

Advanced Technology for the Capture of Carbon Dioxide from Flue Gases

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Abstract

Cost effective carbon sequestration schemes have been identified as a key need for dealing with carbon dioxide's (CO₂) impact on global climate change. Two main approaches are being pursued for sequestration: the enhancement of biological carbon sinks, and the capture and storage of CO₂. Since the bulk of the cost in a capture and storage sequestration scheme stems from CO₂ separation and compression, Praxair has focused on substantially reducing these costs through technology advances. In this paper, we focus on CO₂ capture from flue gases emitted from the existing energy infrastructure. Such large point sources account for nearly sixty percent of global CO₂ emissions. Praxair has developed advanced amine absorption processes that can separate CO₂ from flue gases at much lower costs than current commercial alternatives. These significant capital and operating cost savings have been achieved by developing an oxygen tolerant amine absorption process, and by the application of amine blends.

1. Introduction

The growing evidence that links the greenhouse gas carbon dioxide (CO₂) and global climate change highlights the need to develop cost effective carbon sequestration schemes [1]. CO₂ accounts for over eighty-two percent of all greenhouse gas emissions in the U.S., even after considering its relative greenhouse warming potential (GWP) [2]. Nearly sixty percent of CO₂ is emitted by utility or industrial power systems, which are based on fossil fuel combustion [3]. Future power generation technologies such as fuel cells or gasification need to mature and to lower costs to gain widespread application. Consequently, it is likely that for the next several decades the bulk of the CO₂ will be emitted from the fossil fuel-based energy infrastructure, both existing and that likely to be added in the near term.

Carbon sequestration would enable the continual use of carbon-based fuels to meet the world's growing energy demand without further increasing the atmospheric concentration of CO₂. Because carbon-based technologies dominate about 75% of the world's and 84% of the U.S.' power generation [3], and because they will likely maintain their dominance for the foreseeable future, an effective CO₂ emission control strategy should target these power systems. The flue gas effluents of the corresponding medium to large point sources present a desirable control point due to their centralized location and large scale [4].

CO₂ capture technology retrofitted to the existing energy infrastructure offers the potential to meaningfully reduce worldwide CO₂ emissions in the near term in a practical manner. Some of the emerging technologies e.g. oxyfuel combustion with CO₂ recycle will require unconventional combustion systems. As such, as they become more cost effective, they will mainly find application in new energy installations. This paper describes the technology development efforts at Praxair focused on the recovery of CO₂ from existing flue gases without having to modify the current infrastructure.

The main challenge of CO₂ capture and storage is the high cost of technologies using current state-of-the-art. Separation and compression of CO₂ account for the bulk of these costs, while the costs of transportation and injection are relatively lower [5]. Consequently, Praxair is focusing on developing advanced separation technologies that would significantly lower the cost of CO₂ capture from flue gases for eventual sequestration. This paper presents the successful development work at Praxair in the area of advanced amine absorption technology.

2. Key Aspects of the Sequestration Problem

The separation problem at hand is introduced first by discussing the key characteristics of typical flue gases. It is followed by an explanation of the preferred compression scheme to reach CO₂ sequestration pressure.

Flue Gas Characteristics

Flue gases emitted from medium to large point sources are generally at or slightly above atmospheric pressure. They typically contain 3–15% (by volume) of carbon dioxide. For example, flue gas from a coal-fired power plant typically contains about 14% CO₂, 5% O₂, and 81% N₂. Flue gas from a natural gas turbine is even leaner in CO₂ but higher in O₂ with a typical composition of 4% CO₂, 15% O₂ and 81% N₂. Typical trace contaminants include sulfur oxides (SO_x), nitrogen oxides (NO_x), and particulates. Their levels vary widely, depending on fuel composition, combustion system and operating conditions. For example, the flue gas of a coal-fired power plant may contain 300–3,000 ppm SO_x, 100–1,000 ppm NO_x, and 1,000–10,000 mg/m³ particulate matter. Natural gas firing significantly lowers the contaminant levels to less than 1 ppm SO_x, 100–500 ppm NO_x, and to around 10 mg/m³ particulate matter.

Efficient CO₂ Compression Requires Enrichment

Compression is a major consideration in several sequestration schemes, e.g. ocean or geologic sequestration. While typical power plant flue gases are emitted at around atmospheric pressure, their CO₂ content ultimately needs to be compressed to a high pressure, e.g. around 1500 psia prior to sequestration. One option is to directly compress the flue gas. However as Figure 1 indicates, CO₂ emissions resulting from power consumed in compressing flue gas can significantly reduce or eliminate the net amount of CO₂ that gets sequestered. For example in the case of coal-based power generation, the energy consumed in compressing flue gas containing 10% CO₂ from atmospheric pressure to above 1200 psia will generate CO₂ emissions that exceed the amount being sequestered! The net power consumed in upgrading the flue gas and compressing CO₂ using state-of-the-art technologies is also indicated in Figure 1 for both natural gas- and coal-based power generation. Thus it would be preferable to first upgrade CO₂ and then compress it.

With the above considerations in mind, the preferred route to CO₂ capture and sequestration from typical flue gas sources involves the following four steps. First, the CO₂ content of the flue gas is significantly upgraded by separation. Second, the CO₂-rich

stream is compressed to the sequestration pressure (e.g. about 1500 psia for injection into the ocean or a geologic formation such as an oil well or an aquifer). Thirdly, the dense CO₂ fluid is transported to a secure long-term storage location. Finally, the CO₂ is injected into the storage medium, such as a suitable geologic formation or the ocean.

As discussed earlier, low cost sequestration of CO₂ from flue gases hinges on the economics of the CO₂ capture step [5], i.e. to upgrade from 3 to 15% CO₂ to well above 90% CO₂. Accordingly, Praxair's approach to solve this key problem is discussed next in detail.

3. Approach to Solution

The rationale for making chemical absorption the technology of choice for CO₂ separation from flue gases is given first. It is followed by a general discussion of amine absorption technology including its background, the state-of-the-art, and its key areas for development.

Methods for CO₂ Separation

Since the bulk cost of CO₂ sequestration from flue gases is determined by the CO₂ capture step [5], a comprehensive survey of potential separation methods has been completed at Praxair to select the best technology option(s). A synopsis is given here.

Separation of CO₂ from a mixture of gases can be accomplished through various means: low-temperature distillation, membranes, adsorption, physical and chemical absorption. Because typical flue gases have low CO₂ partial pressures (less than 2.2 psia), the driving force for many of these separation methods is significantly diminished. Consequently, inefficient and costly flue gas compression would be necessary to ensure adequate CO₂ recovery by such methods as low-temperature distillation, pressure swing adsorption (PSA), membrane separation, or physical absorption. Specific considerations in connection with these separation methods are given next.

Low-temperature distillation has widespread commercial use in the purification and liquefaction of CO₂ from streams containing >90% CO₂. However CO₂ cannot be effectively condensed from atmospheric pressure flue gas.

To produce a CO₂-rich stream with high purity from flue gas, membrane or pressure swing adsorption (PSA) processes generally require either a high degree of compression or deep vacuum and/or multiple separation steps. The associated capital and operating costs are high.

Physical absorption processes are temperature and pressure dependent, with absorption occurring at high pressures and low temperatures. Such processes are typically used for CO₂ separation when partial pressures of CO₂ are high, e.g. CO₂ rejection from natural gas. Use of physical absorption for CO₂ capture from flue gas would entail a significant amount of compression, bulk of which (>80%) is consumed in compressing N₂. Thus, a significant energy penalty will be incurred making the process uneconomical.

Chemical absorption, e.g. with amine-type absorbents, is well suited for CO₂ recovery from flue gas. The chemical reaction between CO₂ and amines greatly enhances the driving force for the separation, even at low partial pressures of CO₂. The costs of this

technology are relatively insensitive to the feed CO₂ content. Consequently, chemical absorption with amines provides the most cost-effective means of directly obtaining high purity (>99%) CO₂ vapor from flue gases in a single step.

Background of Chemical Absorption with Alkanolamines

Chemical absorption with alkanolamines has been generally used in processes such as natural gas sweetening and hydrogen production for the rejection of carbon dioxide [6]. However, in these applications, the CO₂ partial pressure is significantly greater than that in flue gas applications. Several alkanolamines such as MEA (monoethanolamine), DEA (diethanolamine), MDEA (methyldiethanolamine), DIPA (diisopropanolamine), DGA (diglycolamine), TEA (triethanolamine) and other sterically hindered amines have found commercial use. The particular choice of alkanolamine is primarily dictated by the requirements of the specific application.

For many years, MEA was almost exclusively used for removal of CO₂ and H₂S. However to reduce operating costs and corrosion rates, the use of MDEA-based solvents became more prevalent. The slower rate of reaction of CO₂ with MDEA was compensated through the addition of small amounts of rate-promoting agents such as DEA or piperazine [6]. In applications such as natural gas treating, the state-of-the-art technology employs MDEA-based solvents, i.e. a blend of MDEA and a faster reacting amine. However, this choice will not be effective for CO₂ recovery from flue gas because reaction rate of MDEA with CO₂ is very slow at low partial pressures leading to absorption columns that are very tall and expensive.

Description of Typical Amine-based Absorption Process

Figure 2 depicts the operation of a typical amine based absorption plant for recovery of CO₂ from flue gas. Prior to CO₂ recovery, the flue gas typically needs to be cooled and treated for reduction of particulates and other impurities such as SO_x and NO_x to tolerable levels. A feed blower provides the necessary pressure for the pretreated flue gas to overcome the pressure drop in the absorber. Flue gas is passed into the absorption column, which typically operates within the temperature range of 40 to 45°C at the top, and 50 to 60°C at the bottom. The flue gas and lean amine solution contact each other countercurrently in the absorber. The amine selectively absorbs CO₂ from the flue gas by chemically reacting with it. Small amounts of oxygen physically dissolve in the amine solution. The CO₂-rich amine solution from the bottom of the absorber is pumped to the lean/rich heat exchanger. The rich amine is heated to about 105°C by means of the regenerated or lean amine solution. The heated CO₂-rich amine then enters the upper portion of the stripper, which typically operates at a temperature of 110°C at the top and 120°C at the bottom. Operating pressure at the bottom of the column and in the reboiler is typically around 30 psia. Pressure drop across the column is about 3 psia. The energy for stripping is provided through the use of saturated steam at a pressure of 45 psia or higher. Heating of the amine solution drives off some water, which enters the stripper as steam and helps desorb CO₂ from the rich amine solution. Most of the lean amine solution is pumped to the lean/rich heat exchanger. A small portion of it is fed to a reclaimer, where heating to a higher temperature and addition of soda ash or caustic soda facilitates precipitation of any degradation byproducts and heat stable amine salts.

The CO₂-rich vapor stream from the top of the stripper is passed through a reflux condenser where it is partially condensed. The resulting 2-phase stream is separated into CO₂ and condensate, which is fed back to the stripper. The CO₂ stream recovered at a pressure of around 25 psia is further dried and compressed to a high pressure required for sequestration, e.g. about 1500 psia for injection into the ocean or a geological formation.

State-of-the-art

Separating CO₂ from flue gas using chemical absorption with alkanolamines is complicated by the following two factors:

1. Low partial pressure of CO₂ (< 2 psia),
2. Presence of oxygen in the flue gas.

The low CO₂ partial pressure necessitates the use of MEA-based systems. While MEA may have the advantage of fast reaction rate with CO₂ at low partial pressures as compared to other commercially available amines, there are significant disadvantages such as high heat of reaction, limited capacity and significant corrosion problems. Oxygen present in the flue gas causes rapid degradation of alkanolamines. The degradation byproducts lead to corrosion problems and cause significant deterioration in the overall separation performance.

To counter the influence of oxygen, the approach currently practiced is the use of chemical inhibitors. For example, the processes licensed by Kerr-McGee/ABB Lummus Global Inc. [7] and by Fluor Daniel [8] use inhibited monoethanolamine solutions. Depending on the exact concentration of the solution, the steam consumption can vary from 4 – 5 MMBtu per metric ton of CO₂ recovered. It is desirable to reduce the capital and operating costs significantly to make sequestration more affordable.

These key issues have been addressed by developing Praxair's advanced amine technology, which is discussed next as the centerpiece of this paper.

4. Praxair's Advanced Amine Technology

Oxygen Tolerant Process

The key aspect of Praxair's successful approach is handling the dissolved oxygen in the amine solution through process modifications instead of the introduction of additional chemicals.

Praxair has recently been granted two patents for these improved oxygen tolerant absorption processes [9],[10]. Figure 3 represents a typical process flow diagram for the improved absorption process. The key idea in this process is to moderately heat the CO₂-rich amine to a temperature within the range of 60 to 90°C and then deoxygenate the solution by depressurization. For this purpose, the CO₂-rich amine is passed from the first heat exchanger to a flash tank where its pressure is reduced from slightly above atmospheric pressure to subatmospheric pressure, generally within the range of 5 to 10 psia by operation of a vacuum pump. Depressurization will cause some CO₂ to be released along with the oxygen. This stream can be directly mixed with CO₂-rich stream from the stripper for subsequent compression. The resulting oxygen depleted CO₂-rich amine solution, typically containing less than 0.5 ppm oxygen, is withdrawn from the

flash tank and passed through a second heat exchanger where it is further heated to a temperature of around 105°C. Since this heating takes place after most or all of the oxygen has been removed from the amine solution, there is no need for inhibitors to slow down the oxidative degradation of the alkanolamines.

Another means for deoxygenation is stripping the dissolved oxygen from the CO₂-rich amine in a stripping column by means of an oxygen scavenging gas. The flow rate of the oxygen scavenging gas and height of the stripping column can be optimized to ensure that the dissolved oxygen content of the CO₂-rich amine solution leaving the stripping column is about 0.5 ppm or less. Examples of gases that can be used as oxygen scavengers are nitrogen or the CO₂-vapor product from this CO₂-separation process. It has been found that less than 2% of the product stream suffices for oxygen stripping purposes. Also, in this case, the oxygen containing oxygen scavenging gas from the top of the stripping column can be remixed with the CO₂-vapor that is subsequently compressed prior to sequestration.

Praxair has recently demonstrated the performance of the oxygen tolerant absorption processes described above.

Amine Blends

Praxair has also been granted another patent [11] that describes CO₂ recovery using amine blends. A study of the different operating cost components of the chemical absorption process indicates that steam costs are the most dominant component. MEA-based systems tend to have higher steam consumption due to high heat of reaction of MEA with CO₂. Also, corrosion with MEA-based systems becomes significant at concentrations above 30 wt.%. Therefore, this patent recommends the use of concentrated amine blends, as high as 50 wt.%. Higher concentrations imply less water to be heated resulting in lower steam consumption rates. Further, use of another amine such as MDEA potentially allows for greater capacity and reaction rates without the operational problems that arise due to corrosion. Examples of such amine blends are solutions containing 10 – 20 wt.% MEA and 20 – 40 wt.% MDEA. Detailed simulations have confirmed the feasibility of the use of such amine blends for CO₂ recovery from flue gases. Pilot tests are underway to demonstrate that use of concentrated amine blends can reduce steam consumption from today's value of 4 – 5 MMBtu/mT of CO₂ to around 3 MMBtu/mT of CO₂ recovered.

Benefits of Application

The economic benefit from the improved processes described above is significant for separating CO₂ from flue gases. Ongoing work at Praxair is expected to further reduce these costs by a substantial amount.

These key technology advancements pave the way to significantly more cost-effective carbon sequestration processes. Praxair's advanced amine technology to capture CO₂ from flue gases promises to be a powerful vehicle for the meaningful reduction of greenhouse gas emissions from medium to large point sources. In addition, these reductions can be achieved readily because Praxair's CO₂ capture technology can be easily retrofitted to the existing power generation infrastructure without any modification to the core of existing systems.

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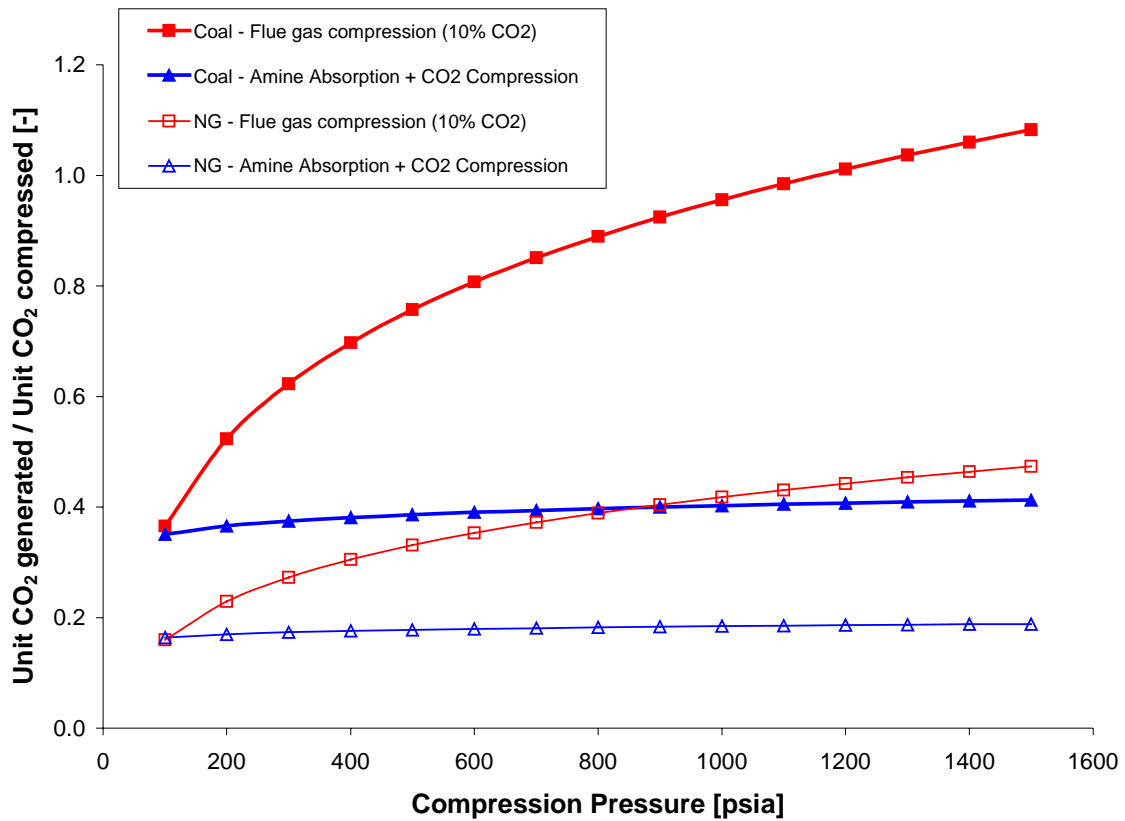


Figure 1. Amount of CO₂ generated by compressing unit amount of CO₂ as a function compression pressure for power generated by coal (full markers) and natural gas (empty markers). Squares represent: the compression of flue gas containing 10% CO₂; triangles show: amine absorption followed by compression of CO₂.

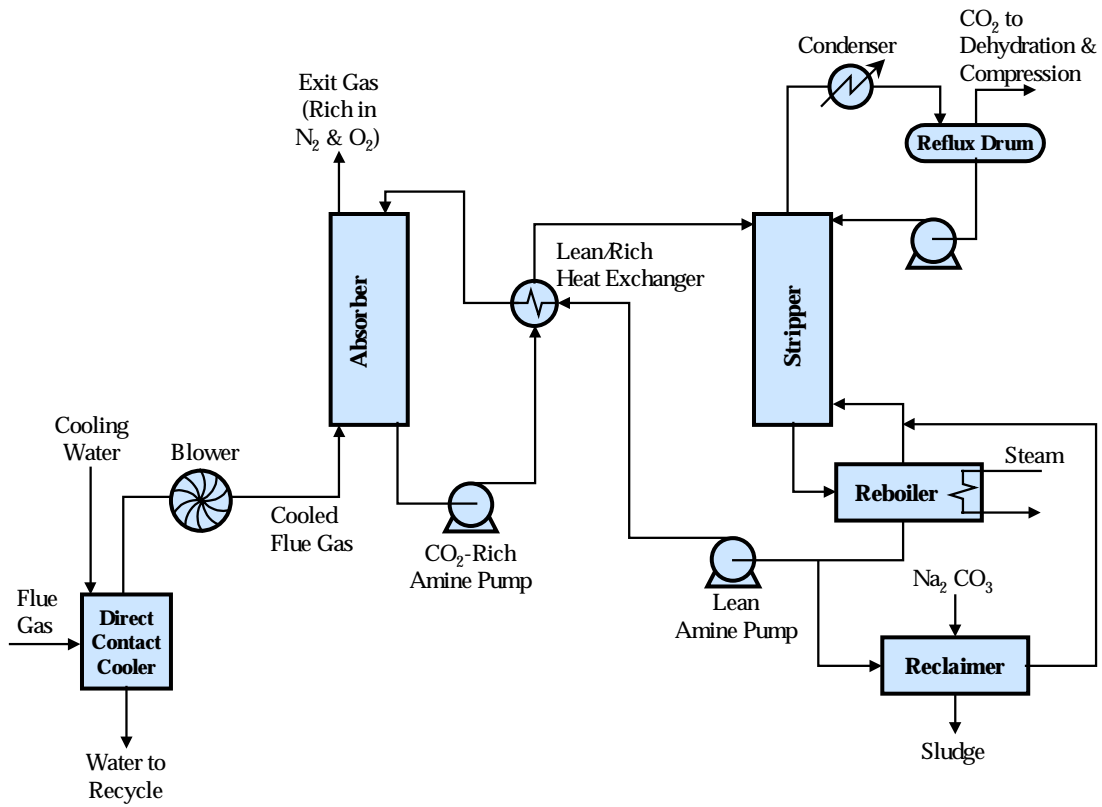


Figure 2. Typical Amine Absorption Process for CO₂ Recovery From Flue Gas

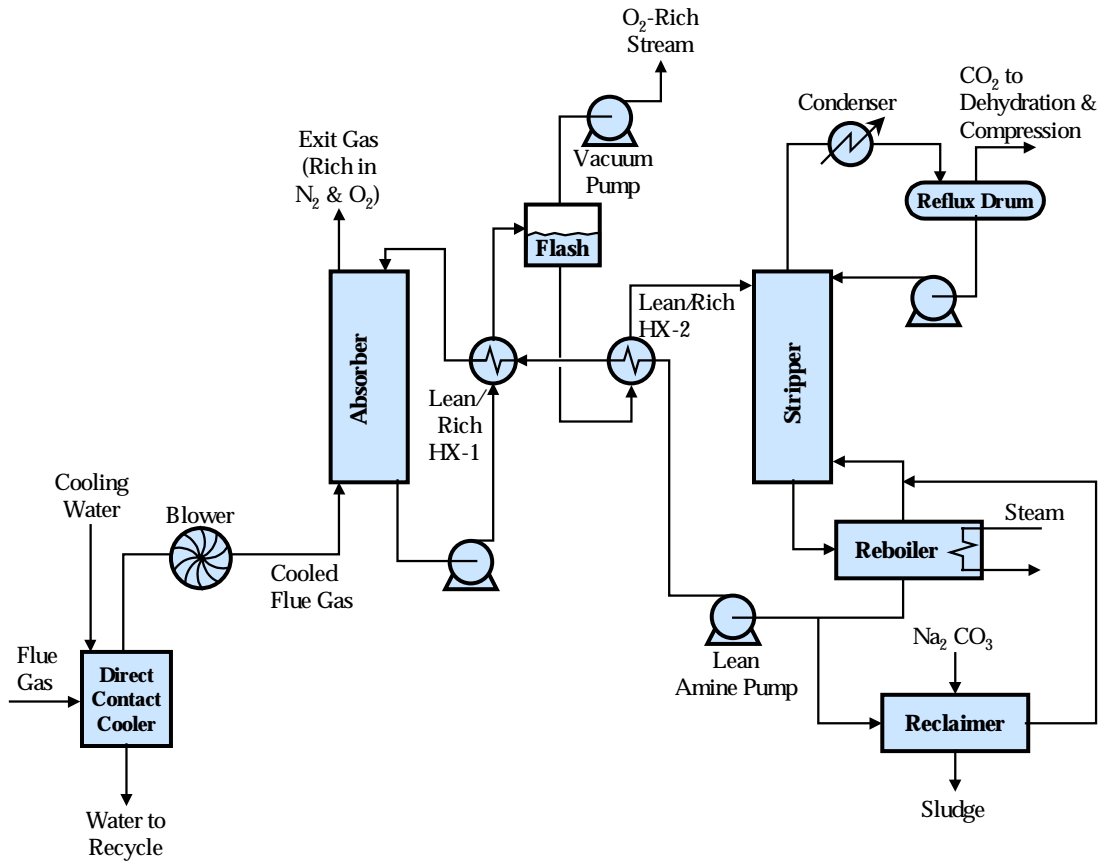


Figure 3. Improved Absorption Process with Vacuum Flash