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Capturing CO_2 from flue gas streams in ammonia plant, waste generation as HSS and its reclamation at CO_2 recovery plant, NFCL, Andhra Pradesh (India)

R. Raghavan, G.V.S Anand, P.H.N Reddy, P. Chandra Mohan, V. Appala Raju* and Amar Nath Giri**
Quality & Environment Management System, NFCL, Nagarjuna Road, Kakinada - 533 003, India
***e-mail:** varaju@nagarjunagroup.com, ******amarnathgiri@nagarjunagroup.com

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Abstract: There are a number of different methods for Mitsubishi Heavy Industries (MHI) has concentrated its extensive research and development programs on the use of sterically hindered amines and the post combustion, chemical absorption process in particular for treating flue gasses from natural gas combustion. The CO_2 recovery plant consists of three main sections: the flue gas cooler, the absorber (for CO_2 recovery) and the stripper (for solvent regeneration). In NFCL Kakinada, the flue gas from primary reformer enters in the flue gas quencher, where it is cooled to 40°C. The flue gas is compressed to a pressure of 1.113 Ksca and enters in the CO_2 absorber. The CO_2 in flue gas is absorbed by KS-1 (Hindered amine) solvent, which is distributed from top through packed bed system. The CO_2 thus liberated is washed with DM water at the top of CO_2 regenerator, cooled to ambient temperature in an overhead condenser and sent to urea plants.

Key words: Flue gas, Carbon dioxide recovery plant, Chemical absorption, Heat stable salts

Introduction

As Wong *et al*. (1999), the emission of carbon dioxide (CO_2) from the burning of fossil fuels has been identified as the major contributor to global warming and climate change. However, for the immediate term over the next 20- 30 years at least, the world will continue to rely on fossil fuels as the source of primary energy. The challenge for the fossil fuel industry is to find cost-effective solutions that will reduce the release of CO_2 into the atmosphere. Reduction of anthropogenic CO_2 emissions into the atmosphere can be achieved by a variety of means, which has been summarized by Prof. Yoichi Kaya from University of Tokyo and can be expressed as:

$$CO_2^{\Uparrow} = POP \times \frac{GDP}{POP} \times \frac{BTU}{GDP} \times \frac{CO_2^{\Uparrow\Uparrow}}{BTU} - CO_2^{\Downarrow}$$

Where $CO_2^{\Uparrow}$ is the total released CO_2 to the atmosphere, POP (population), GDP (Gross Domestic Product) /POP is per capita gross domestic product and is a measure of the standard of living, BTU/GDP is energy consumption per unit of GDP and is a measure of energy intensity, $CO_2^{\Uparrow\Uparrow}$/BTU is the amount of CO_2 released per unit of energy consumed and is a measure of carbon intensity, and $CO_2^{\Downarrow}$ is the amount of CO_2 stored/ sequestered in biosphere and geosphere sinks. Of the first two measures, reducing the population or the standard of living is not likely to be considered. Consequently, only the three remaining methods can be employed (*i.e.* reducing energy intensity, reducing carbon intensity and carbon storage).

Mimura *et al.* (2001) describe their recent work in solvent composition. They have developed a series of amine solvents designated as KS-1, KS-2, and KS-3 as improved Hindered Amine) The composition of these solvents is propriety. The KS-1 solvent has been commercialized in Malaysia where a flue gas containing 8 vol. % CO_2 is being treated with 90% CO_2 recovery. Corrosion problems were reported to be negligible using this solvent and also that solvent degradation during prolonged operation was slight. They indicated that amine consumption was about 2.0 kg ton^{-1} CO_2 recovered using a MEA process while for the Malaysia plant using KS-1, solvent loss was 0.35 kg ton^{-1} CO_2 recovered. With improved solvents currently in the pilot phase, they indicate that solvent loss may be further reduced to ~0.1 kg ton^{-1} CO_2 recovered. Steam consumption was 1.5 ton of low-pressure steam per ton CO_2 recovered. It is claimed that K-3 is better than K-1 and K-2 in terms of energy consumption for solvent regeneration. A pilot plant test using KS-3 under coal fired boiler flue gas containing 14-vol% CO_2 (dry basis) and 50 ppm SO_x showed a CO_2 recovery of 90% (Mimura *et al*., 2004), and sodium hydroxide was believed to be used in the solvent regeneration by converting the heat-stable salt due to reaction of SO_x with the amine to free amine and Na_2SO_3.

The Canadian group has also developed a series of proprietary designer solvents designated as PSR solvents (Veawab *et al*., 2001). The PSR solvents have been designed to specifically for the separation of CO_2 from flue gas streams. The PSR solvents may be used at higher amine concentration than conventional MEA solvents and at a higher loading of CO_2. The key features claimed for the PSR solvents are lower regeneration temperature, lower solvent circulation rate, lower solvent degeneration rate, and lower corrosion rate.

Materials and Methods

CO_2 capture process in CDR plant: The flue gas genereted by natural gas fired application an FGD (Flue Gas Desulfurization) may not be required as the SO_2 content in the gas stream is minimal. Therefore, depending on the fuel type, a deep FGD process may or may not be necessary. The primary objective of the flue gas water cooler (FGWC) is to further cool the flue gas prior to entering the CO_2 absorber. The lower flue gas temperature increases the efficiency of the exothermic CO_2 absorption reaction and minimizes KS-1 solvent loss due to gas phase equilibrium increases. The optimum temperature range for CO_2 recovery is between 95-113°F (35-45°C), however this is flexible in consideration of other factors such as water utility requirements and availability. The FGWC is designed and constructed to not only to cool the flue gas, but to also further remove various impurities such as SOx, NOx, dust and suspended particulate matter (SPM).Clean-burning, natural gas typically has low concentrations of CO_2 and impurities.

The CO_2 absorber has two main sections, the CO_2 absorption section (bottom section), and the treated flue gas washing section (top section). The conditioned flue gas from the FGWC flows upward through structured, stainless steel packing material while the CO_2 lean KS-1 solvent is distributed evenly from the top of the absorption section onto the packing material. The flue gas comes into direct contact with the KS-1 solvent and CO_2 in the flue gas is absorbed. The CO_2 rich KS-1 solvent (rich solvent) is pumped to the CO_2 Regeneration unit for steam stripping. The clean flue gas then moves up into the treated flue gas washing section of the absorber. This section is where vaporized KS-1 solvent is removed and recycled and the flue gas is again cooled to maintain water balance within the system (the absorption of CO_2 in the KS-1 solvent produces some rise in temperature). The clean flue gas then exits the top section of the CO_{2a}absorber. The rich solvent is pre-heated in a heat exchanger using heat from the hot lean solvent coming from the bottom of the CO_2 stripper. The heated rich solvent is then introduced into the upper section of the CO_{2s}stripper, where it will come into contact with stripping steam of around 248°F (120°C). The rich solvent is then stripped of its CO_2 content and is converted back into lean solvent. The high purity CO_2 (>99.9%) exits the top of the stripper vessel and is compressed and dehydrated, prior to transportation. Once stripped, the now lean solvent is cooled to the optimum reaction temperature of approximately 104°F (40°C) before being reintroduced to the top of the absorption section of the CO_2 absorber unit.

CDR plant opted at NFCL (Technology supplier: Mitsubishi Heavy Industries (MHI), Japan and CO_2 Absorbent: KS-1 solution, proprietary supply from MHI, Japan): The flue gas from primary reformer enters the flue gas quencher, where it is cooled to 40°C. The flue gas is compressed to a pressure of 1.113 Ksca and enters the CO_2 absorber. The CO_2 in flue gas is absorbed by KS-1 Solvent, which is distributed from top through packed bed system. Subsequent to contact with KS-1 solution the flue gas is further washed with DM water in the top section of CO_2 absorber. The flue gas after removal of CO_2 is sent out to atmosphere through a stack provided at CO_2 absorber top. The CO_2 rich solution at 55°C is pumped to the lean / rich heat exchanger. The lean solution is recycled back to CO_2 Absorber. The rich solution stream is heated up to 114 °C and sent to CO_2 regenerator, where in CO_2 is stripped off from rich solution by providing necessary heat to reboiler using low pressure steam. The CO_2 thus liberated is washed with DM water at the top of CO_2 regenerator, cooled to ambient temperature in a overhead condenser and sent to urea plants. In view of adequate natural gas supply to NFCL by RIL, it was decided to switchover Unit-II operations to full NG mode from the present operation of mixed feed / fuel (NG + Naphtha). Subsequent to switchover from naphtha / NG mix to full natural gas mode in Unit-II, there will be shortfall of CO_2 which will be met through the CO_2 production from CDR plant.

The power and steam demand required for CDR plant is met through the existing offsite facilities. The flue gas having about 8 to 9% CO_2 by volume is drawn from primary reformer stack and cooled to 45°C or below in a direct contact cooler. It is then fed at the bottom of an absorber through a blower. The absorber is a packed tower. A solvent mainly KS-1 is fed on the top of the absorber. The solvent and rising flue gas come in contact on the bed. The solvent absorbs CO_2 from the flue gas and balance flue gas devoid of CO_2 is vented from the top of the absorber after washing. The solvent after absorption of CO_2 becomes rich and collected at the bottom of the absorber. The rich solution is pumped to the top of a regenerator after heat exchange where heat of regeneration is supplied through a re-boiler. On heating, the solution liberates absorbed CO_2 and solution gets regenerated for further absorption. The CO_2 is collected from the top of the regenerator and sent to Urea plant through a booster compressor for further conversion to urea.

In this process some heat stable salts are generated due to minor decomposition of the solvent which is separated in a reclaimer and disposed off.

Solvent (KS-1 Solution) using for recovery in CDR plant and its environmental consequences: These factors contribute to the use of large equipment, high solvent consumption and large energy losses - leading to increased operating costs. During its comprehensive R and D phases, MHI tested more than 130 different reagents. The most efficient solvents were critically examined in the final stage of pilot plant testing. Following this, a proprietary solvent KS- 1 was developed. In parallel with the development of the solvent, the process itself has also been optimized, leading to superior, demonstrated performance of CO_2 recovery from the flue gases of fossil fuel combustion processes. The development of KS-1 is seen as a breakthrough because

of the significant number of advantages it offers. KS-1 has an exceptionally low corrosive nature and, unlike MEA, does not require a corrosion inhibitor. This factor means carbon steel can be used for the majority of construction within the CO_2 capture plant. Furthermore, the process operates at atmospheric pressure (ensuring a safe work environment), has few exotic materials and a simple configuration. Additionally KS-1 offers superior CO_2 absorption and regeneration, lower degradation, lower circulation rate and, with other patented equipment, has less solvent loss when compared to other amine based systems. All of these features lead to decreased operating cost. Importantly, KS-1 together with the patented "improved" CO_2 recovery process which utilizes the heat of the lean KS-1 solvent, effects a 30% reduction in steam consumption over the conventional MEA process.

HSS (Heat stable salt): Heat stable salts (HSS) have received a lot of attention in the industry. HSS are acid *anions* with a stronger acid strength than the acid gases that are removed from the process gas. These anions may bind to the usable amine and then therefore make it unavailable for acid gas absorption. Heat stable amine salts (HSAS) refers to the salt formed by a HSS (anion) and a protonated amine molecule (cation). HSAS may also be referred to in some instances as bound amine (BA)

HSS vs. HSAS: There has been much confusion about the terminology of HSS versus HSAS. It is important to understand that these HSS anions must be bound to a cation in solution so that the solution is balanced (Mother nature's rule). One must understand what cation forms a salt with the HSS anion to understand the disposition of the anions and their quantity in solution. As referred to earlier, the sum of cations in solution must equal the amount of anions in solution.

Σ Cation.s = Σ Anions

BA + SC = HSS + LL

Where, BA = Bound amine (protonated amine molecule)

SC = Strong cations (sodium or potassium)

HSS = Heat stable salt anions

LL= Residual leanloading (H_2S or CO_2)

From the above equation we can see that HSS will not equal the Bound Amine (HSAS) if there is a substantial amount of strong cations present in the amine solution. This is why we recommend that the total level of HSS anions and strong cations should be measured directly. Measuring the HSAS only may give a false low reading of the level of HSS anions in solution if strong cations are also present in the sample.

It is also important to understand that HSS anions may be reported at least three different ways, and it is important to understand the methodology employed to avoid confusion.

- Weight percent of solution HSS anions (strong acid anions) measured as weight percent of the total solution.
- As weight percent amine, this unit of measurement assumes that the HSS anions are bound to an amine cation (also reported as HSAS). This number is determined by calculating the equivalent amount of amine cations that are tied up with the HSS anion, and is expressed as weight percent of the total solution.
- As percent amine capacity (As percent total amine) HSS expressed as weight percent amine divided by the amine strength (free amine or alkalinity).

Determination and analysis procedure of heat stable salts:

Method: This method is intended to be used to determine the quantity of heal stable salts present in used aqueous amine solutions. A weighed sample of solvent is passed through (or equivalent) a column of DOWEX* 50W-X8, 50-100 mesh hydrogen form resin. The anions present are converted to the corresponding acids, and the solvent is retained or the resin. The effluent containing the acid is then titrated, potentiomctricully, with a standard base.

Apparatus: pH meter, with a combination pH electrode, glass column, ID 16 mm x 610mm L, or 100 ml ion exchange column, stand for ion exchange column, magnetic stirrer with heater, thermometer (0-100°C), beaker (capacity 200 ml, 500 ml), 31, automatic titrator, plastics funnel, electric balance, graduated at I mg

Reagents:

- 0.1N NaOH solution Dissolve 4~4.5g of NaOH in / liter of water. Make standardization as follows.

  $\Rightarrow$ Weigh 0.2~0.25g of sulfamic acid and dissolve the acid in 50 ml of water.

  $\Rightarrow$ Add 3 drops of Bromothymol blue (BTB) solution and titrate the solution until the color of solution turns blue.

  $\Rightarrow$ Normality of 0.1N NaOH solution is calculated as follows.

  $$N = SF/ 97.09 X 10^3 /V$$

  Where: N= Normality of 0.1N NaOH solution (eq/1)

  SF= weight to taken sulfamic acid (g)

  V= 0.1N NaOH solution consumed; in titration (ml)
- 0.1% Bromothymol blue (BTB) indicator dissolve 0.1 g of BTB in 20ml of ethyl alcohol. Then, dilute to 100 ml with water.
- Hydrochloric acid (5 or 10%)
- Cation exchange resin (hydrogen form)
- pH paper, range to include 6~8.

Procedure:

- Fill the glass column with enough wet resin to completely neutralize the solvent and exchange the anions present. (Approximately 2 ml of resin per meq. of solvent)
- Pass 100 ml of 10% HCl through the resin and rinse with deionized water until the effluent is neutral to pH paper.
- Combine 5~10 gm of sample plus or minus one milligram, 50ml of resin and 50 ml of deionized water.
- Heat to at least 71°C for 30 min.
- Add another 50 ml of resin to column.
- Pour entire solution (Including resin) into resin column and follow with deionized water until the liquid eluting from the column is neutral to pH water.
- Combine the rinse water, the eluted sample, and titrate potentiometrically with 0.1 N sodium hydroxide solutions with automatic titrator.
- From the titration curve obtained, determine the greatest point of inflection and consider this to be the end point, that is, the number of milliliters required for complete titration of the system.
- Make the blank test over the whole procedure and correct the result.
- From the quantity of 0.1 N NaOH solution consumed in the titration, the acidity and the concentration of heat stable salts can be calculated as follows.

(i) Acidity $A = \frac{(a-b)xN}{W_5}$

Where:

A = Acidity in sample (eq/kg)

a: 0.1 N NaOH solution consumed in titration in sample test (nil)

b: 0.1 N NaOH solution consumed in titration in blank test (m)

W_s: weight of sample taken (g)

N: normality of 0.1 N NaOH solution (eq/1)

(ii) Heat stable salts (HSS) concentration HSS (eq/kg) = A

Remarks

- If the solution contains carbonates and/or sulfides, in addition to the free acid gases present, voids can form in the column from release of the CO_2 and H_2S, and subsequent channeling will occur. By slurring the sample in a beaker with an additional quantity of resin, until the mixture is acid, the gases will be evolved. The mixture can then be poured over the resin in the column and the determination followed in the normal fashion.
- Before the titration is made, it is advantageous to boil the effluent sample, with vigorous stirring, for a few minutes. This will allow any dissolved acid gases to escape which would buffer the titration. The acids formed from the ion exchange are not affected by this boiling.
- Quantitative analysis for many of the anions found in solvent systems can be made on the titrated effluent, as interference from the solvent and ether cations have been removed by absorption on the resin.
- After the resin has been in contact with a 1 N (or stronger) hydrochloric acid solution for a sufficient length of time, it will attain an equilibrium exchange capacity of about 1 meq/ml of wet resin. In order to avoid column breakthrough, never exchange more than half the original capacity of the resin. Thus, it is best to provide initially a 100% excess of resin capacity over and above the quantity thought to be necessary.

Results

Analysis items and frequency are shown in Table 1. The analysis item and / or frequency may be increased depending upon the requirement in an operating facility.

Table 1: IRON and HSS analysis report as monthly average it its trend of growth

from May 2009	KS1 solution (After Correction of the data)	
- to Jan.2011	Iron (ppm)	HSS (%)analysis
May, 09	1.1	0.1
June, 09	3.2	0.3
July, 09	4.7	0.5
August, 09	5.5	0.6
September, 09	6.2	1.0
October, 09	6.2	1.2
November, 09	7.8	1.5
December, 09	8.5	2.1
January, 10	8.6	2.5
February, 10	13.5	2.7
March, 10	13.9	2.7
April, 10	16.45	3
May, 10	15.8	1.8
June, 10	14.0	1.4
July, 10	15.2	1.0
August, 10	12.5	0.9
September, 10	10.5	0.8
October, 10	7.0	0.6
November, 10	9.0	0.8
December, 10	19.5	1.15
January, 11	14	0.9

Discussion

Several researches have been found and develop solvent to absorb CO_2 which should be cost effective and economically viable. Mimura *et al.* (2004) have developed and observed the alternative of KS-1 solvent as KS-2: The most important issue involved with the chemical absorption method for recovering carbon dioxide from a power plant's flue gas is to develop energy-efficient absorbents. KS-1 absorbent was presented at ICCDR-2 in Kyoto. After the conference, efforts to develop energy-efficient absorbents have been made and a new absorbent KS-2 was developed, as a result and its performance confirmed by the pilot plant. KS-2 has similar energy efficiency as KS-1 both of which require 20% less energy than MEA. KS-2 is however more stable than KS-1 and a more efficient absorbent for low CO_2 content flue gas. MHI has published papers on the performance of its KS-1 solvent in the petronas fertilizer Co. CO_2 capture plant in Malaysia. This is the only commercial installation of KS-1. Using this data, the performance of the EFG Plus ^{SM} technology can be compared to KS-1. The recovery of carbon dioxide from the rich amine stream from the absorber is highly energy intensive. It requires substantial quantities of low pressure steam extraction from the power plant turbine cycle and high power usage for compressing large volumes of flue gas to overcome absorber pressure loss. This results in a significant export power loss. Technology developers have therefore concentrated on developing new generations of technology which minimize steam consumption, by ensuring that a high degree of thermal integration is achieved in the process and/or by using amines with lower stripping steam requirements, either with improved formulations (Fluor), or improved amines (MHI with their KS1, 2 and 3 series of amines which have a much lower specific stripping heat requirement than MEA). Fluor has developed an improved process called Econamine FG Plus^{SM}. Which lowers the energy consumption of the process (Reddy *et al.,* 2003).

There is considerable industrial experience with MEA and most systems at present use an aqueous solution with only 15-25-wt% MEA, mainly due to corrosion issues. Corrosion inhibitors may be added to MEA solution, and these results in an increase in solution strength. In a commercial process, concentration of MEA up to 30-wt % have been employed successfully to remove 80% - 90% of the carbon dioxide from the feed gas (Mariz, 1998). The process has been used to treat flue gas, however, some cooling and compression of the gas is required to operate the system. The solvent composition is proprietary, so royalty costs may be significant. Another commercial process, which uses 20% MEA with inhibitors, is also offered for flue gas treatment (Barchas and Davis, 1992).

It should be avoided to continue CDR plant operation without reclaiming under the condition that iron concentration is 11 ppm. in the case that CDR plant continues to operate under the condition that iron concentration is over 5 ppm, CDR plant has a great risk of corrosion. The allowable limit of iron concentration for starting reclaiming shall be 5 ppm.

Situation regarding the increase of iron concentration, which was happened at IFFCO Phulpur. In 2007, iron concentration in KS-1 solution increased up to 32 ppm. MHI inspected inside after CDR plant S/D, and then found that heavy corrosion occurred at the duct between stack and Quencher. Quencher, absorber and regenerator had no corrosion. After investigation into CDR plant operation, it was found that CDR plant S/D without drying operation caused this heavy corrosion, resulting in entrainment of iron dust to KS-1 solution. So, iron concentration in KS-1 solution increased. Drying operation is necessary after CDR plant S/D for the purpose of preventing CDR plant corrosion. MHI recommended duct coating against entrainment of iron dust, and drying operation after CDR plant S/D.The increase of iron concentration in KS-1 solution had stopped since duct coating was conducted.

MHI designs that reclaiming shall be started when HSS concentration reaches to 2 wt%, and then stopped when it comes down to 0.7wt%. In NFCL case, HSS concentration in KS-1 solution is expected to increase as following figure based on the design basis of the flue gas. First reclaiming should be therefore conducted after approximately 2.5 months passed from CDR plant S/U. Next reclaiming should be done when approximately 1.5 months passed after 1st reclaiming has been finished.

In NFCL the formation of HSS in CDR plant shows exponential growth from starting to till 05-05-10. 3.3 (%)/ 2.9 (%) and the iron content was also very high around 18 ppm after then due to alkanomisation / reclamation the HSS quantity has been decreased 1.0% (21.08.10) now it is gradually decreasing due to reclamation now it has been 0.9% and the iron content is around an around 14 ppm as per the norms of Mitsubishi KM it should be below 0.7 % the query is if continuously analysis by quality control why it has not been reduced of both the HSS formation & Iron. As per my opinion it should be less than 1% (We have to maintain) and the iron content is also should be below 11 ppm for the best performance of the CDR plant then we can increase the ATA in 2011 May. We are daily adding one drum of KS-1 solution around 200 litre and additives to make efficient the chemical properties of KS-1 Solution to absorb 2 molecule of CO_2 by one molecule of KS-1 and to maintain the passivation layer to reduce the corrosion of the equipment

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Reference

Barchas, R. and Davis, R.: The Kerr-McGee/ABB lummus crest technology for the recovery of CO_2 from stack gases. *Energy Convers. Mgmt.,* **33:** 333-340 (1992).

Mariz, C.L.: Carbon dioxide recovery: Large scale design trends. *J. Canadian Petroleum Technol.*, **37**: (1998).

Mimura, T., Simayoshi, H., Suda, T., Masaki I. and Sigeaki M.: Development of energy saving technology for fluegas carbon dioxide recovery in power plant by chemical absorption method and steam system. *http://www.sciencedirect.com/science* (2004).

Mimura, T., Matsumoto, K., Iijima, M. and Mitsuoka, S.: Development and application of flue gas carbon dioxide recovery technology. Proceedings of International Conference on Greenhouse Gas Control Technologies, Cairns, Australia. Published by CSIRO publishing, Collingwood, Victoria, Australia. August 13-16 (2001).

Reddy, S., Scherffius, J., Freguia, J., Roberts, C.A.: Fluor EFG+^{SM} technology, an enhanced amine based CO_2 capture process. Second National Conference on Carbon Sequestration, NETL. DOE, Alexandria VA May 5-8 (2003).

Veawab, A., Aroonwilas, A., Chakma, A. and Tontiwachwuthikul, P.: Solvent formulation for CO_2 separation from flue gas streams. National Conference on Carbon Sequestration, Washington, DC, May 15-17 (2001).

Wong, S., Gunter, W.D., and Bachu, S.: Geological storage of CO_2: Options for alberta, combustion and global climate change conference, Calgary, Alberta, May 26-28 (1999).