

CO₂ Capture by Absorption with Potassium Carbonate

Sata K. A. Ajjam

Babylon University ,College of Engineering

Abstract

Several process improvements have recently been incorporated into this Hot Potassium Carbonate process for CO₂ removal. The influence of steel surface condition and solution chemistry on the critical inhibitor concentration required for spontaneous passivation of carbon steel in typical solutions of hot potassium carbonate plant (HPC) was studied. V₂O₅ solution was used as an inhibitor. It was found that the critical inhibitor concentration depended on solution composition and the steel surface condition. An inhibitor concentration of 14-15 g/l required to ensure spontaneous passivation under all conditions. A minimum level of V⁺⁵ ions is required for inhibition, so that monitoring the V⁺⁵ concentrations above 30% of total vanadium crucial to successfully managing corrosion protection in plant.

الخلاصة

عدة تحسينات أجريت في السابق لعمليات إزالة غاز ثاني أكسيد الكربون CO₂ بواسطة الامتصاص بكاربونات البوتاسيوم الساخنة. تم دراسة تأثير ظروف سطح الحديد وكيميائية المحلول على تركيز المثبط لأجل خمود مستمر في مصنع الإزالة بكاربونات البوتاسيوم الساخنة . محلول خامس أكسيد الفناديوم V₂O₅ استخدم كمثبط. ولقد وجد إن تركيز المثبط الحرج يعتمد على تركيز المحلول وظروف سطح المعدن للمعدات والأجهزة (steel surface condition) . تركيز المثبط بين 14-15 غم/لتر مطلوب لتأكد خمود مستمر (spontaneous passivation) وفي كل الظروف. أقل مستوى لأيون الفناديوم الموجب 5 (V⁺⁵) مطلوب للتثبيط, لذلك يجب ضبط ومراقبة تركيز (V⁺⁵) فوق 30% من الفناديوم الكلي مما يحسم ويوفر حماية من مشكلة التآكل في المصنع.

1. Introduction

The removal of CO₂ is a crucial step in the manufacture of ammonia. Many technologies efficiently remove CO₂ from the process gas. With so many choices there is no "one method fits all" solution. Consequently, process designers must align technological benefits of various techniques with the final product or downstream plant specifications. Ammonia synthesis catalyst (iron) requires pure synthesis gas and the tolerance limit of CO+CO₂ content in the gas is only 10 ppm. In this research the available technologies for CO₂ removal will be discussed in brief with particular focus on the Benfield system that is widely used for Ammonia Plants.

1-1 Process description of Benfield system

Sirte Oil Company, 1983 et al ; The CO₂ content in the process gas downstream of the low temperature converter (LT) is approximately 18%. Carbon dioxide is a strong catalyst poison. It also reacts with the ammonia present in the synthesis recycle gas to ammonium carbamate and ammonium carbonate.

These salt-like products form deposits in the machinery and equipment, and this might cause serious damage.

Various processes are available for removing the CO₂ from the synthesis gas , if the quantity of CO₂ to be absorbed is large, the only efficient method of removing the CO₂ is by a regenerative process using liquid absorbents. One normally differentiates

between physical and chemical scrubbing methods. Physical scrubbing processes are characterized by the fact that the scrubbing agent is chemically neutral and its loading is roughly proportional to the partial pressure of the CO_2 .

The quantity of scrubbing agent recycled depends essentially on the quantity and pressure of the gas to be treated. Physical scrubbing processes are only economical if the process concerned and the external conditions are favorable.

For instance, pressure water scrubbing will only be used if cheap electric power and sufficient quantities of relatively cold water are available. The scrubbing agent is regenerated by flashing and subsequent stripping with inert gas, e.g. air. Stripping with inert gas is equivalent to lowering the partial pressure of the component to be scrubbed out. This effect is improved by operating in countercurrent.

In view of the fact that these prerequisites are not met in the plant a chemical scrubbing process was selected.

For chemical scrubbing, we can choose between the potash, amine and caustic soda solution scrubbing processes. Depending on the activator added to the liquor, the potash scrubbing process can be further subdivided, e.g. arsenic scrubbing (approximately 140 grams/l As_2O_3), glycine scrubbing (30-50 g/l glycine) or the Benfield scrubbing process in which the liquor contains 1 to 6 % diethanolamine (DEA) as activator. The Benfield scrubbing process is used. The best known amine scrubbing processes are based on monoethanolamine (MEA) and diethanolamine (DEA).

See the Block diagrams for Ammonia production facility (fig-1) and Carbon dioxide removal section (fig-2)

ENGINEERING DATA BOOK, 2004 and AIChE Technical Manual, published by the American Institute of Chemical Engineers, 1997

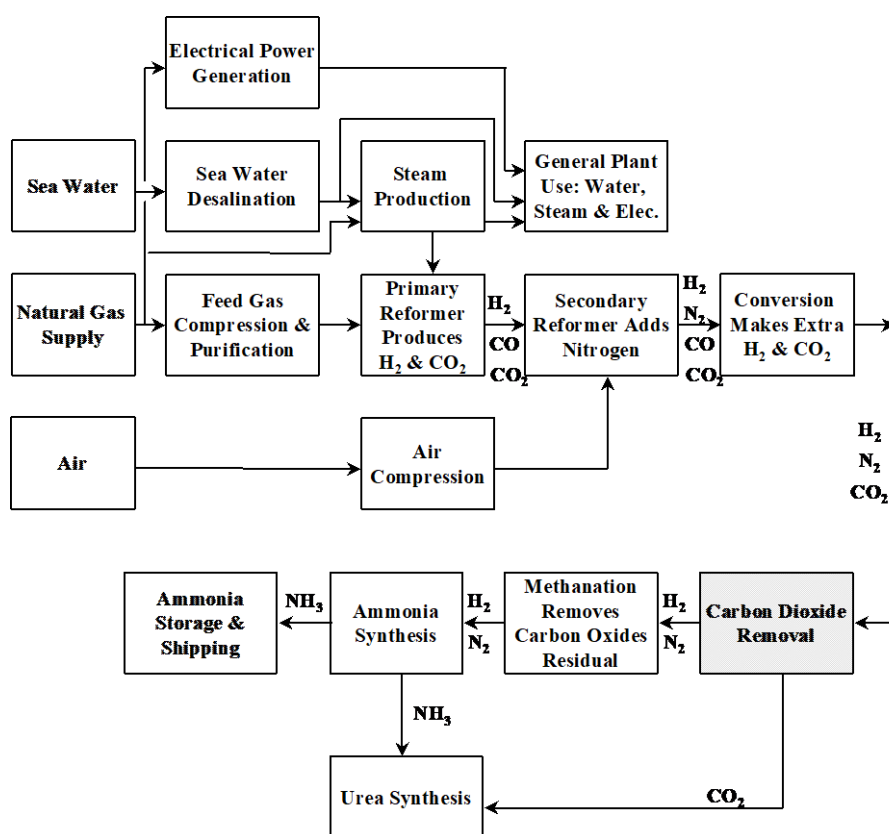


Figure-1 Ammonia production facility block diagram

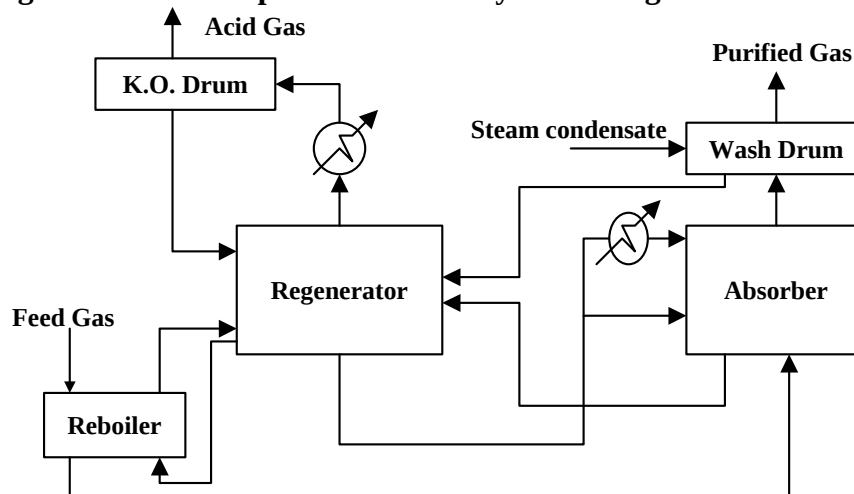


Figure-2 Carbon dioxide removal section

1-2 Maintenance of Corrosion Protection.

In a system where vanadium is being used as a corrosion inhibitor, the iron content of the solution is an important monitor of the overall effectiveness of the corrosion inhibition in the solution in the Benfield system. Normally the solution will have an iron concentration of 10-100 ppm. This is generally a function of how well the plant was cleaned initially and if iron is being brought into the system either via make-up water, impurities in the chemicals, or as a gas contaminant.

Allowing the vanadium concentration to drop to a low value can cause iron from solution lines and vessel walls to go into solution. If higher than normal solution velocity is present and the solution impinges directly upon a steel wall, localized corrosion can occur again putting iron into the solution. An increase in iron concentration over a short period of time would indicate corrosion, unless this can be attributed to a gas or condensate source.

Corrosion coupons which have been put in different points of the system could be removed for inspection to determine if the solution is generally corrosive or whether the source of iron is localized corrosion or possibly from condensate makeup. If the iron content is allowed to continue to increase ultimately concentrations are reached that will cause co-precipitation of both iron and vanadium. If that point is reached, corrosion will accelerate because of loss of vanadium.

Generally iron levels above 200-300 ppm should be considered excessively high. If the iron concentration is in the range of 200-300 ppm we would recommend bringing the V_2O_5 concentration up to 0.7-0.8%. It would be preferable at this point to shut off the process gas and to put the plant through 24-48 hour shutdown.

1.3. Significance of V^{+5}/V^{+4} Ratio .

Shaw, and Hughes, May 2001 et al; Costin Oil, Gas & Process Ltd., Manchester, England Corrosion inhibition of carbon steel with vanadium has been

excellent and in only isolated cases has localized corrosion occurred and this has been due to direct impingement of solution against carbon steel at higher velocities.

Freshly made solution from V_2O_5 is all V^{+5} valence and in a new plant gives a very high film forming rate.

The V^{+5} form is the more active as far as corrosion resistance is concerned.

It is principally the V^{+5} that is responsible for the protective film that protects the iron against bicarbonate and CO_2 corrosion. To do a good vanadation job it is important for there to be a reasonably high concentration of V^{+5} .

The reduced form V^{+4} is probably not capable of building a protective film by itself. A vanadium film once formed, however, can be maintained by V^{+4} , even if no V^{+5} is present. If there is abrasion due to packing movement, dirt in the solution, etc., the film can be thinned and lost and will not be restored unless some V^{+5} is present in the solution. After a time of operation equilibrium is established between V^{+5} and V^{+4} generally with a ratio of about 1. This solution has an adequate amount of V^{+5} to insure good operations. There are successful operating plants where the V^{+5}/V^{+4} ratio is as low as 0.05 and no corrosion has resulted after several years of operation.

1.4. Adjustment of V^{+5}/V^{+4} Ratio.

Shaw, and Hughes, May 2001 et al; As pointed out in the previous section V^{+4} is capable of maintaining a corrosion resistant vanadium film but probably is unable to form a new film in the absence of V^{+5} .

Thus, while the V^{+5}/V^{+4} ratio require increasing the V^{+5} concentration to insure enough formation of a new protective film. Most typically, a high concentration of V^{+5} is needed when a system is revanadated after the towers have been opened and exposed to air, and flushed with water, or have been allowed to dry. Maintaining a high V^{+5} content is also suitable if an unexplained rapid increase in iron content occurs since the increase could indicate localized corrosion caused by loss of the protective film due to abrasion caused by high solution velocity or particulates, packing movement, etc. Whenever a system is revanadated or it is suspected that a portion of the protective film has been lost, the V^{+5} content of the solution should be increased to 0.7 to 0.8 wt.% as KVO_3 .

The V^{+5} content can be increased by adding more vanadium (usually as V_2O_5) or by oxidation of V^{+4} already in solution.

Addition of more vanadium is not objectionable. A total concentration of KVO_3 at least as high as 1.5 wt.% is acceptable. However, oxidizing the vanadium already in solution with KNO_2 (potassium nitrite) will be significantly more economical. Potassium nitrite selectively oxidizes V^{+4} and will not oxidize DEA except if present in excess for a long period. In addition undesirable reaction products do not remain in solution; N_2 and/or NO evolve as a gas. Oxidants other than potassium nitrite (air, hydrogen peroxide, etc.) should not be used since they will oxidize DEA.

When KNO_2 is to be added, it should be prepared as a water solution in the mixing sump and then transferred to the circulating solution. The amount of KNO_2 added should be such that 70 to 80% of the vanadium is converted to V^{+5} . Complete conversion to V^{+5} should be avoided to prevent any possibility of excess KNO_2 slowly reacting with DEA. The amount of KNO_2 required will usually fall between .01 and 0.1 wt. % of the solution inventory, depending on the solution's V^{+4} content and also on the amount of readily oxidized trace components that may be present. The quantity of KNO_2 to be used should be determined by laboratory test prior to addition to the plant solution. A convenient procedure is to prepare several 50 to 100 ml

portions of plant solution to which different amounts of KNO_2 are added. The samples are heated to 90°C in closed bottles for 3 hours to insure complete reaction.

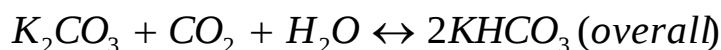
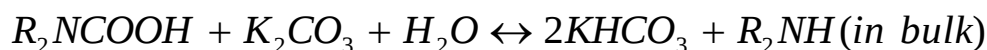
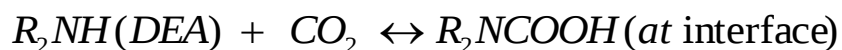
The V^{+4} and V^{+5} contents of each are then determined using recommended analytical procedure, by a spectrophotometer of company's laboratories.

1-5 Chemistry of CO_2 absorption and regeneration in the benfield system.

Samuel Streizoff, 1981 and Ammonia Plant Manual Sirte Oil Company 1983, et al; Operationally, Benfield system in (Ammonia plant) has given its fair share of problems such as high CO_2 slip, foaming problem and corrosion problem due to DEA degradation products and difficulties in keeping the Vanadium in the oxidized form. It has also been found that when operating at about 105% flow sheet feed gas rate, the Benfield system becomes the plant bottleneck.

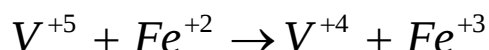
Both high CO_2 slip and foaming problem are common problems.

The chemistry of CO_2 absorption and regeneration involves reaction of the promoter with CO_2 at the gas liquid interface, regeneration of the promoter in the bulk solution and its return to interface (both steps known as [shuttle mechanism] occur in the absorber) and release of major quantity of CO_2 by flashing and heating the solution in the Regenerator. The chemical reactions for the above are shown below.



The chemistry of corrosion inhabitation involves oxidation of iron on the wall surface to Fe_2O_3 while pentavalent vanadium V^{+5} provides the potential required for the oxidation. Simultaneously, V^{+5} gets reduced to tetravalent vanadium V^{+4} .

The chemical reaction for the above is as follows:



As V^{+5} is yellow and V^{+4} blue in colour of Benfield solution would be yellowish green or bluish green depending on which of the contents (V^{+5} or V^{+4}) is major. The solution turns to dark colour when DEA gets degraded.

2- Experimental Procedures and Methods

2-1 Low ratio of pentavalent/tetravalent vanadium in Benfield solution.

This kind of problem is an uncommon one which shall be discussed in this section. In order to avoid corrosion of equipment in Benfield system, $\text{V}^{+5}/\text{V}^{+4}$ ratio should be maintained at 1 or above 1. Ammonia Plant could not maintain this ratio in spite of dosing KNO_2 to the system and the ratio was showing very low values as can be seen in the analysis sheet no. (1).

Daily Benfield Analysis, (No-1)			
V^{+5} g/l	V^{+4} g/l	T-V 10-15 g/l	$V^{+5}/$ V^{+4}
7.54	14.06	21.6	0.536
6.87	14.08	20.95	0.488
5.9	15.26	21.16	0.386
6.5	14.1	20.6	0.461
5.88	14.66	20.54	0.401
7.48	16.04	23.52	0.466
7.78	14.46	22.24	0.538
6.72	15.2	21.92	0.442
6.06	13.28	19.34	0.456
4.56	13.54	18.1	0.337

The ratio varied from 0.44 (minimum) to 0.57 (maximum). It was decided to oxidize in steps the tetravalent vanadium so as to get more pentavalent that would improve the ratio.

First step of oxidize the tetravalent vanadium

Oxidation of V^{+4} was carried out by injection of air to a batch of solution and transferring back to system. This step was done to oxidize V^{+4} to V^{+5} without adding KNO_2 for a week, but there was no significant effect on the inventory of the solution when the batch was transferred to the system (see analysis sheet no.2).

Daily Benfield Analysis, (No-2)			
V^{+5} g/l	V^{+4} g/l	T-V 10-15 g/l	$V^{+5}/$ V^{+4}
7.54	14.06	21.6	0.536
6.87	14.08	20.95	0.488
5.9	15.26	21.16	0.386
7.16	14.18	21.38	0.505
6.22	15.16	21.38	0.41
6.35	14.85	21.20	0.427
6.72	15.2	21.92	0.442

Second step of oxidize the tetravalent vanadium

Air injection and KNO_2 dosing were stopped for one week. Since there was no improvement in the ratio, nitrite was added in installments spread over the next week up to 100 kg, and this amount was added to the process flow during the start-up of Carbon dioxide removal section in the ammonia plant.

Even then no increase in ratio was observed. At the end of this step the Benfield solution composition was as follows:

223.10 g/l of K_2CO_3 , 169.14 g/l of $KHCO_3$, 18.20 g/l of DEA , 6.56 g/l of V^{+5} , 14.44 g/l of V^{+4} , Total -V was 21.00 g/l as KVO_3

The above analysis data were carried out in the site laboratories of SOC (Sirte Oil Company) using recommended analytical procedures, by a spectrophotometer and other equipments.

The total vanadium content was 1.64 wt% KVO_3 against normal value of 1.06 to 1.14%. As higher vanadium content increases the rate of degradation of DEA, the plant was advised to bring down the content of vanadium to normal value.

Third step of oxidize the tetravalent vanadium

The vanadium content of Benfield solution can be reduced only by draining the solution. Since the carbonate and DEA strength also will fall off on draining, addition of potassium carbonate and DEA is necessary immediately after draining. Therefore, the plant could not start draining the solution immediately and after mobilizing these chemicals which took 26 days, the draining commenced. The Benfield solution composition at the commencement of draining was as follows:

220.59 g/l of K_2CO_3 , 174.17 g/l of $KHCO_3$, 20.37 g/l of DEA , 5.24 g/l of V^{+5} , 15.42 g/l of V^{+4} , Total -V was 20.66 g/l KVO_3 as V_2O_5 and 51.8 ppm Fe.

The solution was drained in three installments as the solution strength should not be depleted fast. Otherwise CO_2 slip will shoot up. After draining the first installment, the strength of the solution was made up with 12 MT (metric ton) of K_2CO_3 and 1000 Liters of DEA. On completion of this action the total vanadium came down to 18 g/l. Then, 70 Kg of KNO_2 was added for one week due to low ratio of V^{+5}/V^{+4} (0.289) which improved later to about 0.466 (see to analysis sheet no.3).

Daily Benfield Analysis, (No-3)			
V^{+5} g/l	V^{+4} g/l	T-V 10-15 g/l	V^{+5}/V^{+4}
4.56	13.54	18.10	0.336
4.57	13.67	18.24	0.334
4.78	13.81	18.59	0.346
4.60	13.67	18.27	0.336
4.58	14.0	18.58	0.327
3.97	14.9	18.87	0.266
3.99	13.56	17.55	0.294
4.51	14.01	18.52	0.322

After two weeks the second draining was done with make up of 7.75 MT of K_2CO_3 and 440 kg of DEA. Then, the total vanadium dropped to about 16 g/l and the ratio remained at about 0.90. The final draining was carried out after a few days with a make up of 3.0 MT K_2CO_3 and 450 kg of DEA. The total vanadium dropped to (14-12 g/l) and the ratio improved to 1.0 or above 1 .(see to analysis sheet no.4).

The foaming problem which was persisting in the plant before draining the solution, disappeared completely and V^{+5}/V^{+4} ratio gradually boosted up to 2.83 over a week. It facilitated to raise up the plant load to 105% without any problems. No corrosion was observed in Benfield system since the problem of low V^{+5}/V^{+4} ratio was tackled in proper time.

Daily Benfield Analysis, (No-4)			
V^{+5} g/l	V^{+4} g/l	T-V 10-15 g/l	V^{+5}/V^{+4}
4.74	12.06	16.8	0.393
7.74	8.69	16.43	0.890
7.81	8.69	16.5	0.898
7.83	8.62	16.45	0.908
7.84	8.59	16.46	0.912
7.89	8.46	16.35	0.932
7.87	8.34	16.21	0.943
8.15	7.63	15.78	1.068
8.24	6.98	15.22	1.180
8.31	6.71	15.02	1.238

2-2 Other Facts in Benfield system.

Some of the facts gathered either from experiences of other plants or from my investigation are:-

- Many plants have experienced foaming and bubble retention in Benfield system. The mechanism of this retention is not clearly understood.
 - Solution and gas composition can have marked effects on the quantity retained.
 - Pure Benfield solution is clear with the colour of the vanadium. The colour is dependent on the proportion of the V^{+4} and V^{+5} present in the solution.
 - The absorption/desorption promoter DEA can degrade to give a dark coloration to the solution due to the accumulation of these degradation compounds. These compounds may further degrade to give carbon particles and other solid carbonaceous materials in the solution.
 - A higher vanadium content in the Benfield solution increases the rate of degradation of DEA.
 - The effect of degradation products on foaming and bubble retention is not well known. But it is established that both foam and Benfield liquid and process gas.
 - Oxygen in either air or dissolved in water entering the solution not only increases, the V^{+5} content in the solution but also the rate of degradation of the DEA.
 - Gas bubbles become foam as they rise to the surface where two phases disengage. The rate of the rise of the bubble depends on the size, gravity, the downward velocity of the solution, the gas density and its composition.
- It also depends on the liquid composition and the effects it brought about on the viscosity and surface tension of the interface between the gas and the liquid. This is greatly affected by any accumulation of small suspended solids at the interface which will make the separation of the foam and bubbles from the main body of the liquid more difficult.

3-Conclusion and Recommendation for further work.

3-1 Conclusion

The problem of low ratio of pentavalent to tetravalent vanadium in Benfield solution used in Ammonia was due to high concentration of vanadium in the solution and also, continuous oxidation of solution collected in the Sump Tank. The normal concentration to be maintained is 14- 15 g/l of KVO_3 (1.06-1.14%) whereas the actual value had risen up to 21 g/l. While the continued oxidation by aeration in the Sump tank and periodical dosing of KNO_2 degraded the DEA in the solution, higher concentration of vanadium increased the rate of degradation. When the degraded product($KCOOH$) in the solution exceeds 1.5%, it results in foaming as low V^{+5}/V^{+4} ratio in Benfield system as the format acts as an oxygen scavenger and prevents the formation of V^{+5} .

3-2 Recommendation for further work

The following recommendations were given to Ammonia Plant in order to avoid repetition of the problem.

(1) To keep the total vanadium in Benfield solution at 14-15 g/l.

As the vanadium concentration will vary with the level in the Regenerator, it was advised to keep the level steady as far as possible

(2) To maintain V^{+5} content in the solution above 30% of total vanadium.

(3) To analyze potassium format ($KCOOH$) periodically so as to keep it below 1.5%.

(4) To substitute DEA, with another chemical, LRS-10

LRS-10 (London Research Station-10) is a patented chemical developed by British Gas Company. It is a formulation of several secondary amines. This formulation offers significant improved performance over the DEA promoted hot potassium carbonate systems. The change over to LRS-10 does not demand a shut down of the plant. It can be done on line by dosing the chemical gradually over a period. The concentration of LRS-10 to be maintained is same as that of DEA which is 3%.

3-3 The advantages of using LRS-10 are enumerated below:-

(1) Lower CO_2 slip from the Absorber.

(2) Higher throughput up to 10%, thereby increasing plant production.

(3) Operation at lower steam to gas ratio.

(4) Reduced liquor flow CO_2 absorption.

(5) Saving of hydrogen consumed for methanation.

(6) Extension of methanator catalyst life.

(7) Degradation of amines is reduced.

(8) More stable operation of the plant.

4-References.

Ammonia Plant Manual of SOC (Sirte Oil Company)-1983.

Ammonia Plant Safety, AIChE Technical Manual, published by the American Institute of Chemical Engineers, 1997, 3Park Avenue, New York, NY 10016-5991.

GPSA(Gas Processors Suppliers Association), ENGINEERING DATA BOOK, 2004 Hydrocarbon Processing/ May 2001, Optimize CO_2 Removal, T.P.Shaw, and P.W.Hughes, Costin Oil, Gas & Process Ltd., Manchester, England.

Technology and Manufacture of Ammonia, Samuel Streizoff, 1901, Copyright @ 1981 by John Wiley & Sons, Wiley-Interscience Publication.