 compressor (see Fig. 3). This drum is a vertical vessel accommodate with 150 mm thickness mist eliminator. Checking the design is demanded to know whether this unit does functioning perfectly or not.

5.2.1 Drum Size

Typical dimensions for standard knockout drums cannot always be generalized for all drums and in some cases specific design parameters are making the drum unique. However, it is a good way to compare knockout drum with typical drums dimensions. Four sizing methods were used in this study (the first and second are called the sizing of separator [2,4], the third is called the selecting gas/liquid separator method [5] and the forth is the knockout drum design method [6]).

They produced good demission values and specially the first and second methods. However, some deference values were also found for the other two methods regarding the disengagement. The disengagement height is less than typical values of both methods. The minimum height should be at least half the tower diameter and this important because it reduces non-uniform gas flow through the mesh pad. However, this comment is disregarded as the four methods prove the drum design satisfactory.

5.2.2 Operating Vapor Load

Mist eliminator is important device in order to hold back the entrained liquid droplets. The superficial velocity of gas should be lower than 4 m/sec in order to prevent any re-entrainment from this device. Pressure drop generated across the wire mesh is usually very small; however, it should be monitored but in the existing drum there is not any. Wire mesh may become partially clogged with time, partially or fully flooded. Therefore, it can malfunction due to one of the following suspicious phenomena:

- 1. Damage of mist eliminator,
- 2. Blockage of mist eliminator,
- 3. Entrainments at High loads (high gas velocity),
- 4. Unsuitable of mist eliminator,

The mist eliminator pad is accommodated with 150 mm thickness which is known as a prefect typical size [5]. The first and second points were declined as inspection confirmed that there was no damage or blockage for mist eliminator but even it was clean.

Entrainment can be very high and this depends on droplet size that can be gone out form the mist eliminator. Drum height provides elimination of small droplets in vapor space. Mist eliminator provides the finishing function for the elimination mists of very small droplets. The size of minimum droplet can be determined as follows:

Determination of minimum droplet size settle down by gravity can be found by using Stoke's law [3, 5]. At normal operation vapor velocity, the min. droplet size cannot be settle down is 200 μ m and less than this size will be carried out with vapor. Mist eliminator provides a finishing as the last barrier in face of smaller 200 μ m droplets.

The key design variable for entrainment in separation vessels is the vapour load factor "K value" which was derived by Souders and Brown [4, 6, 7]. Their derivation is based on force balance calculation on a droplet falling through the vapour space.

$$K = V X (\rho_V / (\rho_L - \rho_V))^{0.5}$$
 ----- (3)
Where;

$$K = \text{Load Factor (m/sec)}$$

$$V = \text{Vapor Velcotiy (m/sec)}$$

$$\rho_V \text{ and } \rho_L = \text{density of vapor and liquid (kg/m^3)}$$
For normal operation, the K loading factor is 0.061 m/sec. The K value

For normal operation, the K loading factor is 0.061 m/sec. The K-value for vertical knockout drum typically designed to operate between 0.061-0.106 m/sec which is the optimum range [5].

The mist eliminator might flood during operation if the velocity goes beyond the designed value (1.41 m/sec) leading to high loads mentioned in third point of suspicious phenomena. In our case, the velocity is maintained below this value (i.e. 1.41 m/sec) which confirms the tower design and operation is acceptable. Vapor velocity a cause flooding was checked with recent correlations on performance of mist eliminator [8]. The results show the operation is far a way from flooding. The operating pressure drop is estimated to be 0.001089 kg/cm^2 . Therefore, the third suspicious point is declined.

It can estimate the droplet size that cannot be captured by mist eliminator by using the Fig. 4. Typically, the 150 mm mist eliminator cannot capture the average drop size of 10 μ m and below [5, 6]. From Fig. 4, the droplets sized in range 50 - 4 μ m cannot be eliminated from going to the CO₂ compressor. Estimation of entrainment quantity (Fig. 4) would be approximately between 0.028 – 0.28 mg/m³ (540.8 – 5,408.7 mg/hr).



Fig. 4 Entrained Concentration of Water at Atm. Conditions [5]

Let us assume that this amount of entrainments would contain some dissolved potash in varies concentration as indicated in Table 4 (in wt% potash). The concentration range is assumed from very low and up to the salt concentration of potassium carbonate absorption solution in the Benfield Process.

Potash* in water, wt %	540.8 mg/hr	5,408.7 mg/hr
0.01	0.05408	0.54087
1	5.408	54.087
10	54.08	540.87
30 (absorption solution)	162.24	1,622.61

Table 4 Estimated of Potash Carried Out by Gas Outlet from D-101

* Potash as 87.48 % K₂CO₃ and 12.52% KHCO₃ (Estimated 50% is K⁺)

Generally speaking, liquid entrained droplets have potash concentration vary from very small concentration upto 30 wt. % (Table 4); although the CO_2 gas passes through many scrubbed units. The calculation result was

in *agreement* with estimated values of potash flow rate (1,440 mg/hr Potash) reported by urea plant. This shows that the forth subspecies point is most likely the case. The mist eliminator is not suitable for eliminating potash from going to the CO_2 compressor therefore it should be changed or upgrade to better type.

5.3 CO₂ Pipeline

It is 1,500 m long pipeline carry CO_2 gas (at relative humidity of 100%) from ammonia plant to the urea plant. the pipeline is protected from direct sun and rain, and it is thermally insulated in order to minimize temperature losses and drafts effects on the CO_2 temperatures (the inlet temperature is around 45°C and at outlet is 39°C). Pipeline is provided with 10 condensate drains (traps) to remove condensate at different locations. Inspections confirmed that all drains are working probably. The prediction results were shown that at first traps in the line the water condensate will eliminate any potash to be further carried out with the gas stream even in case of large amount of potash associated with CO_2 gas stream. There was an assumption that CO_2 pipeline might be fouled with potash or potash precipitated in large amount somewhere in the pipe. This possibility was dropped as the internal inspection showed no sign of any accumulation the pipeline.

5.4 CO₂ Cooler

The CO_2 cooler function is to cool and wash the CO_2 gas. This tower is responsible to eliminate of any potash can be available with CO_2 stream. The CO_2 cooler is a packed tower with Raschig Rings (Polypropylene) packing materials. The CO_2 gas outlet should be around $45^{0}C$ (see Fig. 5).



Fig. 5 CO₂ Cooler at Normal Operation Conditions

5.4.1 Performance Evaluation of CO₂ Cooler

1- Packing Pad

Raschig rings packing are used widely as they are usually cheaper per unit of cost but some times less efficient than many other types. This lower efficiency due to production of considerable channelling and directs more liquid to walls of tower rather than distributing them equally. Dumping of Raschig rings is flexible for in loading, operation and handling of dirty fluids. For better design, the column diameter dividing by packing size ratio should be greater than 30. In existing system, it is 54 and fully satisfactory [9].

2- Trough Liquid Distributor

This type of distributor has capability of handling large vapour loads and it allows for good liquid distribution. This type of distributors is usually used with structured packing rather than dumping packing. This is due to desire to have an over flow sheet of liquid on the packing. It has been mentioned [7, 9] that this type of distributor cannot produce uniform distribution over packing and especially in the area near or next to tower walls. Poor distribution reduces the effective wetted packing area and promotes liquid channelling. In the dumped conditions most packing follow a conical distribution down the tower with the apex of the cone at the liquid impingement point. After about 3.5 m of vertical height [5], the liquid tends to flow vertically downward unless redistributed. To overcome this flow behaviour better and efficient packing is recommended.

3- Pressure Drop and Flooding Condition

The pressure drop and flooding condition can be determined based on the generalized pressure drop correlation (GPDC) for packed beds. The check of operability at different loads to improve the performance of separation was investigated. The flooding factor and pressure drop are within safe values even if the water flow rate is increased from 120 m³/hr up to 220 m³/hr. Entertainment would be enhanced by flooding conditions and as the flooding factors predicted within normal range, entrainment would be negligible. There is an agreement between pressure drop measured and predicted.

4- Elimination of Potash

The active area available for contact between water and CO_2 is small (may be due to escaping amount of gas without washing or liquid channeling). This could cause the escape of potash with gas outlet and increases the gas outlet temperature which is what was noticed on site. Calculations were carried out to test a number of possibilities. Fig. 6 shows the tower system with water make-up flow rate.



Fig. 6 Prediction Results with Demineralised Water Make up

Clearly, no potash can escape form tower in any scenario of potash quantity come with CO_2 gas. The possibility of potash escape from this tower is very small (all potash will be dissolved in water). Therefore, potash carry over should be eliminated even if large amount of potash is associated with CO_2 . This is not the actual situation on site.

5- Mist Eliminator and liquid Entrainment

As recommended rule of thumb and to avoid liquid entrainment with the vapour out of the tower, the K load factor value is used. If the tower operates at vapor velocity beyond normal operation velocity of 1 m/sec, it will overload leading mist eliminator be flooded and enhancing heavy reentrainment.

The droplet size that can be captured by mist eliminator can be determined by using the Fig. 4 illustrated previously in the evaluation of knock out drum. As mentioned, the 150 mm mist eliminator cannot capture the drop size less than 10 μ m [5, 6]. From Fig. 4, the droplets sized in range 50 - 4 μ m cannot be eliminated from going to the CO₂ compressor.

6- Disengagement Height

It can be checked with utilization of sizing method given by Amistco [4]. The current height is 0.75 m and in agreement with Amistco sizing method (≥ 0.6 m).

5.4.2 How to Improve CO₂ Cooler Performance

Increase of the water flow rate upto 200 m³/hr can be applied easily without any modification to improve washing efficiency. Pump and current Seawater cooler can handle the increase of circulation water flow. The design and rating tool from Alfa Laval (webCAlc) was used to simulate this unit [10]. There would be increase in heat load on this unit. This means there is a necessity for extra heat transfer area (may be by installed extra plates) or by installing another plate and frame heat exchanger. Normally, this type of heat exchanger can be increased in its capacity by 16% of original designed [10].

5.5 Benfield CO2 Desorber Evaluation

The evaluation of Benfield section at ammonia plant was carried out. This tower is the source of the potash carry over problem. Investigations were concentrated to find out why potash solution is being carried out CO_2 stream. The process simulation obtains the answer. Evaluating of absorber and desorber were done and compared with current operating data mentioned in the plant data recorded.

A number of operating scenarios were investigated to help in identifying any unseen reasons in the process behind the problem. Results have been obtained after many trails. It was concluded that this tower is very sensitive to any small change in the operation conditions such as heat loads from the reboiler or temperatures variation or even the pressure profile across the column.

GPDC Sizing method was used to check sizing of design and operation of this tower. Sizing results were within acceptable ranges with respect to flooding and pressure drop for both original and revamp designs. The tower is fully capable to handle liquid and gas loads in original design and revamp case. Foaming tendency of the solution is monitored and found to be within acceptable level; although there is small degradation of DEA.

5.5.1 Maloperation Checking

After revamp the tower seems to operate in the borderline designing capacity of the desorber. The increase of vapor load and circulation rate was applied. However, the desorber should handle revamping case easily. Checking maloperation of desorber was investigated as follows;

1- Mechanical Configuration of Outlet Nozzle & Mist Eliminator

The outlet nozzle location plays a great role in the vapor flow behaviour. In our case, side outlet can enhance disturbances of the flow which might cause local re-entrainment on the mist eliminator (due to non-uniform velocity profile on the top section).

To overcome this, two options is possible;

1- change the outlet nozzle to be in centre of top section,

2- Or improve mist eliminator to prevent velocity variation and local entrainments.

However, the first option requires investment and many modifications which are not possible in the current situation. The second option is worthy for further investigations. Special design of mist eliminator at different thickness should be applied but no information was found on such type of mist eliminator



Fig. 7 Ammonia Desorber Top Section

In general, mist eliminator typically is capable to eliminate very small liquid droplets (i.e. 10 microns). The pressure drop across a wire mesh pad is sufficiently low to be considered negligible. The mist eliminator is efficient only when the gas velocity is low enough that re-entrainment of the coalesced droplets does not occur. If the flow becomes high enough above normal value of 2.14 m/sec (overloading), the re-entrainment would be occurred as mist eliminator would be under flooding.

2 - Disengagement Height

The disengagement height from top surface of mist eliminator upto the central outlet nozzle of gas is 0.95 m which is not enough as recommended value mentioned elsewhere, 3.1m [4], 2m [5], 2.5m [6], and 1.82 m [11]. This cannot be improved as required further mechanical modification to the tower.

3- Desorber Operation

Operation conditions and equipment's malfunction might be a reason behind the carry-over problem. The conditions can give an indication are increase of process gas flow rate and/or change of tower temperatures. These changes might generate due to upsets in the ammonia plant as a whole (i.e. change of process gas flow rate).

Temperature and pressure at the tower top section have a significant influence on the stability of operation. Top section pressure is usually well controlled through controlling gas outlet flow. However, pressure build up can be experienced at very high flow rate and in very short period of time. This increase will create backpressure to the desorber. The pressure controllers will response immediately to reduce any change in pressure to normal value. Slight increase in pressure enhances increasing of temperature and this can generate huge load differences in operation. Furthermore, the expected sequence of changes that might lead to the overload could be assumed as follows;

- 1. Change of heat load supplied to the reboiler due to changes in temperature or flow rate of process gas coming from shift reaction section,
- 2. Change of temperature profile in the tower leading to create extra water evaporation (high quantity of flow could be generated),
- 3. High load builds up as well as the pressure in the downstream equipments. Pressure increases and control system responses to reduce this increase in pressure.
- 4. Operating at high pressure leads to extra water to be evaporated with respect to that condition. Sudden carry over of solution and washing water due to flashing occurs,
- 5. Overloading of the downstream equipments occur due to over flow rate (high velocity gas flow) travelled as plug flow.

Alternatively, may be in the other way around. Pressure change may occur first rather than change in the heat load supply to the tower. Table 5 summaries results of a number of scenarios on desorber performance. Depend on both top pressure and heat load supplied to desorber, operation performance of tower can be predicted (i.e. outlet conditions obtained). In all cases, CO_2 flow rate is constant and only water causes changes.

As can be seen, over heat load supply can increase the outlet flow rate considerably as well as the outlet temperature with top section pressure. Water evaporation is always the result of this increase as it evaporates significantly with temperature change corresponding to the pressure operating at that situation. Optimum value for removal of CO_2 and evaporation of water should be determined at each operation scenario.

		Тор	Heat Load	Outlet	Outlet Flow	
		pressure,	Supplied to	Temp.,	Rate, (%)	
		kg/cm ²	Desorber, (%)	(%)		
Reference*	Normal	1.4	100 %	100 %	100 %	
Scenario 1	Case 1	1.4	117.13%	102.02%	117.03%	
	Case 2	1.4	136.04%	103.74%	136.40%	
Scenario 2	Case 1	1.45	76.78%	98.02%	83.40%	
	Case 2	1.45	102.34%	100.91%	99.75%	
	Case 3	1.45	134.26%	104.40%	132.05%	
Scenario 3	Case 1	1.47	83.74%	97.41%	78.96%	
	Case 2	1.47	96.15%	99.81%	89.91%	
Scenario 4	Case 1	1.5	117.13%	102.02%	117.03%	
	Case 2	1.5	136.04%	103.74%	136.40%	

Table 5 Desorber	Simulation Results	at Different Opera	ting Conditions
	omulation results	at Different Opera	ung conditions

This is the original reported operating condition according to the design.

Flooding conditions might be experienced even for very short period of time in the top section. It can be concluded that change in operation is the preliminary responsible for malfunction and potash carry over. The higher load will affect handling capacity of all downstream equipments as they will be under overloading situation.

4- Washing Section

Washing section is accommodating with one sieve tray. The liquid flow, which is returned condensate, for this tray is very small comparing to vapor load. However, this type of tray is known that it cannot provide good liquid hold-up equivalently for good contact between liquid and vapor. As mentioned in previous point, washing water in the top section might evaporate completely with CO_2 gas if the operating conditions change

significantly. At current situation, it cannot be modified due to mechanical difficulties. Increase of water flow is already doubled and it is not recommended to increase it much further as it will affect the absorption solution strength.

6. Suggestions to overcome the problem

Suggested solutions are constructed on basis of avoiding any major mechanical change the existing system to reduce any risk as well as to minimize any investments might be needed. These suggested solutions will be implemented in the first opportunity of turn-around.

6.1 CO₂ Desorber

- 1. Better monitoring to the operation parameters (i.e. heat loads, flow rates, temperature and pressures) to insure good controlling on operating conditions,
- 2. The existing mist eliminator should be modified to reduce local entrainments. Consultation with mist eliminators vendors should be made to investigate of applying one of the following suggestions with minimizing pressure drop:
 - Install a new mist eliminator with higher separation efficiency.
 - If unique mist eliminator can be provided, in which it can handle non-uniform flow based on nonuniform mist eliminator thickness (see Fig 8).



Fig. 8 Unique Mist Eliminator to Reduce Non-Uniform Gas Flow

- **3.** Possibility of replacement of the type of activator from DEA to ACT-1 [12] in the Benfield section should be investigated. DEA is not thermally stable and can be easily suffer from degradation, in which it will produce other chemicals that enhance foaming tendency and reduce solution activation,
- 4. Gamma scanning [16] should be utilized for checking desorber and CO₂ cooler during operation to identify if flow patterns and columns' internals function correctly.

6.2 CO₂ Cooler & Knockout Drum

- 1. Upgrading mist eliminators of CO_2 cooler and knockout drum to better performance type. Measuring pressure drop should be applied to monitor their operation,
- 2. The existing CO₂ cooler system is capable to handle an increase of water washing flow rate (from current load of 120 upto 200 m³/hr). Improvement of the scrubbing efficiency is expected at higher flow rates of water,
- 3. Installation of a spraying distributor above the mist eliminator to wash it and CO_2 gas outlet from the column,
- 4. Packaging material can be changed to enhance the scrubbing efficiency,

6.2 New Knock-Out Drum

Installation of another knock out drum before the compressor and after the existing KO drum is highly desirable. This will assure of minimizing the entrainment of very small liquid droplets. The proposal is given with preliminary design [4] and economic estimation [9]. We selected the diameter of slight smaller to the

existing knock-out drum with 2.15m, to consider the slight change in pressure drop might form in the new KO drum. The pay back period of investment will be within short period of time (3 months).

7. Potash Deposits Problem Mentioned Elsewhere

The problem of carry-over associated with Benfield Process is well known in all over the world. Many comprehensive studies (see Table 6) and reports have been found that mentioned this kind of problem; although, they were not given lots of information.

Case No.	Company	Date	Subject	Source of	Action Taken, Suggestion or
				subject	Recommendations
1 [13]	GPIC	2003	Problem_Benfield solution carry	Upgrading and	Improve washing performance and modification on CO ₂
			over	Revamping	compressor.
2 [14]	Ruwais Fertil Industries	1999	Problem- Benfield process foaming and loss performance	DEA Degradation + Upgrading	Using new activator ACT-1 from UOP
3 [15]	UOP	?	Improving- Benfield Process on overcoming old problems	Foaming + DEA Degrading + etc	 1-New random Packing. 2-New stable activator ACT-1. 3-Energy Integration.
4 [16]	COLSCA N	?	Problem- Benfield Solution carry over	Foaming + Tilted tray	Perform remedial actions during the next shutdown
5 [17]	Synetix	?	Problem Kataloc 11-S Catalyst poisoned.	Benfield solution carry over	Washing the Kataloc 11-S with dematerialized water.
6 [18]	Bass Gas Project	2002	Survey CO ₂ removal system - Rejection of Benfield Process.	-Plant complexity - K ₂ CO ₃ Solidify	Amines is better than Benfield Process and Membrane.
7 [19]	www.eng- tips.com	2003	Problem : Benfield solution carry over.	?	Installed a new cleaning scrubber
8 [12]	UOP	?	Modification & Study: Upgrading Capacity, Minimize Activator Losses	DEA loss + High energy consumption	
9 [12]	UOP	2000	Study: Reviewing old DEA activator behaviour.	Degradation + Loss + less absorption	-New activator ACT-1 Performance over DEA.
10 [20]	Kribhco's Fertilizer	1998	Problem-BenfieldSolutionCarryOver(CO2Absorber)	Load Upgrade & Revamping	Solution Changing demisters densities and thicknesses.
11 [21]	www.nh3.c om	2003	Problem- Benfield Solution carry over	Possibility: -Foaming -Loading	Recommendations Improving anti-foam dosing performance and increase demisters density and size.
12 [22]	Orica Engineerin g	1999	Problem Benfield solution carry- over and Ammonia catalyst poisoned	Foaming + Flooding + (Revamping)	Recommendations Improving washing section performance and demisters density and size.

Table 6 Cases of Carry-Over Problem in Benfield Process Elsewhere

8. Conclusion

Process simulation was used to simulate and identify the performance of each unit involved from Desorber to CO_2 Compressor. The aim of simulation was to find out whether each unit has contributed to the carry over problem or not and to how far it is involved. However, results indicated that all scrubbing units are capable to

remove any potash associated with CO2. These scrubbing units will only lose some of their performance, simply, if they operate at overloading conditions.

It is concluded that potash solution could be carried over with CO_2 due to overloading and mechanical configuration in the desorber. Overloading could be due to pressure and temperature variation which could lead to evaporate of large quantities of water especially at certain events such as; start-up, shutdown and feed load change. Mechanical configuration of the top section of the desorber could contribute to carry over problem.

Potash carry-over phenomena in Desorber, CO_2 cooler, CO_2 pipeline, and knockout drum are complex phenomena as it relates to macro sizing of liquid droplets which is difficult to be described in empirical calculations manner or steady state simulation. It is much better to check it with utilisation of Computational Fluid Dynamic (**CFD**) modelling and dynamic simulation on the basis of real time case for a whole process under equipment specifications and conditions. However, simple approach illustrated in this work prove to be enough with less efforts for computational and information.

9. Reference

- 1. Ammonia Process, <u>www.thyssenkrupp.com/uhde</u>
- 2. A. Kohl and R. Nielson, Gas Purification, 5th Edition, Gulf Publishing Co., 1997.
- 3. Frank L. Evans, Equipment Design Handbook for Refineries and Chemical Plants, 2nd edition, Gulf Publication Co., Houston, 1980.
- 4. AMISTCO Mesh & Vane Mist Eliminators, Armistice Separation Products Inc., 2004, www.amistco.com.
- 5. Peter G. Talavera, Selection Gas/Liquid Separators, Hydrocarbon Processing, June 1990.
- 6. The knockout drums design method, Armistice Separation Products Inc., <u>www.amistco.com</u>.
- 7. Ernest E. Ludwig, Applied Process Design for Chemical and Petrochemical Plants, Volume 2, 3rd Edition, Gulf Publishing Company, 1997.
- 8. H. Eldessouky, I. Alatiqi, H. Ettouney, and N. Al-Deffeeri, Performance of Wire Mesh Mist Eliminator, Chemical Engineering and Processing, 39, 2000.
- 9. Robert Perry, Perry's Chemical Engineers' Handbook CD, 7th Edition, McGraw-Hill, 1997.
- 10. www.alfalaval.com
- 11. GPSA, Engineering Data Book, Volume I (1-16), Revised Edition (10th), 1994
- 12. <u>www.uop.com</u>
- Hanan Al-Maskati and Khalid Al-Bin Ali, Overcoming The Potassium Carbonate Carry-Over with CO₂ Gas Vented From Benfield Section (Case Study), The 4th Middle East Refining & Petrochemical Conference and Exhibition, 29 September – 1 October 2003, Bahrain.
- 14. S.A. Alghafli, H. M. Lari, B.Bousmaha and H. I. Bukhari, Energy Conservation Measures: Energy Audit, Process Optimization, Ruwais Fertil Industries FERTIL, UEA.
- 15. S.K. Furukawa and R. K. Bartoo, Improved Benfield Process for Ammonia Plants, UOP, 1997.
- 16. www.mint.gov.my/products/bti/pat/colscan.htm
- 17. <u>www.synetix.com</u>
- 18. "The BassGas Project, Project Alternatives (Environment Effects Statement / Environmental Impact Statement)", January 2002, Australia
- 19. <u>www.eng-tips.com</u>
- 20. P.P. Singh and J. Singh, Moderinsation of Kribhco's Fertilizer Plant, Krishak Bharati Coorperative Limited, India, 4 May 1998.
- 21. <u>www.NH3.com</u>
- 22. J. Underwood, G. Leader, G. Dawson and C. Barney, Design of CO₂ Absorption System in an Ammonia Plant, 10 Nov. 1997. (Preliminary report).
- 23. F. Yu, A quick Guide to Compressor Section Knockout Drum Sizing, Hydrocarbon Processing, June 2003.
- 24. L. Pless and B. Asseln, Using Gamma Scans to Plan Maintenance of Column, Petroleum Technology Quarterly, Spring 2002 (www.eptq.com).
- 25. Hiren Sarma, How to size gas scrubbers, Hydrocarbon Processing, September 1981.
- 26. Scott W Golden Scott A Fulton Daryl W Hanson, Understanding centrifugal compressor performance, Petroleum Technology Quarter, Springing 2002.
- 27. Bernhard Kalis, Compressor Suction Drums: I think I've got liquid carryover. What can I do about it?, <u>www.amistco.com.</u>