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EXPERIMENTAL EQUIPMENT USED IN THE STUDY OF CARBON DIOXIDE ABSORPTION (I)

BY

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Abstract. The continuing increase demand in global energy has led a faster raw material depletion and increased exploitation of hydrocarbon fuels. Before using natural gas, it is necessary to remove acid gases (H_2S and CO_2), to increase the heating value of natural gas, reduce corrosion, prevent atmospheric pollution. Acid gas removal is best accomplished by chemical absorption. Such washing processes are also used in petroleum refining, coal gasification and hydrogen production. This paper presents a brief chronology of experiments conducted in the study of carbon dioxide absorption in amine solutions, focusing on experimental equipment developed in laboratory research.

Keywords: acid gases; carbon dioxide; experimental devices; flow of absorption.

1. Introduction

Natural gas, by its chemical composition, is considered the cleanest fuel. With reserves larger than those of oil, natural gas is practically usable in world. Its extraction and treatment require little energy in comparison with what oil or coal requires.

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Therefore, natural gas treatment is an important technical and economic problem. Depending on the storage, natural gas may contain very variable amounts of acid gases (CO_2, H_2S) and other contaminants (water, mercaptans) that must be removed from the gas. Indeed, H_2S must be completely eliminated from gaseous effluents due to its toxicity and its properties highly corrosive; in addition, it acts as a poison for catalysts. CO_2 acts as a diluent, reducing the energy value of gas, while increasing the cost of transport.

Absorption is a current process used in gas purification (Prausnitz *et al.*, 1999; Damen *et al.*, 2006; Gibbins and Chalmers, 2008). These include chemical absorption processes with amine solutions, physical absorption with physical solvents and hybrid absorption processes (chemical + physical). The choice of the absorbed-absorbing system depends on the equilibrium curve of the system, as well as on the hydrodynamic conditions in which the absorption process takes place. The latter depend on the constructive form of the absorber (with filler, tray, site, etc.) which determines the nature and intensity of the interphase contract, gas velocity, working pressure and temperature.

The schematic diagram of a chemical, physical or hybrid absorption process is similar. The gas to be treated is introduced at the bottom of the absorber and circulates countercurrent with the solvent; the gases to be separated are then absorbed. The solution charged with acid gas is recovered at the foot of the absorber and then introduced into a regeneration column. The difference between the three processes lies in the regeneration of the solvent.

Its efficiency decreases with decreasing absorption gas concentration due to an increase in the flow rate of liquid used as an absorbent relative to the absorbed gas unit. In Fig. 1 is present an absorption process using a chemical solvent.

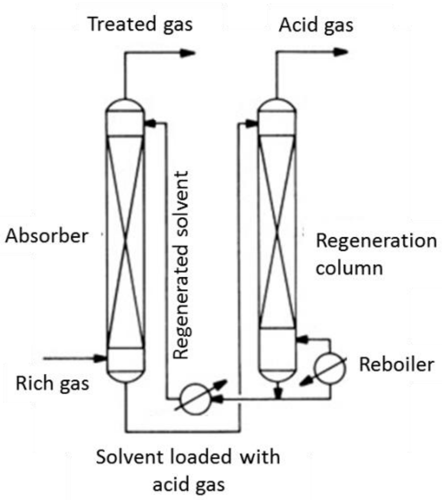

Fig. 1 – The schematic diagram of an absorption process.

2. Experimental Equipment

A bibliographic study of various experimental techniques to measure the flow of absorption for the acid gas into aqueous amine solutions shows that two experimental principles are used. Some authors carry out these measurements in scanning devices or in closed-ended devices: scanning method and closed reactor method.

There is thus found the existence of several types of apparatuses used in the study of gas - liquid absorption in order to determine the reaction mechanism of the acid gases and reaction kinetics.

The second point that differentiates experimental methods is how the device works. Continuous mode requires unnecessary quantities of acid gases and solutions, leading to costly experiences.

Two methods are used to track the evolution of a reaction: the chemical method and the physical method. The chemical method consists of sampling liquid phase samples to chemically analyze them. The concentration of a reagent, generally the concentration of gas, is also obtained in the course of the experiment. For example, in the case of CO_2 absorption, the chemical analysis consists of precipitating the gas as $BaCO_3$ by addition of $BaCl_2$. Physical analysis allows the pursuit of the evolution of a physical, optical or electrical property related to the studied system. One of the most used properties in kinetic measurements is the dominant pressure inside the reactor. The advantage of physical analysis is that it provides data continuously, contrary to chemical analysis.

Chronologically, the experimental devices are as follows:

1973. Levenspiel and Godfrey (Levenspiel and Godfrey, 1974) proposed a contactor for gas-liquid transfer. This new device is made up of two compartments. The lower compartment, in which the fluid is continuously introduced, is provided with a 3 – blade propeller shaker, placed at the end of the contactor. 8 baffles are placed inside this compartment. The second compartment has the same diameter and it is equipped with a 4 – bladed. The gas is continuously agitated.

1977. Vidaurri and Kahre (Vidaurri and Kahre, 1977) studied the absorption of CO_2 and H_2S using aqueous solutions of MDEA, TEA, DGA, DEA and MEA. They used a physical analysis method, which consisted in recording the pressure every 30 seconds after the gas was introduced. The experimental device (Fig. 2) consists of a cell containing a known volume of gas, above which a pressure cap is placed. The cell is connected through a valve to another glass cell containing the solution. After the solution is introduced, it is degassed. The vacuum is then carried out in the second cell before the gas is pressurized. The valve that binds the 2 cells is open, the gas (N_2, CO_2 and H_2S) is absorbed and the evolution of its cell pressure over time is recorded. The authors conclude that MDEA has a better selectivity compared to other amines used.

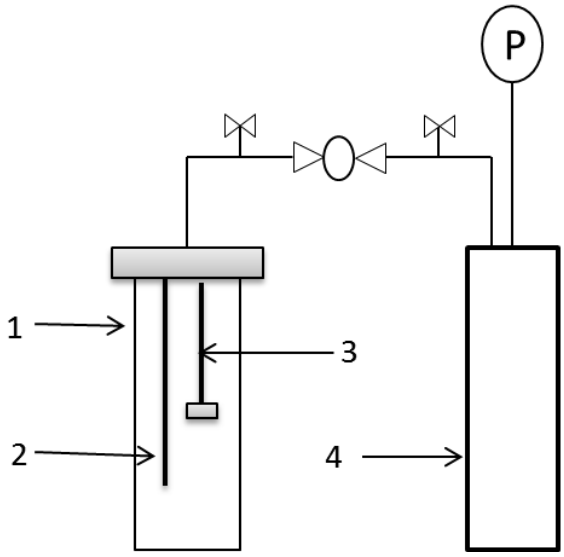

Fig. 2 – Vidaurri experimental apparatus
1 – solvent drum; 2 – thermocouple; 3 – stirrer; 4 – gas tank.

1984. In a reactor equipped with double walls and thermostated at 298 K (Blauwhoff *et al.*, 1984) studied CO_2 absorption in aqueous solutions of DEA, DIPA, TEA and MDEA (Fig. 3). The gaseous and liquid phase stirrers are magnetically driven, which avoids the generation of heat. The total pressure in the reactor is recorded by a mercury manometer. The solution is vacuum degassed in order to remove all inert gases, then is introduced into the reactor. When liquid vapor equilibrium is reached, CO_2 is introduced into the reactor at a CO_2 pressure, t = 0. The evolution of pressure during absorption is recorded. The absorption flow is obtained from the mass balance of the components in the gaseous phase. The kinetic constants were obtained by pseudo-ordering, considering the zwitterion mechanism and the participation of OH-alkanolamine, water and ions in zwitterion deprotonation. In the case of CO_2-loaded DEA and DIPA solutions, the partially apparent order of alkanolamine increases with concentration and decreases when the CO_2 load increases.

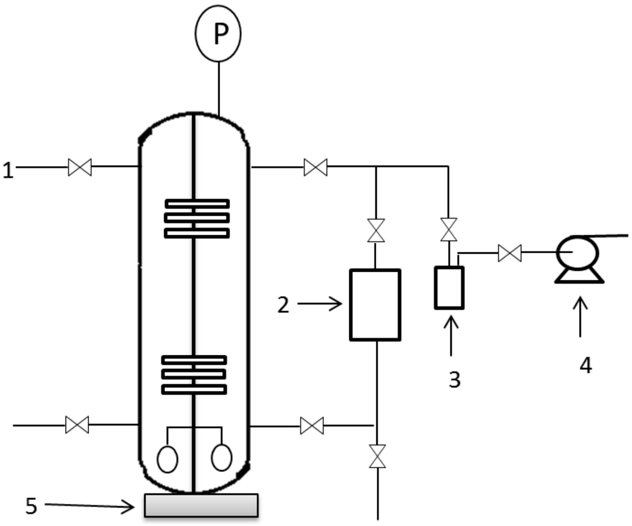

Fig. 3 – Blauwhoff experimental apparatus
1 – Carbon dioxide source; 2 – degassing cell; 3 – vacuum cell;
4 – vacuum pump; 5 – stirrer.

1985. Sada and his collaborators have used chromatographic analysis to determine the composition in CO_2 of the gaseous phase (Sada *et al*., 1985). A sample of this phase is taken at the inlet and outlet of the gas. The experimental technique remains the same as that used by Hikita in 1975 (Hikita *et al*., 1975). These authors studied the kinetics of CO_2 absorption in 2 types of solvents at T = 303 K: aqueous solutions of MEA or DEA and alcoholic solutions of DEA or MEA. The alcoholic solvents used are methanol, ethanol and 2-propanol. The value of the ratio for each type of solvent was determined by measurements in a downstream column. Considering the pseudo-order reaction regime I, the experiment determined the partial reaction order with respect to the amine in each solvent and found that it approaches the value 2 when the polarity of the solvent decreases.

1986. Haimour (Haimour and Sandall, 1987) carried out CO_2 absorption measurements in aqueous MDEA solutions in an open-shake reactor with a flat interface. The latter, unlike the previous one, was equipped with 2 thermocouples, placed in the immediate vicinity of the interface, in the liquid phase, respectively in the gas phase (Fig. 4). The agitator system was composed of two similar turbines having independent axes crossing the reactor. A volume of solution is introduced at the bottom of the reactor through a tube passing through the double walls. This volume is kept constant thanks to a continuous withdrawal. The gas is first saturated at ambient temperature before passing into a soap dispenser flow meter, then introduced at the top of the reactor. The gas absorption flow is obtained by the difference between the gas flow introduced and that flowing out of the reactor, divided by the exchange surface. These authors compared the experimentally determined acceleration factors and those calculated by considering only the bicarbonate reaction, explaining the high values obtained experimentally by the catalytic effect of alkanolamine on CO_2 hydrolysis.

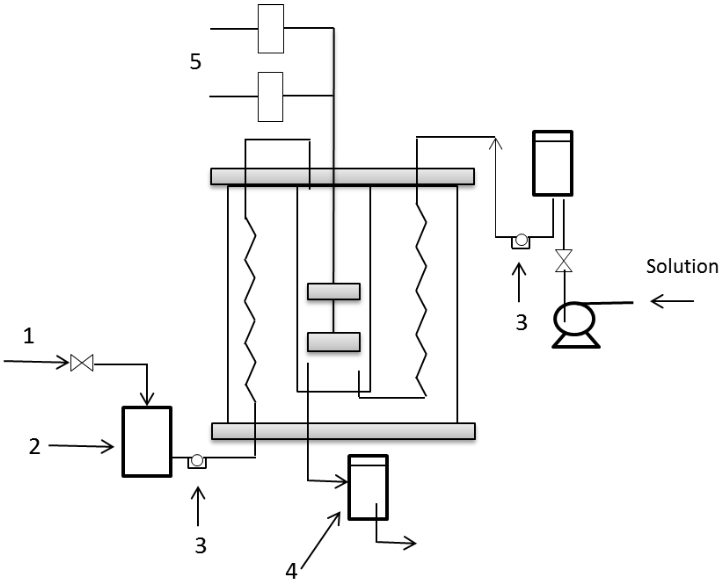

Fig. 4 – Haimour experimental apparatus
1 – gas source; 2 – saturator; 3 –flowmeter; 4 – level controller; 5 – stirring motors.

1987. Haimour and Sandall's study (Haimour and Sandall, 1987) was carried out in a laminar jet reactor consisting of two concentric tubes, one of 4.4 cm internal glass (absorption chamber), the other of plexiglass diameter 12.5 cm. The liquid injection tube is fixed to the top of the jet chamber. The other end is provided with a hole of 0.051 cm in diameter. At the bottom of the jet chamber, a 0.1 cm diameter tube is attached to a teflon plate. The fluid level in this tube is adjusted by a level controller. The liquid flow is set to the desired value, then the gas is introduced having sufficient time to purge the air in the reactor. The air flow is measured at the outlet with a soap dispenser. Considering that the reaction between H_2S and MDEA aqueous solution is instantaneous, these authors determined the kinetic constant of this reaction at 298 K. They also determined the diffusion coefficient of MDEA at this temperature.

1988. Versteeg and van Swaaij (Versteeg and van Swaaij, 1988) used the same device as Blauwhoff (Blauwhoff *et al.*, 1984), but replaced the mercury manometer with a pressure gauge connected to a computer. The experimental method remains the same. These authors studied the reaction between CO_2 and aqueous solutions, namely alcoholic solutions of DEA or DIPA. Carbon dioxide absorption in DEA + ethanol solutions, respectively DEA + n butanol was studied at 293 K. The zwitterion mechanism was chosen to interpret the experimental results. The authors corrected the values of kinetic constants obtained under pseudo - order regime I by using a numerical transfer model that takes into account the reversibility of the reaction.

1995. Rinker (Rinker *et al*, 1995) used a flowing spherical absorber (Fig. 5). The device consists of 2 concentric cylinders of Pyrex glass. The cylinder is placed between 2 stainless steel flanges. A solution distributor is attached to the upper flange. The base of the lower flange is in Teflon. The inside of the cylinder contains a sphere from Hastelloy (the commercial name of a Ni-Mo alloy) attached to a tube of the same material. The upper part of the tube is connected to the solution distributor, which is introduced at the top of the reactor through a tube that runs through the double walls. The solution flows on the surface of the sphere and the tube, then is collected in a pyrex glass tube fixed to the teflon block. After saturation of the gas into a solution of alkanolamine, it is introduced into the absorption chamber through another tube that crosses the double walls and crosses the teflon block. A second opening made on the teflon block allows liquid to be discharged in case of overflow. A soap film flowmeter placed at the top of the reactor allows the evolution of absorption to be followed after the gas supply has been shut off.

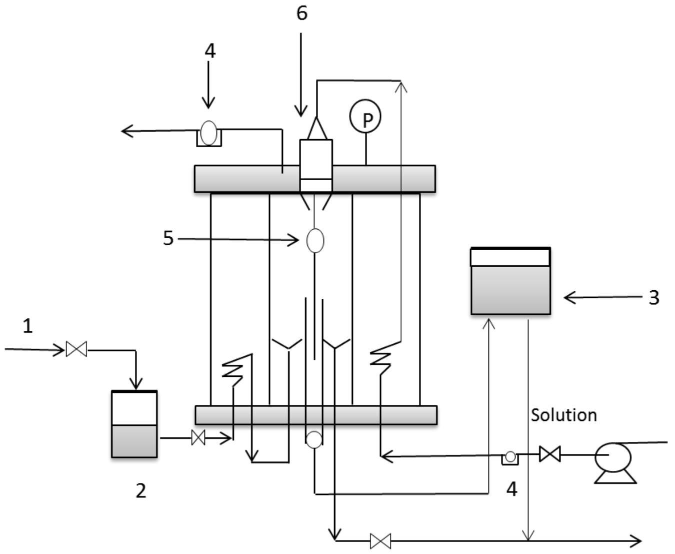

Fig. 5 – Rinker experimental apparatus
1 – gas source; 2 – saturator; 3 – level controller; 4 – flowmeter;
5 – sphere; 6 – liquid dispenser.

1999. Sheng Lin and Ching Shyu (Lin and Shyu, 1999) used another type of CO_2 absorption device in aqueous alkanolamine solutions (MEA, MDEA). This is a double-walled pyrex glass (Fig. 6). The column is filled with ceramic Rashig rings. It is first filled with 1 L alkanolamine solution. While the equilibrium temperature is reached, the CO_2-N_2 mixture is introduced at the base of the column. The CO_2 concentration of the mixture at column exit is determined by chromatography every 5-10 min. These authors have found that aqueous solutions of MEA have a net absorption capacity well above that corresponding to MDEA solutions (absorption capacity expressed in moles of CO_2 absorbed. After regeneration in a distillation column at 483 K, the amine solution was used in an absorption experience. The absorption capacity of the MEA solution decreased by 40% (after the first absorption / desorption cycle), whereas in the case of the MDEA solution, there was a decrease of only 11% between the first and the last series of tests.

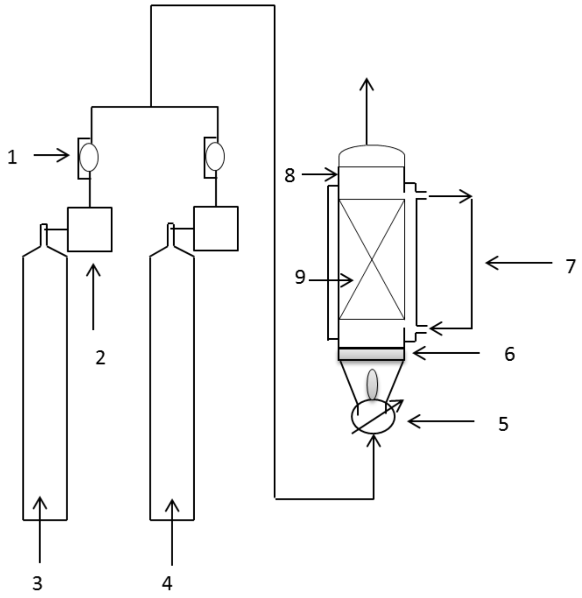

Fig. 6 – Sheng Lin experimental apparatus
1 – flowmeter; 2 – heating; 3 – gas tank CO_2; 4 – gas tank N_2; 5 – valve;
6 – dispenser; 7 – temperature regulation; 8 – filling; 9 – column.

2000. A different experimental technique was used by Ali (Ali *et al.*, 2000). This is the method called *interrupted flow*, whose principle is to track the evolution of the conductivity of the mixture over time. In this study, the mixture consists of two solutions, first prepared from amine and ethanol and the second from ethanol diluted in gas. The two solutions (same volume) are injected with a syringe into the cell where it is rapidly mixed (Fig. 7). A cell-bound conductivity meter allows tracking carbamate formation over time. The output signal of the conductometer is proportional to the conductivity of the solution. Experiments are performed with an excess of amine to achieve the pseudo-order regime I. The recorded conductometer curves allow direct calculation of the global kinetic constant, [k_{obs}, s^{-1}]. The advantage of this method is the direct calculation of the constant without resorting to physicochemical properties. The authors noted that the participation of ethanol in the deprotonation of zwitterion is negligible in cyclohexamine based solvents, in contrast to solvents using aniline and hexamine. They concluded that depending on the alkalinity of the alkanolamine, the degree of contribution of ethanol depends (it is higher when the solvent contains a weaker base, *e.g.* aniline).

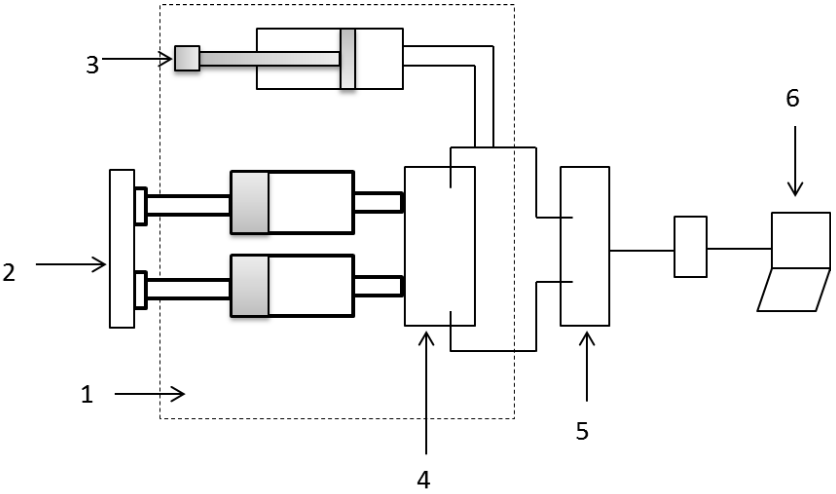

Fig. 7 – Ali experimental apparatus
1 – thermostat; 2 – injection syringe; 3 – stop syringe; 4 – mixing cell;
5 – conductometer; 6 – computer.

2000. In the research undertaken by Pacheco (Pacheco *et al*., 2000), a downstream reactor was used in the CO_2 absorption study in DGA and MDEA solutions (Fig. 8). The column is made of stainless steel. The pressure varies in the column between 1 and 8 atm. The gas is saturated at the working temperature before being introduced into the column at the bottom of it. Its concentration is determined continuously at column exit by IR analysis. It is first diluted with N_2, then introduced into a condenser that allows removal of all traces of water in order to protect the analyzer. The solution is introduced inside the reactor, the flow being kept constant and the temperature measured at the inlet and outlet of the column by means of thermocouples. Liquid phase samples are periodically sampled, then analyzed with IR to determine the amount of CO_2 load. The absorption flow is obtained from the mass balance of the gaseous phase using the inlet and CO_2 outlet concentration respectively.

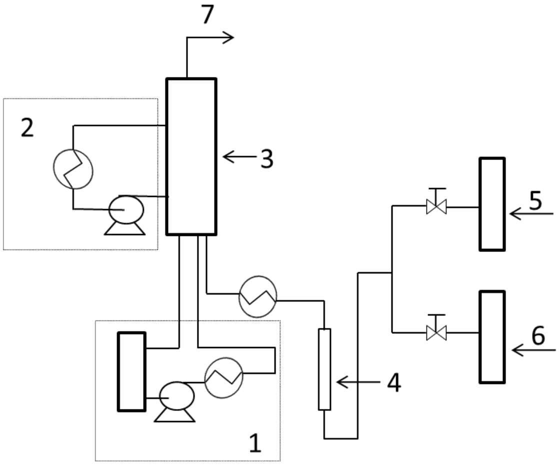

Fig. 8 – Pacheco experimental apparatus
1 – oil circuit; 2 – amine circuit; 3 – downstream reactor; 4 – saturator;
5 – gas tank N_2; 6 – gas tank CO_2; 7 – CO_2 tor analysis.

3. Conclusions

Over time, original laboratory equipment has been developed to measure the rate of absorption at certain temperature intervals using various aqueous amine solutions. We conclude this work with the idea that the main experimental techniques described in this paragraph are distinguished by:

- device type;
- how the device works;
- the method used to track the chemical reaction.

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ECHIPAMENTE EXPERIMENTALE UTILIZATE ÎN STUDIUL ABSORBȚIEI DE DIOXID DE CARBON (I)

(Rezumat)

Creşterea continuă a consumului global de energie a dus la o epuizare mai rapidă a materiilor prime și la o exploatare sporită a combustibililor de tipul hidrocarburilor. Înainte de utilizare, este necesar să se elimine din gazele naturale așa numitele gaze acide (H_2S și CO_2) în scopul reducerii coroziunii, prevenirii poluării atmosferice. Eliminarea gazului acid este cel mai bine realizată prin absorbția chimică. Astfel de procese de spălare sunt de asemenea utilizate în rafinarea petrolului, gazeificare și la producerea hidrogenului. Această lucrare prezintă prima parte a cronologiei experimentelor efectuate în studiul absorbției dioxidului de carbon în soluții de amine, concentrându-se pe echipamentele experimentale dezvoltate în cercetările de laborator.