



Mini Review

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The Changing Paradigm in Sour Gas Treating Processes



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The sour gas treating is the removal of hydrogen sulfide (H₂S), carbon dioxide (CO₂), and organo sulfides from gases. It is a common unit process used in refineries, and is also used in petrochemical plants, natural gas processing plants, and other industries. Currently, removal of carbon dioxide from thermal power plant flue gas seems to be a great challenge as well, which generically is different from natural gas and refinery off gas treating technology. Before chronicling the technologies and their changing spectrum in sour gas treating, the author would like to have a brief opportunity to discuss simply the plight of non-treating of sour gas. The CO₂ enriched gas is having greenhouse effect and global warming potential, untreated hydrogen sulfide may corrode the pipelines in downstream processing, untreated gas incurs the reduction in fuel value of the gas. In LNG (liquefied natural gas) plants, CO₃ should be removed to avoid freezing in the low temperature chillers. Moreover, in the manufacture of ammonia, it would poison the catalyst. The drastic change in climate has triggered an imbalance in ecology, socio-economic structure, energy security and sustainable development. CO2 emission, being one of the exponential components behind this changing climate and that has challenged the environmental poise. Carbon dioxide (CO₂) capture and sequestration or utilization (CCS/ CCU) has taken the centre stage globally due to the increasing adversaries of CO₂ emissions.

Among the most widely practiced gas treating processes, absorption into physical solvents or chemical solvents, and hybrid solvents (blends of chemical and physical solvents) have been the major ones [1,2]. Propylene carbonate (in Flour process), Dimethyl ether of Polyethylene Glycol (in Selexol process), N-methyl-2-pyrolidone (in Purisol Process), Chilled methanol (in Rectisol process) are the physical solvents used for has treating. DIPA-sulfolane-water (40-40-20 wt %) under the trade name Sulfinol D, MDEA-sulfolane-water (40-40-20 wt %) under the trade name Sulfinol M and many more

hybrid solvents are in use for gas treating. Among the different technologies available for CO, mitigation, capture of CO, by chemical absorption is the technology that is closest to get implemented commercially. The technology was patented for natural gas sweetening as early as 1930 by R.R. Bottoms [2]. Triethanolamine (TEA) was the first alkanolamine commercially available and used in early gas-treating plants. In the present context, the role of alkanolamine solvents in sour gas treating research should be revered. Chemical absorption processes for gas treating may be divided into three conceptual categories distinguished by the rate at which the solvent reacts with CO₂. The first group of processes can be termed "bulk" CO₂ treating processes, and are well-known by their ability to remove CO₂ to very low levels. Aqueous primary or secondary alkanolamines and promoted hot carbonate salts are prominent solvents in this category. Though the reaction of CO₂ with these alkanolamines is fast, it is accompanied by a highly exothermic heat of reaction [2], which must be supplied in the regenerator to regenerate the solvent. Consequently, these processes can be energy intensive [1]. The second group of processes employing tertiary or hindered alkanolamines to avoid the faster carbamate formation reaction represents the second group of "selective" treating processes. These selective processes are capable of removing as much as 90% of the CO2 in the feed gas while removing H2S to very low levels (less than 4ppm) [2]. The tertiary alkanolamine MDEA can be regarded as a selective treating agent. A third category of processes is selective treating category. Blended alkanolamines and sterically hindered alkanolamines (2-amino-2- methyl-1propanol (AMP), 2-amino-2-(hydroxymethyl)-1, 3-propanediol (AHPD)) are suitable candidates of this category, which reduces the regeneration energy requirement for the recirculating solvents. Solvent loss, high capital investment for absorbers and strippers, high regeneration energy requirement of alkanolamines have necessitated still better solvent formulation suitable for large scale industrial process applications.

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Gas treating research has witnessed several transitions. Room temperature ionic liquids (RTL's) and their mixtures with alkanolamines, alkali metal salts of a number of tertiary amino acids promoted with reactive amines such as MEA have been used in CO₂ absorption. Some solvents have been proposed with multiple amine functionalities and among them, Piperazine (PZ) has been used as a promoter specially in treating coal based power plant flue gas [3]. The molecular structure and spatial arrangement of the attached functional groups in alkanolamines may be crucial in CO, absorption [4,5]. Apart from absorption, adsorption (Solid Surface), and physical separation (membrane, cryogenic Separation) process have been used in sour gas treating. Paul et al. [6] have studied theoretically the absorption of carbon dioxide in different single and blended alkanolamine solvents using flat sheet membrane contactor (FSMC). Wang et al. [7] have studied the absorption of CO, into water using parallel-plate gas-liquid membrane contactor. The largest membrane based natural gas processing plant in the world is located at Qadirpur, Pakistan (Dortmundt, UOP, 1999). Process integrated membrane and absorption unit are advantageous because of reduced size of membrane gas liquid contactors and weight, wide range of liquid and gas flows, lower capital costs, reduction in energy (if membranes are integrated with the stripping unit), reduction in solvent losses, no entrainment, flooding or channeling. The fascinating facts could not be transformed in to a full flagged, commercially viable CO2 capture technology at large scales. The real issues are low selectivity & flux - large scale systems not economically viable (yet), thermal stability of polymer membranes, degradation & lifetime of membrane, and immature technology.

Commonly used adsorption processes are; the iron oxide, zinc oxide, MOFs and molecular sieve (zeolite) process. In recent years, there has been considerable research on the use of zeolites, metal organic frameworks (MOFs), and zeolitic imidazolate frameworks (ZIFs) for selective adsorption of CO2 from $\rm CO_2/H_2$, $\rm CO_2/CH4$ and $\rm CO_2/N_2$ mixtures [8-13].

A promising novel option is to freeze out (desublimate) CO2 from flue gases using cryogenically cooled surfaces. High cooling costs could be minimized by exploiting the cold duty available at Liquefied Natural Gas (LNG) re-gasification sites. A novel process concept has been developed by [14], based on the periodic operation of cryogenically cooled and

dynamically operated packed beds. An extensive R&D effort has been envisioned towards conversion of CO_2 to hydrocarbon by chemical, and biochemical routes, possibly it is one of the strategic routes leading to our future survival in this planet.

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