CHEMICAL ENGINEERING TRANSACTIONS

VOL. 39, 2014

A publication of AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet

Guest Editors: Petar Sabev Varbanov, Jiří Jaromír Klemeš, Peng Yen Liew, Jun Yow Yong

ISBN 978-88-95608-30-3; **ISSN** 2283-9216 DOI:10.3303/CET1439187

Utilization of Emissions of CO_2 by Production of Mineral Fertilizers

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In recent years various methods of reduction of emissions of CO_2 of the cement enterprises, such as use of alternative fuels, more efficient kiln process, and co-production of synthetic fuels are developing (Mikulcic, 2013). Results of research which was made for Macedonian cement works are presented in article. The special attention is paid to improvement of cement calciners as increase of their efficiency also promotes decrease in emissions of CO_2 (Mikulcic, 2012). However along with change of the main technological process it is necessary to provide methods of utilization of formed CO_2.
Minimization of emissions of CO_2 in the atmosphere can be reached by a combination of utilization and CO_2 burial in the form of mineral fertilizers or carbonates as in this case the carbon cycle becomes isolated, and the carbon extracted from bowels of the earth as a part of fuel, comes back again on initial environment. Other ways of utilization can bring some economic effect, but don't solve an environmental problem. CO_2 after carrying out technological operations, as a rule, nevertheless gets to the atmosphere. Extracted CO_2 can be directed on production of mineral fertilizers, in for example bicarbonate of the ammonium.
The new technology of recycling carbon dioxide contained in the emissions of cement industry, which includes the steps of purification of gases from cement dust, carbon dioxide emission through the use of highly compact vortex apparatus and recycling to produce effective fertilizer - ammonium bicarbonate, which has better performance compared to the traditionally used in agriculture economy of ammonium nitrate. The technological scheme of the process of separation carbon dioxide gas and production of ammonium bicarbonate worked out.

1. Selecting a method for separating and utilization CO_2

The problem of choosing the method of CO_2 utilization is due both to an increase in its emissions and the need of many industries in the use of concentrated CO_2 as a raw material. For solving of this problem it is necessary to conduct systematic research in the following areas: identifying the sources of CO_2 emissions in the context of specific objects and processes; the study of properties of CO_2 in gas, liquid, solid and supercritical states, the development of effective ways of CO_2 utilization, preventing it from to re-entering the atmosphere and providing its binding or long-term sequestration.
Considering the ways to utilization of carbon dioxide necessary to take account the regional aspect, as regions may differ significantly from each other in terms of industrial development, the volume of emissions, the presence of potential consumers of captured CO_2. As practice shows, the highest level of emission is observed in the most industrialized regions, and in the regions with large thermal power plants operating on solid fuel. The interaction between enterprises-issuer and enterprises-consumer CO_2 is very important because they can be in close proximity to each other.
The production of carbon dioxide is well organized both in Russia and in other countries. The gases of chemical and petrochemical industries related to the production of ammonia, methanol and other products have a high content of CO_2 - 98-99 % and can be used without special equipment to increase the

Please cite this article as: Mingaleeva G.R., Nikolaev A.N., Shamsutdinov E.V., 2014, Utilization of emissions of CO_2 by production of mineral fertilizers, Chemical Engineering Transactions, 39, 1117-1122 DOI:10.3303/CET1439187

concentration of CO_2. The food industry in terms of CO_2 utilization are quite self-sufficient, because there is a steady balance between the release of carbon dioxide in fermentation processes and its using for the production of carbonated beverages.

The flue gases which generated by the combustion of fuel creates a special problem. Analysis of statistical data for emissions enterprises of various industries shows that a significant share of carbon dioxide emissions account (over 80 %) of the flue gas of thermal power plants and boilers produced by burning fossil fuels. These gases with CO_2 content of 8 - 20 % and a large amount of gaseous and particulate contaminants at the same time have a high temperature - 130-150 °C. The preparation of the concentrated CO_2 in this case very difficult.

The another significant source of CO_2 emissions are enterprises of cement production, waste gases contain 30-40 % CO_2. In the cement production process CO_2 is released as a byproduct of the reaction during calcination of the raw meal containing $CaCO_3$ and $MgCO_3$, and burning fuels, especially coal. Calculations revealed that the preparation of 1 t of Portland cement clinker consumes about 1.6 t of raw material mixture containing about 75 % $CaCO_3$ and 1-3 % $MgCO_3$, is allocated about 520 kg of CO_2 due to decarbonisation of raw mixture and 600 kg of CO_2 from the combustion of coal fuel. Thus, in the production of 1 t of clinker CO_2 emissions are about 1.12 t With the average performance of a cement plant of 1,000,000 t of clinker per year the CO_2 emissions may reach 1,120,000 t/y.

Recycling of carbon dioxide is its purification from moisture and high boiling impurities, whereby the volume fraction of CO_2 is increased to 99.99 %. A key indicator of product quality, such as the dew point at atmospheric pressure is reduced to -61 °C, and the content of detrimental impurities (carbon monoxide, hydrogen sulfide, oil, etc.) is reduced to the level of their solubility in carbon dioxide.

At the present time of produce methods of pure carbon dioxide from industrial gases: the method of absorption-desorption using a liquid chemical or physical sorbents, the method of adsorption-desorption using a solid sorbent; cryogenic process stream by desublimation in expanding the gaseous mixture, concentration by means of membrane systems.

With a large choice of technology it is difficult to find out one that would be universal for all occasions. Selecting the appropriate technology is determined by several factors: the concentration of CO_2 in the feed gas and product, presence of contaminants and their properties, pressure, temperature, state of the gas and even the geographical position of the company.

The absorption methods have advantages of CO_2 absorption using amine absorbers in the case of large volumes of gas emissions which contain carbon dioxide. The major equipment used in this process is an absorber.

At the present time, a large number of absorption apparatus, which have a substantially different in their characteristics and operating conditions are known. Apparatuses can be classified by the method of formation and structure of the phase contact area, which may be dropping, film, foam and bubble. Drip contact surface is formed by spraying a liquid into a gas stream, which can be used for jet ignition apparatus with a camera or various types of sprayers and sprinklers (irrigation chamber). The film contact surface is formed in fluid flow through a nozzle apparatus with irrigated or tubular film devices. In bubbling apparatuses the contact surface phases formed surface bubbles in a liquid layer. When large gasing of bubble layer the conditions are created for the formation of foam the gas-liquid contact surface formed emulsion consisting of the foam cells. Foam apparatuses isolated in a separate class, since the conditions of heat transfer in them differ from other devices.

As absorber absorption of CO_2 absorption schemes are mainly used packed and plate absorber whereas desorption of carbon dioxide from the rich absorbent solution used tower plate apparatuses.

The factors that determine the intensity of the processes in the contact devices are high relative velocity of the phases developed contact surface, uniform distribution of liquid and gas in the cross-sectional unit, sufficient time of contact phase countercurrent nature of the interaction phase, small energy losses. These factors appear differently in different types of apparatuses. The main problem is to purify large amounts of gases – tens hundreds of cubic meters per second, which is traditionally used packed absorbers cannot provide. Therefore, an apparatus in which the process was carried ethanolamine purification of gases CO_2, the use of a vortex unit, in which the absorbent is sprayed, and reacting it in a swirling flow of the gas. In vortex devices ensures high gas velocity - 1.5 to 2 times higher than in packed absorbers.

The another direction of research related to the different ways of using or disposing of carbon dioxide. Invention by way of recycling carbon dioxide are consider various aspects of production of chemical products. Products of this production must be sustainable materials or substances durables, otherwise due to decomposition or oxidation again turn carbon dioxide. Energy intensity should be low, otherwise the linked stream of carbon dioxide emissions will be offset in the production of its energy requirements.

Agriculture is an important area of recycling CO_2. Application of fertilizers largely solves one of the most pressing problems of agriculture - production of ecologically pure products without reducing the volume of agricultural production, as decomposition products fertilizers - ammonia, carbon dioxide and water - provide vital functions of living organisms and non-antagonistic nature.

The most natural way is the combination of recovery and disposal of CO_2 in the form of fertilizers or carbonates, since in this case the closed carbon cycle and the carbon, recovered from the subsurface in the fuel composition, is again returned to its original environment. Other methods of disposal, although they can bring some economic effect, yet do not solve the environmental problem - CO_2, spent in one of the process steps are typically still released into the atmosphere. CO_2 emissions can be directed to the production of mineral fertilizers, especially ammonium bicarbonate.

The high efficiency of nitrogen fertilizer in agriculture causes prospect of large-scale manufacture as an alternative or supplement to traditional chemicals such as urea and ammonium nitrate. Ammonium bicarbonate and their decomposition products readily react with the elements of the soil, to a much lesser extent compared with ammonium nitrate and urea are removed from it, do not pollute the ground water and the environment and, thus, are more environmentally clean drug (Pozin, 1974).

2. The description of technology separating of CO_2 and production of ammonium bicarbonate

In relation to the cement production the following scheme of production of ammonium bicarbonate is suggested (Figure 1).

Pre-cleaning gas from solid particles can be produced in a separate unit by means of devices with a double purification zone (Gimranov, 1982), in which the first zone is carried out dry gas cleaning from solids. Water supplied to the second zone and the deposition of particles takes place on the film and the liquid droplets. Calculation is based on the condition of low concentration of cement particles in the water, at which there is a suspension of cementation. The effectiveness of this type of apparatus reaches 99 %.

The hot gas to be purified is fed into the apparatus with a double purification zone 1, then in a vortex apparatus 2 for additional cleaning and gas cooling.

Cooled and cleaned gas is supplied to the underside of the absorber plate 3. As the absorbent to the fourth top plate enters the regenerated absorber solution is ethanolamine. In the preparation of a fresh solution is introduced a corrosion inhibitor. Water is supplied at the top of the absorber 3 in the first plate. Carbonating the solution from the absorber via a heat exchanger 3 is fed to the desorber for regeneration to regenerator 4. The purified gas is fed to the separator - clarifier 5 where the grout washing solution are occur. Purified gas is withdrawn from the section. The gas phase from the separator 5 - purified carbon dioxide - is directed to the section of production of ammonium bicarbonate.

Ethanolamine solution, discharged from the bottom of the absorber 3, is split into two streams. One of them - about one third - the two parallel streams of the filtration passes through the filters 6 and 7. Then streams are combined and pass through the tube of the heat exchanger 8 where heat regenerated ethanolamine solution. After heating, they are fed to the desorber for regeneration regenerator 4. The heat required for regeneration of ethanolamine is entered through a reboiler 9, heated coolant. Vapor-liquid stream of ethanolamine after reboiler 9 comes into a vapor space under of the first plate of regenerator 4.

Ethanolamine solution 4 from the regenerator enters the heat exchanger 8 in vessel 10 from where pump 11 partially passes through the filters 12, 13, 14 (parallel flow), and 15, then through the air cooler 16 is sent to the absorber 3. Optimal conditions for absorption of the regenerated absorbent stream must be cooled to about 40 °C. The separated carbon dioxide together with vapours from the top of the absorber 3 enters the air cooler 17, and then after cooling fed to the separator 18. The separated gas flows to a section of production of ammonium bicarbonate and the liquid phase is supplied to the pump 19, the regenerator 4 of irrigation line. In order to prevent entrainment of liquid phase separator 18 is provided with a vertical mesh - demister and a vertical partition.

Necessary for the production of ammonium bicarbonate, ammonia is sent to a collection drive 21 and further into the vortex absorber 22 irrigated with condensate of water vapor. Swirling absorber works with recycling absorbent to better use and reduce consumption. After saturation of the absorbent is supplied to the tank 21 and then is pumped through a heat exchanger 22 to the reactor 23 where it is carried out the reaction between ammonia and carbon dioxide in an aqueous medium to form ammonium bicarbonate. Ammonium bicarbonate solution near to saturation, is pumped via a heat exchanger to reduce its temperature to 15 °C.

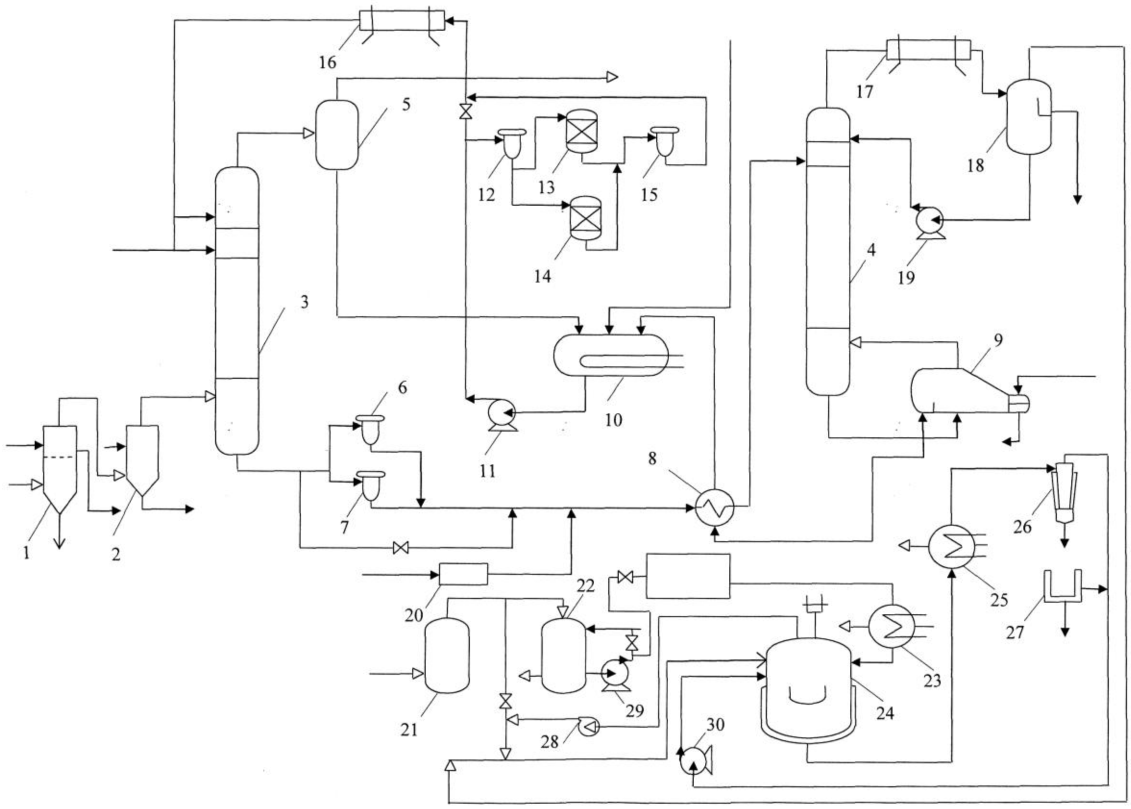

Figure 1: Technological scheme for ammonium bicarbonate based carbon dioxide utilization

Further supersaturated solution enters heat exchanger 25 through the hydrocyclone 26 with a cooling jacket, where crystalline ammonium bicarbonate are separated from the main part of the mother liquor, which is again sent to the reactor. The crystalline precipitate from the hydrocyclone 26 is fed into a centrifuge 27 for dewatering and further the final drying.

To provide the necessary hydrodynamic conditions and full utilization of the carbon dioxide, circulation of gas phase is organized in the reactor using a gas blower 28. The accumulation of inert gases in the system is eliminated periodically purging. This gas stream is directed into the vortex absorber 22. Since ammonium bicarbonate is a thermally unstable substance and is completely decomposed into components at the temperature 60 °C, in process scheme the cooling of fed ammonia water and gas is provided in the reactor. The finished product from the centrifuge 27 is fed to the drying and further package. Heating heat exchangers 23 and 25 is performed with steam.

3. Estimation of efficiency the production of ammonium bicarbonate

Material balance for the reprocessing of 25 t/h of gas is given in Tables 1 and 2. Calculations were carried out with a small content of CO_2 in gases (10 %). At a higher content of the effectiveness of its allocation will increase.

Estimation of efficiency of the technology was carry out by thermodynamic method, which performed based on the definition of exergy flows into each inlet unit and the outlet there from (Szargut, 1967). Exergy efficiency was 28.4 %.

Techno- economic evaluation of recycling systems CO_2 has some features that significantly distinguish it from similar calculations of projected technological schemes.

When creating technological systems for production or output of raw materials, technical and economic indicators reflect the possibility of a given company to produce products range and quality, customer satisfaction, and a predetermined amount. This criterion allows to establish the economic feasibility of the organization of production and profitability. Moreover, new products must have the best consumer qualities compared to peers and to be in demand in the market, which is estimated in the course of preliminary research and prospecting and marketing research. Investment attractiveness of the systems are designed by the possibility of profit, profitability and payback on investment.

Table 1: Material balance on the main components section absorption and regeneration (capacity 25 t/h gas)

Main components	Gas to cleaning in the absorber, kg/h	Gas after cleaning, kg/h	A solution of ethanolamine after regeneration, kg/h	Saturated solution of ethanolamine, kg/h	Concentrated CO_2, kg/h	Water after regeneration, kg/h
CO_2	2,500.0	231.2	160.4	2,429.2	2,268.8	0.0
H_2O	725.0	1,121.4	20,471.6	20,591.0	119.4	515.8
Ethanolamine	0	0.1	11,124.7	11,124.8	0.1	0.2
Mass flow	25,000.0	23,127.7	31,756.7	31,145.0	2,388.3	516.0

Table 2: Material balance on the main components section absorption and regeneration (capacity 25 t/h gas)

Capacity, t/h gas	Concentrated CO_2, kg/h	Ammonia, kg/h	Water, kg/h	Ammonium bicarbonate, kg/h	Water from the centrifuge, kg/h
25	2.39	0.88	6.17	4.02	5.42

For CO_2 utilization systems and other emissions core revenue part is of the prevention of environmental damage, which is expressed by the sum of environmental charges. The resulting products, such as ammonium bicarbonate or refrigerant, having consumer qualities, also form part of the revenue, but in this case they may not be the best available analogues. Therefore, if state control of emissions to the environment, including carbon dioxide, an undertaking these emissions should be interested in reducing environmental payments so that it is ready to attract investors or invest their own funds in the creation of recycling systems.

In European countries payment of CO_2 emissions is 8 - 50 €/t depending on the size of the state quota and the need to purchase additional quota. The level of profitability of production is determined by the formula:

$$ROI = \frac{(P - T) \cdot 100}{FA - CA}, \%, \tag{1}$$

where *P* - annual profits of the enterprise; *T* - tax on profits; *FA* - cost of fixed assets (typically 95 % of the investment costs); *CA* - normalized value of the current assets (10-12 % *FA*).

For utilization systems for charging you for CO_2 emissions to determine the expression level of profitability takes the following form:

$$ROI = \frac{(P - T + PE) \cdot 100}{FA - CA}, \%, \tag{2}$$

where *PE* - sum of environmental payments for CO_2.

Economic evaluation showed that the capital cost of the organization of production will be repaid in less than 2 years, while the profitability of production will be 8.1 %. If environmental payments amount to at least 10 €/t CO_2, the profitability of production is already 10 %, respectively payback period drops to 1.5 y.

4. Conclusions

Process of production of bicarbonate of ammonium is widely applied in the food and chemical industry, but can be successfully used in processes of utilization of carbon dioxide of power plants and plants due to highly effective vortex devices at a stage of a cleaning from dust and CO_2 extraction from gases. According to calculations from each ton of the emitted and cleared carbon dioxide 1.68 t of bicarbonate of ammonium can be made that at existing norms of introduction of mineral fertilizers for increase in fertility of farmlands provides the huge potential of their realization.

To implement ways to utilization of CO_2 necessary to develop basic principles of interaction of various industries on environmental security and raw material supply and to develop a methodology of optimal variant of utilization CO_2 of industrial facilities, including estimation of thermodynamic and technical-economic indicators.

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