ABSTRACT
The literature concerning the application of CCS to industry is reviewed. Costs are presented for different sectors including “high purity” (processes which inherently produce a high concentration of CO$_2$), cement, iron and steel, refinery and biomass. The application of CCS to industry is a field which has had much less attention than its application to the electricity production sector. Costs range from less than $2011_{10}/tCO_2$ up to above $2011_{100}/tCO_2$. In the words of a synthesis report from the United Nations Industrial Development Organisation (UNIDO) “This area has so far not been the focus of discussions and therefore much attention needs to be paid to the application of CCS to industrial sources if the full potential of CCS is to be unlocked”.

Keywords: CCS, industry, cement, iron, steel
INTRODUCTION

Carbon capture and storage (CCS) is frequently associated with coal-fired electricity generation, and to an increasing extent with gas-fired generation. However, there are many other sources of CO\textsubscript{2} which can also benefit from the technology and many of these are substantially easier to retrofit with CCS than are power stations. Due to rising energy costs, many energy intensive industrial processes have made significant advancements in energy efficiency over the past 40 years and are now operating close to their thermodynamic limits. The options for further reduction are highly limited. Furthermore, for process-related emissions (those inherent to the process itself, such as the emission of CO\textsubscript{2} during the calcination of limestone for lime or cement manufacture) there is little choice other than to apply CCS if the industry is to be substantially decarbonized. In light of this, it is surprising that the power industry, where technologies such as wind, tidal and hydropower offer serious alternatives to the application of CCS (through clearly there are issues with intermittent generation) has dominated the research and development agenda.

A synthesis report for the United Nations Industrial Development Organisation (UNIDO) [1] states that “This area has so far not been the focus of discussions and therefore much attention needs to be paid to the application of CCS to industrial sources if the full potential of CCS is to be unlocked”. In this paper, the major classes of industrial CO\textsubscript{2}-emitting processes are discussed, the most suitable types of carbon capture equipment for each of them, and the likely costs of implementing the technology. One thing which is immediately apparent is that there is a very much reduced set of literature pertaining to industrial emissions when compared with the large and growing literature on the application of CCS to power stations. Much of the literature refers back to a small number of IEA studies [2,3], there is much less independent validation of costs by different researchers. This is most likely owing to the breadth of different processes in the industrial CCS arena, and the proprietary nature of many of the processes leading to a paucity of freely-available knowledge.

The extent of future reductions in CO\textsubscript{2} emission attributable to CCS in the industrial sector could be very large. The IEA blue map scenario [4] attributes 19% of total global CO\textsubscript{2} emission reductions vs the “business as usual” scenario to CCS, and this is roughly split 55:45 between power generation and industrial emissions applications. The share of total direct (i.e. excluding process emissions and indirect emissions from electricity production) industrial emissions of CO\textsubscript{2} from the major CO\textsubscript{2}-emitting sectors is shown in Fig. 1.

UNIDO classifies [4] the industrial sector into five different sub-sectors; “high purity” (natural gas processing and the production of hydrogen, ethylene oxide or ammonia); cement; iron and steel; refinery; and “biomass”, and we will use the same classifications here. It is important to note that the partial pressures of CO\textsubscript{2} in the exhausts of different industrial processes vary greatly (see Fig. 2), with

![Figure 1. Share of direct industrial CO\textsubscript{2} emissions attributable to the major industrial sectors.](image-url)
consequent effects on the cost of separation and compression (CO$_2$ will in general be injected at a pressure of 100 bar or more [7]).

The costs of separating CO$_2$ from the other gases in a power plant exhaust vary depending on the partial pressure of the CO$_2$, the technology chosen and a number of other factors. However, for reference, the estimated costs of CCS range between around $29–$107 for CO$_2$ capture from coal or natural gas-fired power stations [4,8–10]. Some care is necessary though, given the recent significant increases in capital cost indices. The costs of separation currently outweigh the costs of transport and storage, with transport costs estimated at 0–$16/t, depending upon the distance transported, with storage costs at $2–3/tCO$_2$ [11]. All costs in this paper are expressed in 2011 USD and escalated using the Power Capital Costs Index (PCCI) where appropriate [12]. A word of caution is necessary at this stage—academic estimates of costs are generally a little lower than industrial estimates, so care is necessary in comparing them.

The size of the plant also has an impact on cost. A single large blast furnace (Annual steel production of around 3 Mt) typically emits about 3.5 Mt of CO$_2$ per year. A large steel plant can often consist of up to five large blast furnaces on one site, emitting a total of 17.5 Mt CO$_2$ per year and making it one of the largest stationary sources of CO$_2$ emissions in the world. Table 1 compares the size of a variety of stationary point sources of emissions.

Table 1. Comparison of the size and quantity of a variety of point sources of CO$_2$ emissions (Adapted from [8]).

<table>
<thead>
<tr>
<th>Source</th>
<th>Average emissions/source</th>
<th>No. of sources in 2005</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power station flue and fuel gas</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Natural gas fired boilers</td>
<td>1.01</td>
<td>743</td>
</tr>
<tr>
<td>- Gas turbines</td>
<td>0.77</td>
<td>985</td>
</tr>
<tr>
<td>- Coal fired boilers</td>
<td>3.94</td>
<td>2025</td>
</tr>
<tr>
<td>Chemical and petrochemical</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Refineries</td>
<td>1.25</td>
<td>638</td>
</tr>
<tr>
<td>- Ammonia</td>
<td>0.58</td>
<td>194</td>
</tr>
<tr>
<td>- Ethylene oxide</td>
<td>0.15</td>
<td>17</td>
</tr>
<tr>
<td>Iron and steel</td>
<td>3.5</td>
<td>180</td>
</tr>
<tr>
<td>Cement</td>
<td>0.79</td>
<td>1175</td>
</tr>
</tbody>
</table>

In the power generation sector, CO$_2$ capture processes can be classified into three different schemes: 1) pre-combustion capture, 2) post-combustion capture and 3) oxy-firing. Owing to the heterogeneity of industrial processes, capture from industrial sources is more complex; however some similarities can be drawn. The different capture processes from industrial sources are discussed in more detail in the next section.
SECTORAL ASSESSMENTS

High purity
This is a classification based on the output concentration of CO\(_2\) from the process (30–100%), rather than a particular industrial sector. There are a number of processes which currently separate CO\(_2\) from process streams for the purposes of product quality or because a required reaction produces CO\(_2\) as an outlet gas. This sector includes natural gas processing. Clearly, the opportunities for CCS are significant in this sector, because the most difficult job of separating the CO\(_2\) from the remaining streams has already been accomplished. Unfortunately, the emissions of high purity CO\(_2\) are relatively small, at [1] only 426 Mt/yr, only 6% of the total industrial emissions. However, the opportunities for demonstration of the technology are large, with a number of significant projects already up and running, as discussed below. The industry is well developed, with solvent-based CO\(_2\) capture already utilized to improve natural gas quality.

Costs in this area are generally low, essentially being those associated with removal of minor contaminants, compression and storage alone [1], leading to a price per tonne of CO\(_2\) of between $9 for retrofit to an existing LNG plant, $15–8 for an onshore natural gas plant, $17–20 for an offshore natural gas plant in shallow waters and rising to $29 for a deep water installation [1]. Early work in this area [14] suggested a mitigation cost of $30/tCO\(_2\) for fertilizer production and $34/tCO\(_2\) for ethylene oxide production (note that these costs were estimated in 1990, so that the capital cost escalation factor and hence the potential error caused is large).

Cement
Cement manufacture contributes over 5% of global CO\(_2\) emissions [15], and with the total demand for cement expected to double by 2050 [16] it will continue to be a large source of CO\(_2\) for many years. There are two major sources of CO\(_2\) in the cement production process—from the calcination of limestone (CaCO\(_3\)) to form CaO (around 60% of the total emissions, excluding the fuel used to effect the calcination [17]), the major constituent of ordinary Portland cement, and from the fuel used to raise the temperature in the cement kiln and to effect the calcination (approximately 40% of the total emissions) to effect the chemical reactions necessary to produce cement [18]. These figures agree with recent ones presented by Cemex [19], the world’s third largest cement manufacturer. Interestingly, Bosoga et al. [20] present a different split of CO\(_2\) emissions (50% for calcination including fuel use in the calciner, 40% for fuel combustion in the kiln, 5% for electricity use and 5% from transportation). Whilst the fuel used can and is frequently biogenic waste-derived material (at least in part), the calcination produces CO\(_2\) which cannot be decarbonized in any other way than CCS.

To date, most of the research on CCS applied to the cement industry has been theoretical modeling and costing of potential processes. The European Cement Research Academy (ECRA) began research on the application of CCS technology to the cement industry in 2007 and recently begun Phase III (laboratory scale and small research activities) of its five-phase project timeline [21]. One pilot study currently in the pipeline is based at a NORCEM cement plant in Brevik, Norway. A post-combustion capture unit will be retrofitted to an existing cement kiln and is intended to start operation by 2018, capturing around 10 kt of CO\(_2\) per year. The estimated cost of this project was 1.7 million Euros [22] in 2010.

Post-combustion capture of CO\(_2\) from the cement industry uses the same capture technologies as those in the power sector (e.g. MEA scrubbing) and has the advantage that it can easily be applied as retrofit to existing plants at low technical risk [23]. However, unlike power plants, cement plants have limited low-grade waste heat available for solvent regeneration (typically only up to 30% of the total heat required for regeneration can be supplied by waste heat [24]). Thus, additional steam has to be generated or imported from elsewhere, increasing the cost of capture significantly.

Oxy-firing, where the kiln is heated by burning the fuel in oxygen diluted with recycled CO\(_2\), has been shown to be a more cost effective option than post-combustion capture [23]. Oxygen enrichment, where the kiln air is supplemented by short bursts of pure oxygen, has already been applied in the cement industry. Oxygen enrichment has the advantage of creating high value energy through increased kiln temperatures, which increases the kiln capacity. With each percentage point increase in the oxygen concentration, the fuel consumption decreases by 1.4–1.9 kJ/kg clinker [25]. Although, oxy-firing with CO\(_2\) capture can be retrofitted to existing plants, it is more suitable for new builds since most of the core units have to be rebuilt. Current research is focused on overcoming three
major challenges: 1) the effect of a high CO$_2$ concentration on the calcination reaction, 2) limiting damage to the kiln refractory at higher temperatures and 3) prevention of air intake into the kiln.

Pre-combustion capture in the cement industry is generally not considered suitable for the cement industry since CO$_2$ emissions arising from limestone calcination, representing around 50% of the CO$_2$ emissions, would remain uncaptured.

Figure 3 shows the application of another promising technology, the calcium looping cycle [26], to decarbonize a cement plant. The flue gas from the cement plant is passed to a reactor (∼650°C, the “carbonator”) where CO$_2$ from flue gas is reacted in an exothermic reaction with CaO at high temperature to form CaCO$_3$, which is then regenerated at ∼950°C (in a “calciner”), with the cycle then repeated. A significant purge flow of CaO is necessary to maintain the average sorbent reactivity, but one key aspect of the technology is that this flow can simply be purged into the cement kiln [17]. In addition (and contrary to most other CO$_2$ capture schemes) the energy given out in the exothermic CO$_2$ capture reaction can be profitably used, because of its high temperature, to produce electricity. Though the technology can be applied to power generation [27], it is a natural fit with cement manufacture because of the integration of the waste products from the cycle with the raw materials for cement manufacture.

Figure 3. The application of the Ca looping cycle on a cement plant.

However, there is a powerful synergy between electricity production and cement manufacture, in that the cycle can be used to decarbonize a power station, with a purge removed in the form of CaO, which eliminates the requirement to calcine CaCO$_3$ in the cement process. This removes a very substantial fraction of the hard to eliminate process-related emissions and eliminates the requirement for a precalciner for the cement works. Of course, it is also possible to remove the emissions via a standard post-combustion scrubbing route, such as MEA scrubbing. However, the estimated cost of decarbonisation is significantly higher (see below).

One significant area of research is into the fate of trace elements and minor species in cement manufacture when CCS is applied, most particularly in processes which make significant changes to the clinker production process. In the words of Bhatty (Portland cement research association) [28] “The likely concerns from alternative or new natural sources [of raw materials required for cement production] are the incorporation of trace elements into clinker and their effects on the performance of cement.” The cement industry is by nature cautious, which is understandable given the consequences if the cement does not perform to the required standard. Current research at Imperial College [29] is investigating the likely build-up of trace elements during repeated cycles of calcination and carbonation for CO$_2$ capture from cement Fig. 4 demonstrates the steps undertaken during the testing of cement produced from spent sorbent at a laboratory scale.

So far, there have been no significant effects on the cement quality noted by pre-using the CaO to capture CO$_2$ [29]; in fact (and as expected), the ratio of alite to belite in the cement (a crude measure of the cement quality) formed improved with increasing cycles of calcination and carbonation: see Fig. 5, which compares the alite/belite ratio for cases with and without the addition of coal to effect the calcination reaction.

Large pilot-scale demonstrations of the Ca-looping process are underway at two locations (both for power-related applications), the University of Darmstadt (Germany), at a scale of 1 MWth [30] and at
La Pereda (Spain) at the scale of 1.7 MWth [31]. As of March 2012, both are operating as expected. Cemex also have a pilot-scale carbonator at Monterray, Mexico [32].

The cost for decarbonisation of cement manufacture has been estimated for calcium looping as ∼$20/tCO₂ [18], and for general post-combustion capture using this process of $15–20/tCO₂ [26]. Kuramochi et al. [23] quote costs (per tCO₂) for a variety of short/medium term processes of between $35 for Ca looping precalcination (based on [18]) to $47–67 for advanced solvents (the lower figure is for steam import from a power station, the higher figure for boiler steam import), around $56 for oxyfuel operation and $85–117 for MEA-based scrubbing (again, the lower figure is for power station steam and the higher for boiler steam). The IEA GHG programme [33] has assessed the costs of an oxyfired cement kiln in the UK, and estimated a cost of $54 for decarbonisation of the calciner only, or $29 for an Asian developing country. This was in contrast to their assessment of $138 for post combustion capture using MEA for the entire plant in the UK, or $93 for a developing country.

Iron and steel

The manufacture of iron and steel is another sector where the use of carbonaceous fuels is currently intrinsic to the process, leading to significant difficulties in decarbonisation through routes other than CCS. The current primary manufacturing route involves the heating of coke, pulverized coal, bulk iron ore and sinter in a blast furnace, with oxygen injected to produce both high temperatures (1500 °C) and a highly reducing environment through partial combustion of the coke. The raw materials pass down the furnace and contact countercurrently with hot reducing gases produced by the combustion
of the coke (and potentially a small amount of coal), and (potentially O₂-enriched) air. The requirement for coke (which supports the ore as it passes down the furnace and prevents collapse of the bed) is one of the main drawbacks of the blast furnace, since the production of coke is costly in both environmental and monetary terms, and the substitution of coke with coal is a subject of significant research [34]. Research in the area of CCS from iron and steel production is being carried out by the Ultra-Low CO₂ Steel (ULCOS) programme [35]; a consortium of 48 EU companies and organisations from 15 EU countries. The programme began in 2004 and has since focused on research and small pilot demonstrations of a number of alternative iron and steel production processes, which enable the capture of CO₂ and its subsequent storage. Following good progress, the program now aims to demonstrate the processes on a larger scale.

The gas produced from the blast furnace consists of CO (17–25%) and CO₂ (20–28%), H₂ (1–5%), N₂ (50–55%) [23]. Post-combustion capture using chemical sorbents, such as those proposed in the power sector, could be used to capture CO₂ from the blast furnace exit gas stream, however much of the carbon then remains uncaptured in the form of CO. Through reforming and the water–gas shift reaction, the CO₂ concentration can be increased to 60% CO₂ [3], making physical solvents such as Selexol, which has been developed for IGCC pre-combustion capture, technically and economically feasible.

The TGR process proposed by ULCOS eliminates the N₂ content by injecting the blast furnace with oxygen rather than air. The gas exiting the top of the blast furnace consists of concentrated CO₂, which can be separated from the other gases using Vacuum Pressure Swing Adsorption (VPSA) or Pressure Swing Adsorption (PSA) together with cryogenics separation to remove final impurities. The CO₂ is transported to underground storage, and the separated CO and H₂ are recycled and injected at the bottom of the blast furnace, where they act as reducing agents. This has the additional benefit of decreasing the amount of coke required as a reducing agent.

An alternative (or possible supplement [36]) is the COREX process. The key feature of this process is that iron ore melting is separated from iron ore reduction. This eliminates the need for the stabilizing properties of coke and allows coal or gas to be used instead. The COREX process exports a significant volume of calorifically-rich gas (mainly CO and CO₂), which can be used for either power generation or (after CO₂ removal) as a reducing gas for a conventional blast furnace [37].

Direct reduced iron (DRI) is an alternative raw material to scrap for the electric arc furnace. In the DRI process, the iron ore remains in the solid phase. This means that the furnace can be operated at temperatures below the melting point of iron and either gas or coal can be used as the reducing agent instead of coke. The DRI process offers promising opportunities for CO₂ capture. Natural gas, enriched with H₂, is partially oxidised to synthesis gas (CO and H₂) by reacting it with oxygen. This reducing gas is then fed to the reactor and reacted with the solid iron ore, producing a mixture of CO, CO₂, H₂ and H₂O. In order to improve the efficiency of the separation process, the CO₂ concentration (and consequently the hydrogen concentration) is increased via the shift reaction and CO₂ can then be separated using either physical or chemical sorbents. The resulting hydrogen is recycled.

There are a number of potential changes to iron and steel manufacture to enable the capture of CO₂, some entailing significant changes to the production process, but others such as post combustion capture requiring minimal alterations.

Kuramochi et al. [38] have compared a number of these technologies and estimate that an avoidance cost of less than $64/tCO₂ for ~50% of the CO₂ emissions is achievable in the short term by converting conventional blast furnaces to top gas recycling. Alternatively, it is possible to add conventional solvent scrubbing to remove CO₂ from the blast furnace off-gas at a cost of $51–64/tCO₂, though because of the high CO concentration in this gas, it is only possible to remove around 15% of the total CO₂ emissions [23].

Again, because of the high temperatures inherent in the iron and steel production processes, coupled with the potential to export significant quantities of energy-rich gas, there are significant potential synergies with the power generation sector.

**Refineries/petrochemicals**

Refineries produce CO₂ through both process heating and intrinsic chemical transformations (such as regenerating the catalyst used in a fluid catalytic cracker). Refineries are variable in scale and processes used, leading to a significant challenge when defining the constitution of a “typical” refinery, never mind its optimization. Some 30–50% of the CO₂ emissions in a refinery result from
process heating and utilities, i.e. large volumes available at a small number of locations [39] (n.b. reference [1] appears to misquote this value as 30–60%). Around 5–20% of the emissions are high purity, and the remaining ~50% is comprised of a number of small sources. Initial experiments being conducted Petrobras into oxyfiring their FCC regeneration [40] as part of the “Carbon Capture Project” ( CCP). Figure 6 shows a breakdown of CO\textsubscript{2} emissions from refineries worldwide by source [23].

Farla [14] conducted one of the first studies into CO\textsubscript{2} capture from industry, and concluded that the costs of CO\textsubscript{2} abated was \$175/tCO\textsubscript{2} for capture from the petrochemical industry. Table 2 (after [1]) contains the estimated costs to decarbonize at a variety of locations within an oil refinery.

Table 2. Estimated costs of decarbonisation from a variety of locations in an oil refinery (after [1]).

<table>
<thead>
<tr>
<th>Process captured</th>
<th>Capture type</th>
<th>Retrofit or new build</th>
<th>Cost of CO\textsubscript{2} avoided $/tCO\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Low</td>
</tr>
<tr>
<td>Utilities, combined cycle gas turbine</td>
<td>Post-combustion</td>
<td>New</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>Pre-combustion</td>
<td>New</td>
<td>38</td>
</tr>
<tr>
<td>The Heaters and boilers (UK)</td>
<td>Post-combustion</td>
<td>Retrofit</td>
<td>108</td>
</tr>
<tr>
<td></td>
<td>Pre-combustion</td>
<td>Retrofit</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>Oxy-combustion</td>
<td>Retrofit</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>Post-combustion</td>
<td>New</td>
<td>134</td>
</tr>
<tr>
<td></td>
<td>Oxy-combustion</td>
<td>New</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>Chemical looping combustion</td>
<td>New</td>
<td>46</td>
</tr>
<tr>
<td>Fluid Catalytic Cracker</td>
<td>Post combustion</td>
<td>New</td>
<td>119</td>
</tr>
<tr>
<td></td>
<td>Oxy-combustion</td>
<td>Retrofit</td>
<td>77</td>
</tr>
<tr>
<td>Hydrogen production SMR</td>
<td>Post-combustion</td>
<td>New</td>
<td></td>
</tr>
</tbody>
</table>

It is clear from Table 2 that the costs of CO\textsubscript{2} capture vary significantly between different parts of the refinery. The major reasons for this are the inherent efficiencies of the capture technologies studied, the sizes of the unit operations being captured from and whether the CCS system is new build or retrofit. Costs appear to be a little higher than for power stations, and significantly higher than for decarbonisation of the cement industry. Similar costs might be expected to those for heaters and boilers for other applications where raising steam is key, such as “Steam-Assisted Gravity Drainage” to produce heavy oils.

Biomass processes

This sector is currently very small, but the combination of biomass and CCS allows the possibility of “negative” emissions of CO\textsubscript{2} [41]. In the non-power-related sector, the main potential sources of CO\textsubscript{2} are from breweries/ethanol production plants (which have the advantage of also yielding high-purity CO\textsubscript{2} streams), and potentially in the future from either biomass gasifiers/Fischer-Tropsch reactors to produce hydrocarbon fuels, or the direct production and upgrading of pyrolytic oils [42].
The potential for this sector should not be underestimated—there are around 3 billion tonnes of biomass residues (i.e. from farming, timber production, etc.) produced per year [43]. In the UK, the TESBIC project [44] has assessed the commercial potential of the integration of biomass combustion for power generation and CCS as a method to capture CO₂ from the atmosphere.

Given the low technology readiness levels (TRLs) of many of the proposed technologies for production of e.g. liquid fuels (excluding ethanol) from biomass (e.g. pyrolysis, gasification + Fischer-Tropsch), combined with the low TRL of CCS and the significant uncertainty regarding the biomass value chain, costs are speculative at best. However, for the case of ethanol production [45], which produces a nearly pure stream of CO₂ as a byproduct of the fermentation process, costs are extremely low, being only associated with drying and compressing the CO₂ for transport. However, by far the most interesting finding from their paper is that adding CCS to the bioethanol plant (and capturing only 13% of the carbon reduces the cost of carbon avoided from $729 to, figures which probably say more about the value of first generation biomass fuels for the mitigation of global warming than they do about the cost of CCS.

UNIDO [1] considers that the application of CCS to biomass processes is an extremely important area for future research. To quote from a workshop to discuss the application of CCS to industry “More detailed scientific studies are needed on costs, long-term contribution on GHG reduction and early opportunities. Dedicated pilot and demonstration projects should be facilitated.”

CONCLUSIONS

The wide variety of industrial sources of CO₂ leads to a large variation in the estimated costs. These range from significantly below the cost of application in the electricity production sector, to much higher. The field is underdeveloped in comparison to the power sector, with fewer studies conducted. This is for two major reasons: firstly, much of the information relating to industrial processes is proprietary, and secondly the industrial sector as a whole (with the exception of gas processing) has been less forward in embracing the technology.

Future research in the area should focus on developing integrated models with common cost models, in collaboration with industry, and explore the potential synergies between power generation and industry, particularly in the cement and iron and steel sectors. Good economic modelling is important. There are also significant experimental research challenges under investigation in the Iron and Steel and Cement manufacturing sectors. Owing to the high temperatures employed in both of these sectors, there are unique possibilities for both to be integrated with high temperature looping cycles, which are being explored in particular in the cement industry.

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