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CO_2 Capture and Sequestration in the Cement Industry

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Abstract

The cement industry is coming under increased scrutiny for its CO_2 emissions. The industry has reduced its CO_2 footprint through energy efficiency measures, reduction of clinker factor, and the use of alternative fuels. However in a carbon-constrained world, more significant reductions are anticipated and thus CEMEX has been investigating the deployment of CO_2 capture and sequestration (CCS) technologies for its own cement plants. The goal of this paper is to present the groundwork for the development and demonstration of a commercial-scale CCS project at one of CEMEX Inc.'s U.S. cement plants. The first part of this paper presents the criteria to determine the most suitable CO_2 capture technology in an integrated CCS system for a cement plant. The second part of this paper summarizes how CO_2 sequestration potential in proximity to one of CEMEX's cement plants was a critical factor in determining the suitability to host a commercial CCS demonstration. Findings of this work showed that the development and demonstration of a commercial-scale CCS in the cement industry is still far from deployment. Retrofitting a very compatible CO_2 capture technology for the cement industry is a limiting factor for early implementation of CCS. A pilot phase under actual cement plant flue gas conditions is a must to develop this technology to a commercial level. Uncertainties regarding the level of CO_2 purity for transportation, geological sequestration, and enhanced oil recovery (EOR) warrant further investigation.

Keywords: *Cement, CO_2 Capture, Calcium Loop, CO_2 Sequestration*

1. Introduction

It is estimated that the cement industry is accountable for about 5% of the global anthropogenic CO_2 emissions [1]. The cement industry has identified measures to reduce its carbon footprint through energy efficiency, reduction of clinker factor, and the use of alternative fuels (including carbon-neutral fuels) [2]. However, this industry recognizes that these measures will only go so far in mitigating CO_2 emissions. There is a limit to how much CO_2 emissions can be reduced by the very nature of cement production. One of the main reasons for this is that typically only around 40% of our emissions are related to combustion of fuels, the rest stems from a chemical reaction in our raw material, the calcination of limestone. Given the limited potential for the conventional levers to reduce emissions, it is clear that carbon capture and sequestration (CCS) will play a crucial role if the cement sector is to reduce its absolute emissions at a global scale [3].

In late 2009, the U.S. Department of Energy (DOE) – National Energy Technology Laboratory (NETL) solicited applications for carbon capture and sequestration from industrial sources. CEMEX Inc. was awarded funding to

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conduct groundwork for the development and demonstration of a commercial-scale CCS project at one of CEMEX Inc.'s U.S. cement plants. The first part of this paper presents the criteria to determine the most suitable CO_2 capture technology in an integrated CCS system for a cement plant. The second part of this paper summarizes how the CO_2 sequestration potential in proximity to one of CEMEX Inc's cement plants was a critical factor in determining the suitability to host a commercial CCS demonstration.

2. CO_2 Capture Technologies – The Cement Industry Application

Three strategies for CO_2 capture in new and existing cement plants are currently being considered: 1) pre-combustion, 2) post-combustion, and 3) oxy-combustion [1, 3]. Pre-combustion CO_2 capture will be more applicable to new cement plants integrated with gasification technologies to produce Syngas (a mixture of H_2, CO, H_2O, and CO_2) from the main plant fuel. H_2 would be then fired in the cement kiln after capturing CO_2 from this Syngas. The main drawback of this approach is that only CO_2 from the fuel will be captured; CO_2 released by calcination of limestone will not. In addition, a new generation of burner technology and cement kiln lines will be required. Post-combustion CO_2 capture involves the separation of CO_2 from the flue gas leaving the clinker kiln. The main advantage of this approach is that CO_2 from fuel and calcination will be captured. New and existing cement plants can be retrofitted with this approach. Oxy-combustion involves the use of purified oxygen for combustion in the cement kiln to produce a N_2-free flue gas (mainly consisting of CO_2 and H_2O). Upon condensation, a pure CO_2 stream will be obtained. However, combustion with purified oxygen in existing cement kilns will require major modifications to burner design, kiln, and plant configuration. Therefore, post-combustion CO_2 capture seems to be the easiest retrofit in a cement plant.

Post-combustion CO_2 capture technologies exhibiting the following characteristics show the most promise for application to the cement industry: 1) technical compatibility with cement manufacturing operating conditions, 2) non-toxic, non-hazardous materials, 3) minimal impact on cement plant operations, and 4) affinity to operational experience of cement plants (equipment, materials, etc). Conventional solvent-based technologies are attractive from the perspective that they are commercially available and are effective at removing CO_2 from flue gas. However, the energy-intensive nature and presence of hazardous materials on plant location make them less suitable for use at a cement plant. In addition, the cement industry, inherently a gas and solids handling/processing industry, has minimal experience with handling and processing liquid chemical processes operating liquid solvent-based systems (i.e. absorption columns). Membrane technologies are proven technologies to separate industrial gases but are still under development for separating and recovering CO_2 from exhaust gases of stationary CO_2 emission sources [4]. Therefore, solids-based technologies for CO_2 capture apparently seem to offer less stringent process retrofit and flue gas conditions compared to other post-combustion CO_2 capture technologies making it a good fit for the cement industry. A "suitability" comparison of general post-combustion CO_2 captures technologies (including oxy-combustion) for the cement industry is shown in Table 1.

A solids-based CO_2 capture technology was studied during this work. It is a calcium-based, high-temperature CO_2 capture technology [5, 6] that follows the reversible chemical reaction (1). This calcium-based CO_2 capture technology consists of the calcium oxide-carbonate cycle using limestone, an abundant and inexpensive raw material already found at most of the cement plants, to separate CO_2 from cement kiln flue gas at elevated temperatures, approximately 650°C. By heating the calcium carbonate to 750 to 950°C firing the main plant fuel within an oxy-fired reactor, the calcination reaction would release CO_2 that can be converted into a CO_2 pure stream after cooling and clean-up.

$$CaO_{(s)} + CO_{2(g)} \leftrightarrow CaCO_{3(s)} \quad (1)$$

Integration of this calcium-based CO_2 capture technology at a cement plant was conducted and is shown in Figure 1. Contrary to our initial reasoning, it can be noted from these block flow diagrams that this post-combustion solids-based CO_2 capture technology would also require extensive retrofit compared to a solvent-based CO_2 capture technology for full CCS integration. Seven process blocks were defined for a cement plant including: 1) CO_2 capture, 2) fuel grinding, 3) air separation, 4) waste heat power generation, 5) CO_2 purification and compression, 6) CO_2 pipeline and injection and 7) cooling water systems. The CO_2 capture block removes CO_2 from the cement plant flue gases using $CaO_{(s)}$ to form $CaCO_{3(s).}$ CO_2 is then released by decarbonation of $CaCO_{3(s)}$ while firing a stream of the main plant fuel in a pure oxygen environment. Sorbent make-up and purge is supplied and used by the cement plant to produce clinker or cement (i.e. blended cements). The fuel grinding block supplies pulverized fuel to the CO_2 capture system. This block can either be a stand-alone system or be part of the existing cement plant fuel grinding facility. Air separation is set to supply pure O_2 (>97% purity) to the CO_2 capture system for sorbent regeneration. Due to the high operating temperatures of the exhaust streams (lean-CO_2 flue gas and CO_2 product gas), waste heat recovery becomes essential as significant power generation can be obtained. The waste heat power generation block is added to generate power from waste heat to offset power consumption due to operation of additional process equipment, air separation and CO_2 compression systems. The CO_2 purification and compression cleans up CO_2 coming off the CO_2 capture system to deliver pipeline-ready CO_2. A cooling water system is included for the cooling needs of the air waste heat power generation, air separation and CO_2 purification and compression blocks.

Table 1.Qualitative Comparison of General CO_2 Capture Technologies for the Cement Industry

Parameter	Post-combustion			Oxy-combustion
	Solid-based	Solvent-based	Membranes	
Energy Demand	Intensive to regenerate sorbent	Intensive to regenerate solvent	Intensive to pressurize gases	Intensive to operate air separation unit
Equipment Materials Processes	In development	Well-developed	In development	Conceptual retrofit on cement kilns
Flue Gas Conditioning	Extensive to avoid sorbent contamination	Extensive to avoid solvent contamination	Extensive gas to avoid membrane deterioration	Removal of other gas constituents from CO_2 product
Other Gases (O_2, CO, NOx, $H_2O_{(v)}$)	Insensitive	Need inhibitors to avoid degradation	May interfere with CO_2 separation rate	Need to assure CO_2 purity
Acid Gas Control (SO_2, HCl)	May be required	Required	May not be required	May be required
Hazardous Toxic Corrosive	No	Yes	No	No

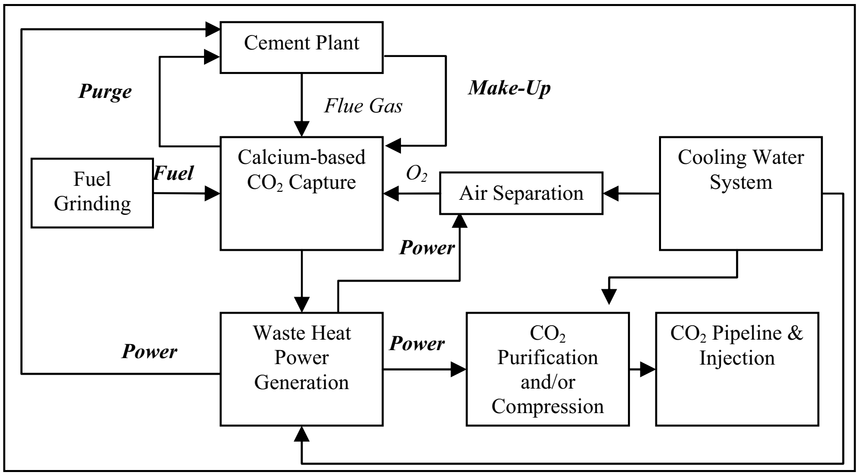

Figure 1. Calcium-based CO_2 capture technologies integrated to a cement plant.

For comparative purposes, a full CCS integration scheme was set up for a cement plant using a conventional solvent-based CO_2 capture technology as shown in figure 2. In this case, seven process blocks were also defined including: 1) flue gas conditioning, 2) CO_2 capture, 3) fuel grinding, 4) steam generation, 5) CO_2 purification and compression, 6) CO_2 pipeline and injection and 7) cooling water systems. The flue gas conditioning block remove gas contaminants (Particulate Matter, SO_2, HCl, etc.) known to deteriorate conventional amine solutions. The CO_2 capture block removes CO_2 from the conditioned cement plant flue gases by using a conventional amine solvent.

Using indirect heat, the amine solvent is regenerated to release the CO_2 product. Due to the inherent lack of process steam at cement plants, a dedicated steam generation block is set to supply the steam for solvent regeneration.The main plant fuel is prepared in a fuel grinding system to supply fuel to this dedicated steam generation block. As previously mentioned, this block can either be a stand-alone system or be part of the existing cement plant fuel grinding facility. The CO_2 purification and compression cleans up CO_2 coming off the CO_2 capture system to deliver pipeline-ready CO_2. A cooling water system is included for the cooling needs of the steam generation and CO_2 purification and compression blocks.

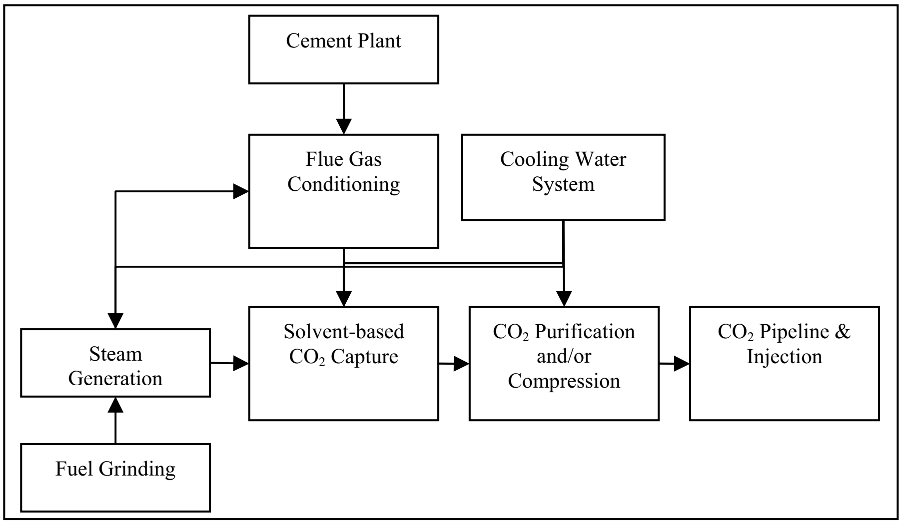

Figure 2. Solvent-based CO_2 capture technology integrated to a cement plant.

An engineering assessment of this calcium-based CO_2 capture technology integrated to a cement plant showed that this technology requires:

- A pilot testing program to better define:
  - Reactor and system designs,
  - Identify final auxiliary equipment needed for optimum operating conditions and,
  - Test long-term sorbent performance under actual cement kiln flue gas conditions.
- Careful process design considerations to minimize the impact on the cement plant's integration, operation and emissions
- Considerable water availability to meet process demands of steam/power generation and cooling water system operation

Another important finding of this engineering assessment was the high synergy with a cement plant configuration for the calcium-based CO_2 capture technology due to the beneficial use of resources: 1) use of spent sorbent for clinker and cement production onsite and/or offsite, 2) recovery of available waste heat for onsite power generation to offset additional power consumption, and 3) use of the same main plant fuel to operate the CO_2 capture system. Process engineering analysis of various process designs showed that the best set of retrofit conditions for the calcium-based CO_2 capture technology offer flexibility to the use of different: 1) fuels (coal, petcoke, natural gas and/or alternative fuels (i.e., biomass), 2) oxygen purities, and 3) types of sorbents (i.e., onsite or offsite limestone sources).

Overall, results of this engineering assessment suggested that the calcium-based CO_2 capture technology has large opportunities to retrofit the CO_2 capture component of an integrated CCS system in a cement plant. However, maximization of waste heat power generation and the extent of CO_2 purity (minimum CO_2 purification requirement) for a particular CO_2 sequestration setting are technological areas that require further research and development work to optimize the technology design, integration and cost. This latter challenge is very important because this calcium-based cycle is unlikely to deliver a raw CO_2 stream that meets current specifications for pipeline transportation, sequestration, or EOR, that typically require oxygen concentrations in the range of parts per million (ppm). The resulting costs for purification of this raw CO_2 stream are expected to be significant. Understanding to what level these extremely stringent requirements could be relaxed and/or to develop novel oxygen removal technologies is a key component of the development of this technology.

3. CO_2 Sequestration Potential – The Right Cement Plant

While the earlier part of this paper described the most suitable CO_2 capture technology in an integrated CCS system for a cement plant, this section details the CO_2 sequestration potential of one of CEMEX's cement plants and its suitability in hosting a commercial CCS demonstration project as well as the process used in selecting the specific cement plant.

CEMEX Inc. owns and operates 14 cement plants in the United States representing approximately 15% of the domestic USA cement production capacity [7]. These 14 plants are located in 10 different states with each site offering different geologic settings as well as varying regulatory, legal, and public relations environments. In general, CEMEX owns the property where the cement plants are located and also owns the land where the adjoining limestone quarry rests. This ownership ranges from a few hundred acres at some sites to over thousands acres at other sites. Because of CEMEX's significant land ownership, combined with the expedited nature of the DOE CCS demonstration project, one of the key focuses of the project was being able to maintain the sequestered CO_2 plume beneath property which CEMEX owned. In other words, while the subsurface geology of the site is most critical, the site also had to be large enough to contain the subsurface CO_2 plume vertically extrapolated to CEMEX's surface controlled boundaries. While ownership of the surface and how the land's surface is utilized is usually quite clear, ownership of the subsurface is often complicated due to the fact that oil, gas and other subsurface mineral entitlements can and often are separated from the surface ownership.

To select the host cement plant site, a multi-phase process of increasingly specific and detailed data analysis was created. As it is illustrated in Figure 3, the initial phase involved a screening of the general geologic setting as it pertains to CCS potential. Using the DOE-NETL's 2008 Carbon Sequestration Atlas for the United States [8], the location of CEMEX's 14 plants were overlain onto detailed maps depicting the three most common geologic setting for which CO_2 can be stored, those being: 1) Oil and Gas Reservoirs; 2) Unmineable Coal Seams; and 3) Deep Saline Formations.

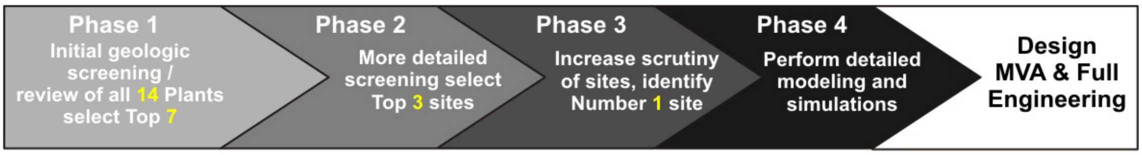

Figure 3. Multi-phase screening process

Because oil and gas reservoirs have many of the same attributes that make for ideal CO_2 storage areas, the presence of both existing and depleted oil and gas reservoirs at or adjacent to the cement plant was considered a positive. Existence of oil and gas reservoirs also created an added potential benefit for utilization of the captured CO_2 for enhanced oil recovery (EOR). However, there are two potential drawbacks to having oil and gas operations on or near site, these are: 1) compromising and/or complicating the necessary monitoring, verification and accounting (MVA) of a CCS site; and 2) interference with subsurface oil and gas mineral recovery. The location of the 14 CEMEX cement plant sites superimposed on a map displaying the oil and gas reservoirs within the Unites States is shown in Figure 3. Identified on the map are the two CEMEX plants overlying or adjacent to oil and gas reservoirs: 1) CEMEX Odessa Plant in the Permian Basin of West Texas; and 2) CEMEX Wampum Plant in western Pennsylvania.

Utilization of Unmineable Coal seams (those coal deposits which are too deep to be conventionally mined) as a CCS site via coal-bed methane recovery methods (CBM) was also considered. Because this particular CCS site would require methane gas recovery systems in addition to the CO_2 injection systems, CEMEX did not believe that the short duration of the demonstration project would allow for full development of such sites and as such did not pursue Unmineable Coal seams as a viable screening component.

The third and final CCS geologic setting considered by CEMEX was the presence of deep saline formations under or adjacent to the cement plant boundaries. The 7 CEMEX plants that reside over areas of deep saline formations are also shown in Figure 4.

The Phase 1 screening effort involved analysis of general data from the respective Regional Carbon Sequestration Partnerships in which the cement plants reside. The conclusion of the Phase 1 portion of the project identified 7 potential CCS host sites. The goal of Phase 2 was to reduce these 7 sites down to 3 and eventually in Phase 3 to the single cement plant site that offers the greatest potential for success.

The types of information analyzed in Phase 2 consisted primarily of regional geologic maps and review of technical literature journals and research documents pertinent to the subsurface. The focus was on identifying porous and saline water filled geological formations at depths ranging from 4,000 feet at minimum to depths not exceeding 10,000 feet below ground surface. The minimum depth of 4,000 feet was based upon a desire to insure that there would be adequate seals to prevent possible CO_2 migration to the surface, as well as to prevent contamination of any freshwater aquifers. The maximum depth of 10,000 feet was simply the practical limit for economics and engineering. However, geologic data alone would not be the basis for reducing the 7 sites down to 3 and ultimately 1. A screening matrix was developed to score each site against criteria affecting the potential viability for on-site sequestration or for EOR. The list of 12 specific criteria developed for the project along with a basis for scoring the criteria for the individual plant site are shown in Table 2.

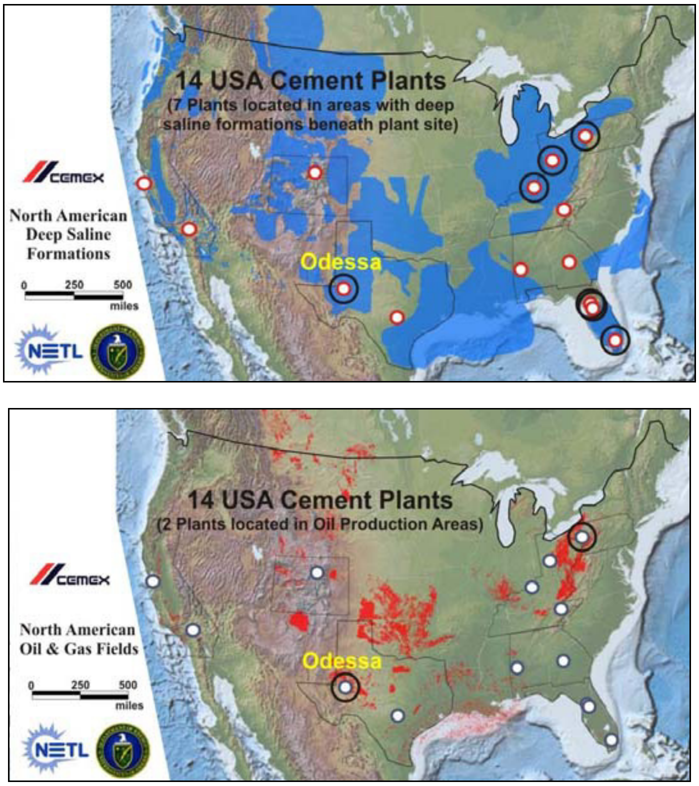

Figure 4.Cemex Plants and North American Deep Saline Formations (up) and Oil & Gas Fields (down)

Using these screening criteria, each plant was “scored” and consequently ranked in terms of CCS potential. The higher the score, the greater the potential for CCS. Using this approach, the 14 plants could be trimmed down to 3 with the highest potential for on-site CCS. While appearing straightforward, the scoring basis may in certain circumstances appear somewhat subjective. It is also arguable that some criteria are more important than others and that some criteria directly influence other criteria. However, for this project, each criteria was weighted equivalently. With 12 criteria and a scoring system based upon a 1 to 10 scale, the maximum score a plant could achieve was 120 and the minimum score would be 12. For the 14 cement plants analyzed, the scoring results ranged from a high of 94 to a low of 48. CEMEX Odessa Plant ranked highest with a score of 94 followed by two more CEMEX USA cement plants with scores of 93 and 76.

The Phase 3 analysis involved extracting higher levels of data including site specific legal and technical data for the highest 3 ranked sites. Data analysis included procurement and development of regional and local geologic cross sections for the plant sites as well as creating maps of local and regional water supply sources and other key factors affecting the CCS potential. Through this process, it became evident that the CEMEX Odessa plant site had clear advantages over the other 2 sites. These advantages included the fact that the immediate area around the Odessa site was undergoing significant EOR operations, and a CO_2 pipeline used in the regional EOR projects was actually present on the CEMEX Odessa plant site. The existence of a local EOR project meant that even if on-site sequestration proved too costly, there was an alternative mechanism for handling the CO_2 generated from the capture technology.

Table 2. Screening Criteria for Cement Plant CCS Potential

Criteria	Scoring Basis: Range 10 (high) – 1 (low)
1. Reservoir type	10 = Thick sands at good depth; 1 = No viable reservoirs
2. EOR potential	10 = EOR projects nearby and pipelines available 5 = EOR projects potentially available >50miles away 1= No EOR projects within 200 miles
3. Primary Storage Potential	10 = Reservoir thickness > 1500’ 5 = Reservoir thickness 500’ 1 = Reservoir thickness < 100’
4. Secondary Storage Potential	10 = Reservoir thickness > 1500’ 5 = Reservoir thickness 500’ 1 = Reservoir thickness < 100’
5. Number of Seals Above Injection Zones	10 = > 3 and/or thousands of feet; 1 = No seals
6. Confidence in Existing Data	10 = large amount of on-site data; 1= regional data only
7. Pre-existing Wells with Potential to Create Leaking Points	10 = Few in any water wells and no oil wells penetrating zones of injection 5 = some nearby water wells and a few oil wells 1 = many nearby water wells, several oil wells
8. Land Ownership	10 = Full ownership of land; 1= Leases on surface land
9. Public/Political Acceptance	10 = Existing CCS projects nearby; 1 = Public rejection of CCS projects
10. Subsurface Mineral Ownership	10 = Full ownership of subsurface minerals; 1 = No ownership of minerals
11. Risk of Tectonic Activity	10 = Very low threat of earthquakes; 1 = High risk of earthquakes
12. Capture Potential	10 = Cement plant can be easily retrofit with capture technology 1 = Cement plant cannot be easily modified for capture technology

The Odessa site also had two other clear advantages over the other two sites: 1) a major DOE sponsored CCS project had been evaluated nearby and consequently a large and high quality database of geologic information already existed; and 2) the Odessa plant site had active oil production within and immediately surrounding CEMEX’s property. The existence of oil activity was viewed as “good news” and “bad news” at the same time. The “good news” was that with oil activity comes a great deal of data including geophysical and seismic data that is critical in evaluating on site sequestration potential, specifically as it pertains to identifying key injection zone targets and the reservoir characteristics which are fundamental in modelling storage potential. Areas without oil activity rarely if ever have such data available. On the “bad news” side, the existence of oil activity on site and around the area can complicate the selection of the desired injection zones because there is a concern that the CO_2 injection could migrate into the oil producing areas or that improperly abandoned oil wells could represent potential CO_2 leakage pathways. Additionally, because the use of the subsurface as a CO_2 storage facility could impair future oil and gas exploration and development on the property, serious legal and economic considerations could arise. Simply put, in the future pursuit of oil and gas, the operator would not want to drill through a CO_2 plume resting above the oil and gas target. Despite the stated complications, the CEMEX Odessa site had clear benefits over all other sites including the important consideration that the particular cement plant technology and layout at this plant would make the retrofit of a CO_2 capture process easier.

The last phase of the analysis involved creating detailed modelling of the selected reservoirs at the Odessa site and then performing computer simulations on various CO_2 storage scenarios with variable reservoir characteristics. Locations for two potential injector wells were chosen by CEMEX at the Odessa site. Using publically available and acquired well data and 2D seismic lines, an initial geologic subsurface model was constructed to ascertain potential storage for 300,000 tons per year of CO_2 for a three year injection period.

4. Conclusions

The development and demonstration of a commercial-scale CCS in the cement industry is still far from deployment. The groundwork conducted during this study showed that retrofitting a very compatible CO_2 capture technology for the cement industry is a limiting factor for early implementation of CCS. This calcium-based sorbent technology is in its infancy to advance with design and construction of an industrial-scale demo CCS plant. A pilot phase under actual cement plant flue gas conditions is a must to develop this technology to a commercial level. Research and development in areas of sorbent regeneration using pure oxygen, waste heat power generation, plant integration and CO_2 purity is needed. In general, CO_2 sequestration seems to be technically viable for the cement industry (particularly for CEMEX Odessa plant). However, very careful considerations must be taken when planning for CO_2 storage. Uncertainties regarding the effect of impurities (O_2, N_2, Ar, NOx, SOx, etc.) in the CO_2 product on transportation and storage in geological reservoirs, and CO_2 storage in areas of oil and gas exploration due to potential CO_2 leakage and access to subsurface minerals are areas that warrant further investigation.

5. Acknowledgments

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