CARBON DIOXIDE CAPTURE AND SEPARATION TECHNIQUES FOR ADVANCED POWER GENERATION POINT SOURCES

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ABSTRACT
The capture/separation step for carbon dioxide (CO2) from large-point sources is a critical one with respect to the technical feasibility and cost of the overall carbon sequestration scenario. For large-point sources, such as those found in power generation, the carbon dioxide capture techniques being investigated by the in-house research area of the National Energy Technology Laboratory possess the potential for improved efficiency and costs as compared to more conventional technologies. The investigated techniques can have wide applications, but the research has focused on capture/separation of carbon dioxide from flue gas (postcombustion from fossil fuel-fired combustors) and from fuel gas (precombustion, such as integrated gasification combined cycle – IGCC). With respect to fuel gas applications, novel concepts are being developed in wet scrubbing with physical absorption; chemical absorption with solid sorbents; and separation by membranes. In one concept, a wet scrubbing technique is being investigated that uses a physical solvent process to remove CO2 from fuel gas of an IGCC system at elevated temperature and pressure. The need to define an ideal solvent has led to the study of the solubility and mass transfer properties of various solvents. Fabrication techniques and mechanistic studies for hybrid membranes separating CO2 from the fuel gas produced by coal gasification are also being performed. Membranes that consist of CO2-philic silanes incorporated into an alumina support or ionic liquids encapsulated into a polymeric substrate have been investigated for permeability and selectivity. An overview of two novel techniques is presented along with a research progress status of each technology.

INTRODUCTION
Carbon sequestration is a viable alternative to reduce the emissions of the greenhouse gas, carbon dioxide, from large point sources. It holds the potential to provide deep reductions in greenhouse gas emissions. As mentioned in the Carbon Sequestration Program, managed by the U.S. Department of Energy, of particular interest are power generation point sources that use fossil fuels.[1] Since nearly one-third of the anthropogenic CO2 emissions are produced by these facilities, conventional coal-burning power plants and advanced power generation plants, such as integrated gasification combined cycle (IGCC), present opportunities where carbon can be removed and then permanently stored. Although pulverized coal-fired-base steam cycles have been the predominant electric power generation technology for many years, it is projected that advanced power generation technologies (for example, gasification-based IGCC) will

make in-roads in the power generation sector in the near future. FutureGen, a power and chemical generation system with negligible atmospheric emissions, is just one example of future gasification-based systems.[2]

In IGCC power plants, a fossil fuel is reacted with oxygen and steam in a gasifier to produce a fuel gas (also frequently referred to as synthesis gas or syngas) consisting mainly of carbon monoxide and hydrogen. This mixture is then cleaned and burned to generate power in a gas turbine combined cycle. The high efficiency of this process can be exploited by fuels, such as residual oil and coal.[3] Plants consist basically of three main building blocks: coal gasification, gas cleaning, and power generation.[4] A process diagram can be seen in Figure 1. Assuming oxygen-blown gasification with coal (near pure oxygen is used to eliminate the pressurization of the diluent nitrogen), the main products of the gasification process are CO, H_2, CO_2, H_2O, H_2S, some gaseous hydrocarbons, and trace amounts of certain pollutants, including mercury. The gas cleanup system of the plant involves particulate removal and acid gas scrubbing. In a typical IGCC plant, the crude fuel gas is first fed to a facility to remove the particulates from the gas stream. The gas leaving the particulates scrubber is then cooled and dewatered and, at this point, consists mainly of CO, H_2, and CO_2. It also contains the acid gas H_2S, which will be removed in the desulfurization system. The acid gas scrubbing process (cold gas cleanup in Figure 1) is generally designed for the removal of sulfur-bearing compounds with very little CO_2 removed in the process. However, removal of CO_2 at this location is possible. Some designs employ sulfur-tolerant shift catalysts followed by acid gas removal at low temperatures. This approach is preferable when CO_2 recovery is desired due to the increase in CO_2 partial pressure after the shift reaction.[5] The power generation consists of a gas turbine system followed by a steam turbine bottoming cycle. The desulfurized gas is first injected with steam and partially expanded in gas expanders to recover some work. The partially expanded gas, which is rich in CO and H_2, is then burned with air and expanded in a gas turbine to recover more work. The residual thermal energy in the gas turbine exhaust is used to produce steam for the steam turbine bottoming cycle.
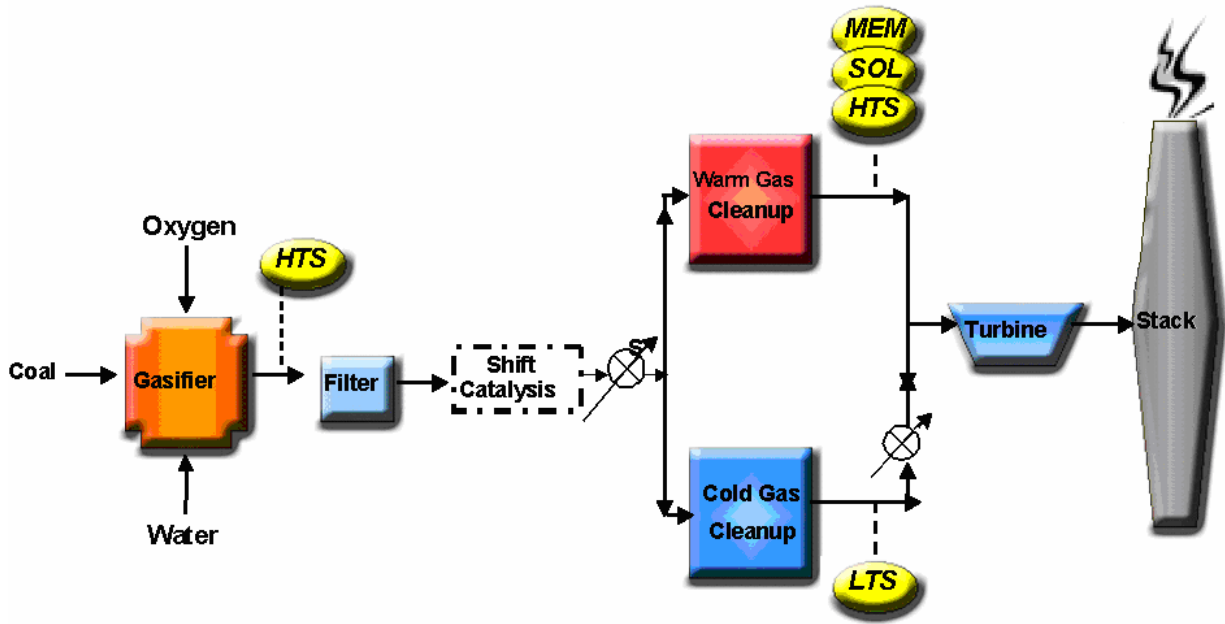
Figure 1: General Case: Advanced Gasification/IGCC – Fuel Gas

The upper flow path in Figure 1 indicates the option where acid gas cleaning occurs within a warm gas cleanup system rather than at the previously described cold (lower) temperatures. The main advantage in cleaning the gas in an IGCC application at higher temperature is that the thermal plant efficiency will be as much as 2-3% greater as compared to the lower temperature acid gas cleaning scenario.[5] The areas of efficiency improvements are that the transfer of heat and latent heat to the more efficient gas turbine cycle are maximized; the capital and operating costs are lowered by reducing the duty on the heat exchangers; and the need for waste water treatment facilities are eliminated.[6]

With respect to CO_2 capture in an IGCC system, post-combustion and pre-combustion technologies can be used. With coal utilization and after the gas turbine, about 9% carbon dioxide exists in the flue gas and partial pressure of the carbon dioxide is low. However, precombustion techniques with the IGCC system offer the opportunity to remove CO_2 from the fuel gas before it is combusted in the turbine. The high pressure of the system and the possible shifting of the CO to CO_2 produce a high partial pressure of CO_2 that could be advantageous with certain removal technologies.

In a carbon sequestration scenario, the cost of the capture/separation step is much higher than that of the storage step.[1] For IGCC systems, commercial processes for CO_2 removal, such as Selexol, are used as a baseline from which other capture technologies can be compared. The U.S. Department of Energy's National Energy Technology Laboratory (NETL) is conducting in-house research investigating novel techniques to capture/separate CO_2 from gases from advanced power generation systems. These technologies fall within the process categories of wet scrubbing with physical absorption; chemical absorption or adsorption with solid sorbents; and separation by membranes.

Except for membranes, all capture technique must be regenerable due to the excessive amount of carbon dioxide produced in a power generation plant.

With respect to the first category, physical solvents for CO_2 removal at high temperatures in IGCC applications are being studied. The higher temperature of operation for these solvents enhances the thermal efficacy of the IGCC power generation system. Depressurization or flashing of the CO_2 from the rich solvent is the means for regeneration. (See "SOL" in Figure 1.)

The use of solid sorbents is another method to remove CO_2 from gas streams. Past work has included alkali and alkaline earth metals as the basic component of sorbent structures. [7] These sorbents could be used in higher temperature absorption processes. More recent work has included lower temperature sorbents for potential use as a substitute for the Selexol process. The regeneration step is crucial for these types of sorbents and either pressure swing and/or temperature swing can be effectively utilized. Regenerable low temperature sorbents that operate below 300°F are identified as "LTS" in Figure 1 whereas regenerable high temperature sorbents "HTS" operate above an arbitrary 300°F level. The 300°F cutoff temperature was arbitrary since, in an IGCC application, this temperature typifies the lower end of the warm gas range for obtaining the 2-3% thermal efficiency advantage.

Another method is separation of carbon dioxide from fuel gas by the use of a membrane system. Simplicity, flexibility, the ability to maintain high CO_2 pressure, and the potential to perform separations at low energy penalties make membranes interesting for CO_2 removal for IGCC applications. In addition to the standard requirement of obtaining high permeability, challenges exist in the development of membranes capable of selectively separating CO_2 from the process gas stream. In addition, the reducing conditions and the presence of water and various minor contaminants necessitate the design of membranes with exceptional chemical and physical stability. (See "MEM" in Figure 1 as a potential location for these membranes.) Development of hybrid membranes for the separation of CO_2 presents a method that can satisfy the requirements for a durable membrane, especially at elevated temperatures.[8-10]

The research status of two of the above novel capture technologies that fall within the in-house research area at NETL are described below along with implications of the experimental research on technical direction and costs. An overview of these novel techniques is presented.

RESULTS AND DISCUSSION

Hybrid Membrane
For the hybrid membrane technology, the membrane is envisioned to separate CO_2 within the pre-combustion zone of an IGCC plant. The high pressure of the gasification-based power generation cycle provides an excellent driving force for the membrane and other inherent advantages of membranes exist, i.e. non-moving parts, etc.[9] If the water-gas-shift reaction within the IGCC scheme is performed to increase the hydrogen production

for the gas turbine combustor, the CO_2 concentration, and thus partial pressure, increases substantially and further enhances the driving force across the membrane. Additionally, if the membrane is fabricated to withstand higher temperatures (300-700ºF), an additional benefit with respect to maintaining the higher thermal efficiency of the plant (as compared to cold scrubbing of CO_2) is obtained.[5]

The initial foray into developing such membranes involved the modification of an inorganic substrate, such as a stable and permeable alumina, with organic groups to increase selectivity towards CO_2. A surface diffusion mechanism was desired. The grafting of organosilanes onto the inorganic surface is a well-studied method. Attachment is accomplished when halogen atoms on the silane molecule interact with hydroxyl groups on the inorganic surface, eliminating HCl and forming a covalent attachment. As many as three such interactions can occur per silane molecule, anchoring it to the surface. Since the silane molecule can also contain nearly any organic group, this method provides an extremely flexible tool for surface modification.[11] Membranes useful in CO_2 abatement for IGCC have been developed using this method. Specifically, the hybrid membranes consist of a rigid frame with an organic being the active membrane layer. CO_2-philic groups on the ends of the organosilanes enhance the preferential surface diffusion of the CO_2 across the membrane.

Testing of these silated membranes was conducted in a concentric tube, continuous flow screening unit describe elsewhere.[11] Results indicate that although the permeance of CO_2 was adequate, the selectivity of CO_2 over He (used in place of hydrogen) was low.[13] Direction of this work shifted to a new membrane design. To summarize this initial phase, a survey of available literature helped to determine that hybrid membranes can be a reasonable technique to separate CO_2 from various gas streams. The initial study laid the foundation for more ambitious work aimed at developing membranes capable of selective CO_2 removal in reducing environments, such as those found in the IGCC process. A pretreatment had been developed and this, combined with a certain silation procedure, allowed pore penetration and development of a silane monolayer capable of significantly affecting membrane performance.

In a recent phase of work, one approach to enhancing flux through solution diffusion membranes is the fabrication of those membranes in a liquid rather than solid state. Higher liquid phase diffusivities allow significant improvements in permeability over most solid state counterparts. Supported liquid membranes (SLMs) are prepared by impregnating porous substrates with a liquid transport media. Though performance results have often been encouraging [14, 15] a major problem has been encountered with respect to long term stability. Evaporation of the liquid transport medium eventually leads to incomplete filling of the substrate pores and membrane failure.[16]

Ionic liquids are a class of salts which are liquid at or slightly above room temperature. The unique nature of the materials leads to a number of interesting properties including negligible vapor pressure. Because the variety of available anions and cations make the number of potential ionic liquids nearly limitless, it is possible to tailor them with high solubility selectivities, particularly for CO_2, over most other gases. Together with these

properties, stability of many ionic liquids to temperatures above 200°C has led us to examine them as transport media in membranes designed to selectively remove CO_2 from fuel gas.

In a collaborative effort with the University of Notre Dame, supported liquid membranes have been prepared by impregnation of commercial porous polymer films with a specific ionic liquid. The ionic liquid has been characterized, and the membranes have been tested in a testing device similar to the one previously referenced to determine performance in the selective separation of CO_2 from He (helium being used as a surrogate for hydrogen). Experiments were conducted in a constant pressure system, and pure gas permeability/selectivity data are reported. Membranes prepared with polysulfone supports have been found to be stable to 125°C. The CO_2 permeability of the membranes increases from 744 to 1200 barrer as the temperature increases from 37 to 125°C. The CO_2/He selectivity decreased from 8.7 to 3.1 over the same temperature range. With the properties of the supported ionic liquid membranes already promising at such an early stage in development, it seems possible that they will make a major contribution to carbon dioxide separations in the future.

Physical Solvents
Conventional processes for acid gas (H_2S and CO_2) removal from coal-based gasification streams include a chemical/physical process using methyl-diethanolamine (MDEA), a physical solvent process using chilled methanol (Rectisol), and a physical process using mixtures of dimethylethers of polyetheleneglycol (Selexol). The MDEA process requires high thermal energy (heat) for solvent regeneration. The Rectisol process is complex, and refrigeration makes it a very expensive acid gas removal process. The Selexol process is more expensive than the MDEA process, and the chilling option could increase the process costs. However, as mentioned earlier, in an IGCC application, these physical and chemical processes for acid gas removal require cooling and subsequent reheating of the stream before the gas turbine, which decreases the plant thermal efficiency and thus increases the overall costs. Consequently, there is a need for the development of an alternative process which should be economical and absorb carbon dioxide without significant cooling of the humid gas streams.[17]

The objective of the physical solvent research is to investigate the potential use of chemically and physically stable compounds as physical solvents for selective CO_2 capture from post water-gas-shift reaction streams under elevated pressures and temperatures that are representative of gasification conditions. The first family of candidates that has been studied is perfluorinated compounds (PFCs). Candidate solvents were manufactured by Flutec Ltd. UK. After a comprehensive literature review for PFCs, an experimental program was devised to obtain the equilibrium gas solubility and the hydrodynamic and mass transfer parameters (gas holdup, Sauter mean bubble diameter, and volumetric mass transfer coefficient) for CO_2 and N_2 in three different PFCs, namely perfluoro-perhydrofluorene ($C_{13}F_{22}$), perfluoro-perhydrophenanthrene ($C_{14}F_{24}$), and perfluoro-cyclohexylmethyldecalin ($C_{17}F_{30}$), known as PP10, PP11, and PP25, respectively.

The literature review [17] revealed that the PFCs have high chemical stability due to the high energy of their C-F bonds. They have high boiling points and low vapor pressures because of the strength of the C-F bond and high molecular weight. They also have no dipole and very low molecular interactions due to the repulsive tendency of fluorine atoms. These unique properties lead to high gas solubility, low vapor losses, and low forces required for expelling the gas molecules upon decreasing pressure or increasing temperature. Thus, PFCs show a high potential for selective CO_2 capture from post-shift fuel gas streams at elevated pressures and temperatures.

Testing of these physical solvents occurred in an experimental setup that consisted of a reactor, preheater, vacuum system, and data acquisition system. The reactor is a gas-inducing 4-liter ZipperClave reactor with two sight-windows. The reactor is equipped with four symmetrically located baffles, a cooling coil, a specially designed heating jacket, a thermowell, and a six flat-blades impeller with hollow shaft. Holes located at the upper and lower end of the shaft allow the reactor to operate in a gas-inducing mode. The transient physical gas absorption technique was employed to measure the volumetric mass transfer coefficient, and the gas solubility was determined when the thermodynamic equilibrium was reached in the reactor. The expanded liquid height method and a photographic method were used to obtain the gas holdup and the Sauter mean bubble diameter, respectively. The experiments were statistically designed for the reactor operating in a gas-inducing mode. A wide range of operating conditions for the central composite statistical design matrix was investigated: pressures (6 - 30 bar), temperatures (27 – 227ºC), mixing speeds (10 - 20 Hz), and liquid heights (0.14 - 0.22 m).

The equilibrium solubilities of CO_2 and N_2 in PP10, PP11, and PP25, expressed in mole fraction, appeared to increase with pressure at constant temperatures, where the values at infinite dilution were found to follow Henry's law. Figure 2 relates the scrubbing temperature with the Henry's constants for the three PFCs and for Selexol data that were obtained from the literature.[18] The solubilities for both gases were greater in PP25 than in the other two PFCs. Under similar operating conditions, the solubility of CO_2 in the three PFCs appeared to be about 7 times that of N_2, which was attributed to the closeness of the solubility parameter of CO_2 to those of the PFCs when compared with that of N_2. The results showed that CO_2 is more soluble in the Selexol solvent than in the PFCs only at low temperatures (≤ 60ºC). The Selexol process, however, is customarily operated at temperatures of about 39ºC, indicating that the Selexol solvent would not be effective at higher temperatures typifying those at the exit of the gasifier system in a warm gas cleanup application. This study revealed the thermal and chemical stability and the ability of the PFCs to selectively absorb CO_2 at temperatures up to 227ºC and pressures as high as 30 bar.[19]
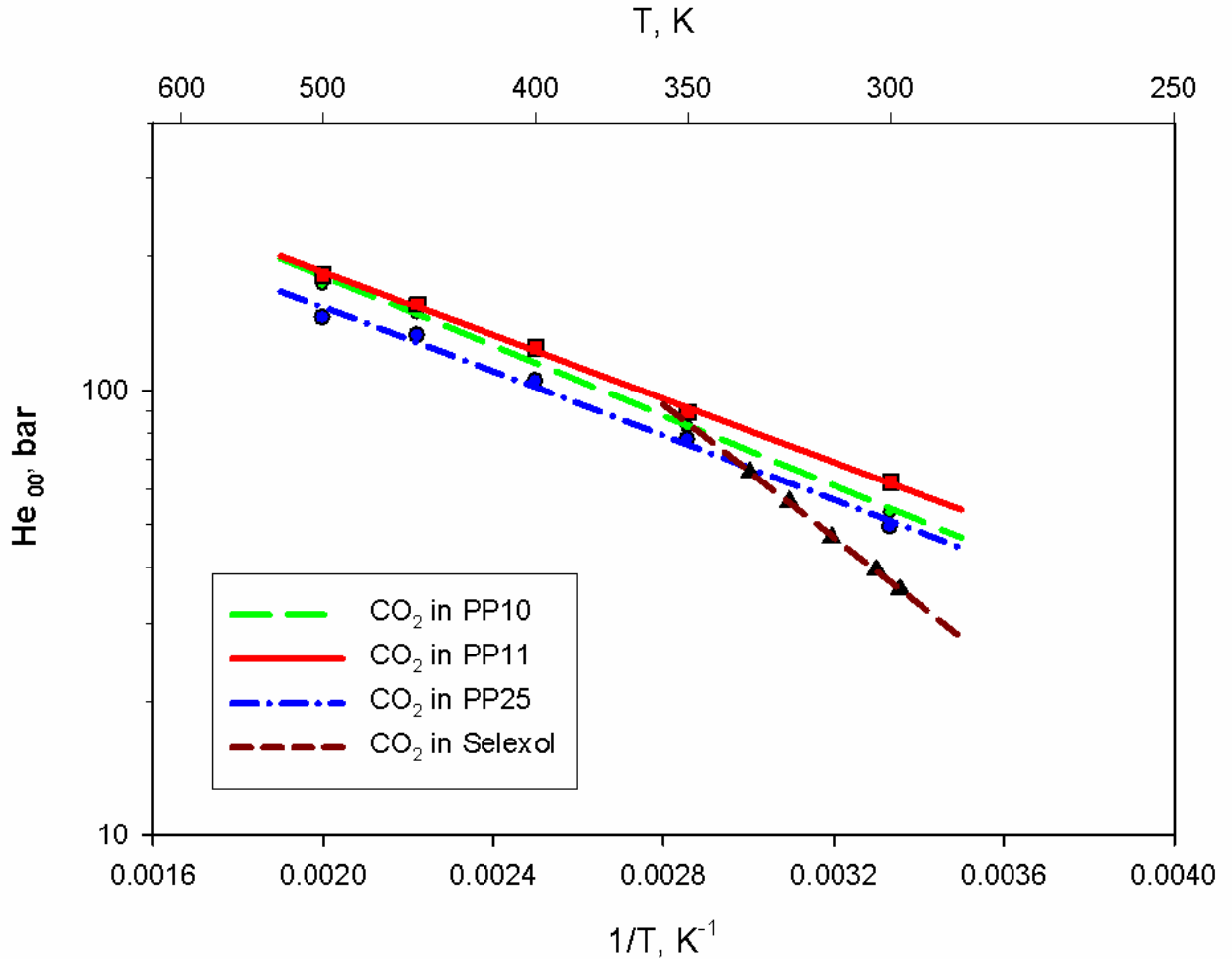
Figure 2: Solubilities of CO_2 in Fluorinated Solvents and Selexol

The volumetric mass transfer coefficients (k_La) of CO_2 and N_2 in PP10, PP11, and PP25, increased with increasing mixing speed, pressure, and temperature due to the increase of the gas-liquid interfacial area (a) and the liquid-side mass transfer coefficient (k_L). The increase of the gas-liquid interfacial area with these operating variables was attributed to the increase of the gas holdup and the decrease of the Sauter mean bubble diameters. The volumetric mass transfer coefficients of CO_2 and N_2 in the three PFCs, however, decreased with increasing liquid height above the impeller due to the decrease of the gas holdup and increase of the Sauter mean bubble diameter, which led to the decrease of the gas-liquid interfacial area. The volumetric mass transfer coefficients of CO_2 in the three PFCs were found to be always smaller than those of N_2 due to the smaller gas-liquid interfacial areas (smaller gas holdup and larger Sauter mean bubble diameter) of CO_2 when compared with those of N_2 under similar operating conditions. The volumetric mass transfer coefficients for CO_2 and N_2 in PP25 were smaller than those in PP11, and both were smaller than those in PP10, indicating that the volumetric mass transfer coefficients decrease with increasing viscosity of the PFC. Also, under the operating conditions investigated, the gas-liquid interfacial areas of CO_2 and N_2 in the three PFCs appeared to control the behavior of the volumetric mass transfer coefficients in the gas-inducing reactor.

Testing with mixtures of gases to simulate representative fuel gas mixtures is being completed. One aspect of this work where improvement could be made was in the vapor pressure of these solvents. Potentially PFCs with higher molecular weight could have a significant impact. With this in mind, future work will include an in-depth investigation of ionic liquids, which have negligible vapor pressure, used at elevated temperatures as a physical solvent for CO_2 removal.

SUMMARY

Various techniques for the capture/separation of CO_2 from power generation point sources are being investigated within the in-house research effort at NETL. The novel technologies include a wet scrubbing physical solvent process to remove CO_2 from fuel gas of an IGCC system at elevated temperature and pressure and hybrid membranes separating CO_2 from fuel gas produced by coal gasification. All these techniques have the potential for significant cost savings and plant thermal efficiency improvements as compared to more conventional CO_2 capture techniques. Future system analyses will attempt to integrate these methods into various power generation schemes with the intent of further optimizing the process with respect to plant efficiency.

DISCLAIMER

Reference in this report to any specific commercial process, product, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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