Containment, Capture, Recycling and Sequestration of Emitted Carbon Dioxide in the Context of the Indian Cement Industry

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1. Introduction

The cement industry in general is widely perceived as a generator of a large quantum of pollutants embracing a wide variety. While the industry has performed well in containing and trapping suspended particulate matters as well as some of the volatiles and toxic elements, its success in maneuvering the carbon dioxide emission is rather limited. Whatever has been achieved is due to maximizing the production of blended cements, minimizing the energy consumption and use of alternative fuels.

According to the world energy outlook, issued by the International Energy Authority (IEA), in 1995 the worldwide carbon dioxide emissions from all sources amounted to 21.6 billion tonnes. In 2002, the last year for which comprehensive data are available in the recent data book of World Bank, the carbon dioxide emission is estimated at 24 billion tonnes. During these seven years the global cement production increased from 1.4 to 1.8 billion tonnes per year. Going by an assumed approximate specific emission of 0.85 tonnes of carbon dioxide for every tonne of cement produced in the nineties, the contribution by the global cement industry to the total emission of carbon dioxide has, thus, increased from 5.5% to 6.4% during this period.

In this global backdrop, India as the second largest producer of cement in the world will have to play an effective role in minimizing the carbon dioxide emission. Humphreys and Mahasenan [1] had shown that between 1990 and 2000, India brought down the specific carbon dioxide emission from about 0.98 kg CO_2 per kg of cement to about 0.94 kg CO_2 per kg of cement and yet it ranked amongst the very high emitters of carbon dioxide (Fig.1). This paper aims at assessing the current CO_2 emissions level achieved due to product and process changes, potential of reduction by 2015, and the strategy for recycling and sequestration outside the battery limits of the cement plants, if such measures become necessary.

2. Status of the Cement Manufacture in India

From the database of Cement Manufacturers' Association of India it is known that at the end of 2005 the total installed annual capacity in India was 170.9 million tonnes with corresponding production of 142.7 million tonnes of cement. The total capacity and production comprise a wide mix

of vintages, manufacturing processes, kiln capacities, plant configurations, etc. as the industry already has a history of over nine decades. The above capacity and production figures include those of mini and small grey and white cement plants to the extent of 11.10 million tonnes capacity and 6.0 million tonnes of production, which have not been considered in later computations in our attempt to assess the carbon dioxide emission.
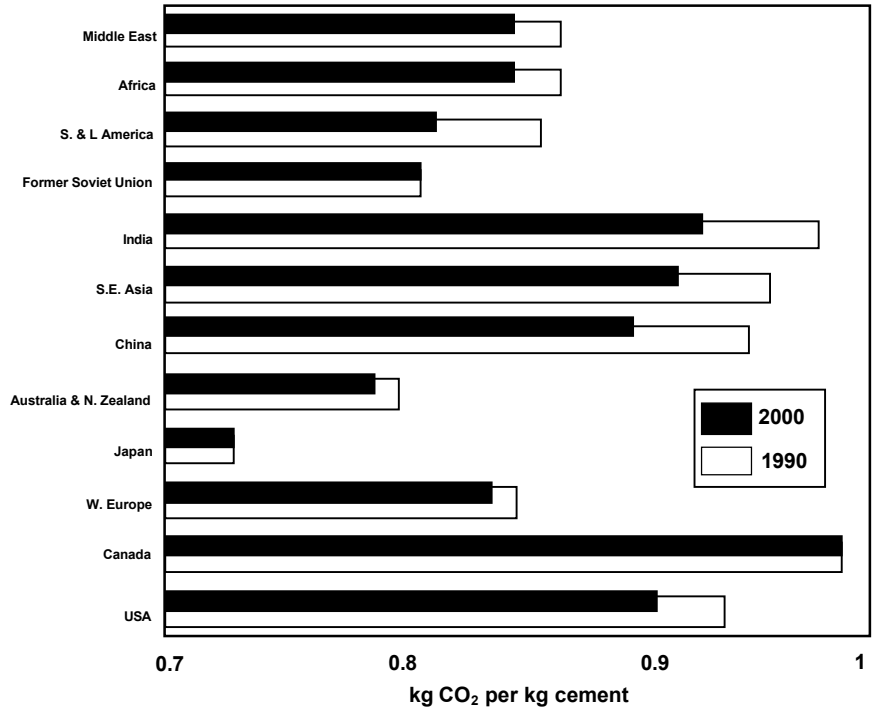

Figure. 1 Carbon dioxide release in some regions in the nineties.

2.1   Kilns and Specific Heat Consumption

There are in total 162 kilns in the industry with total annual clinkering capacity of about 142 million tonnes. Out of these ones 134 kilns are currently operational with annual clinkering capacity of 136 million tonnes. The process and size distribution and average specific heat consumption of these kilns as compiled by the author from various sources are given in Table 1.

The capacity and production of cements of various types over the last five years are shown in Table 2. From the above data it is evident that the proportion of blended cements to total cement production in the last five years has increased from 37.2 per cent to 55.6 percent or by 18.4 per cent and at the same time the usage of clinker has reduced by 6 percent. These developments have certainly contributed towards reduced carbon dioxide emission.

Table 1: Process,Capacity & Energy Based Distribution of Operating Kilns

Serial No.	Capacity range tpd	Average specific heat consumption kcal/kg cl	Process type	Number of Kilns
1	7500 – 7000	690	5 / 6 stage preheater-precalciner	6
2	6500 – 6000	700	- Do -	3
3	5900 – 5200	720	- Do -	2
4	5000 – 4500	720	- Do -	11
5	< 4500 – 4000	735	- Do -	9
6	< 4000 – 3500	770	- Do -	16
7	< 3500 – 3000	780	- Do -	15
8	< 3000 – 2500	800	4 / 5 stage preheater-precalciner	10
9	< 2500 – 2000	820	- Do -	8
10	< 2000 – 1500	850	- Do -	15
11	< 1500 – 1000	970	Older generation preheater	16
12	< 1000	980	Precalciner - Preheater	7
13	< 1000	970	Semi dry	6
14	< 1000	1200	Wet	10

Table 2 : Capacity and Production Trends of Various Types of Cement

Year	Capacity x 10^6 t	Production x 10^6 t				
		OPC [+]	PPC [++]	PSC [+++]	Others	Total
2004 - 05	151.34	55.97	60.23	10.73	0.64	127.57
2003 - 04	144.30	53.51	52.12	11.26	0.61	117.50
2002 - 03	136.97	56.05	43.08	11.63	0.59	111.35
2001 - 02	129.76	57.68	32.29	11.89	0.54	102.40
2000 - 01	114.91	58.06	24.50	10.34	0.71	93.61

+   Ordinary Portland Cement.
++   Portland Pozzolana Cement.
+++   Portland Slag Cement.

2.2 Fuel Usage

So far as the fuel usage pattern is concerned, the industry is primarily dependent on bituminous coal of about 35 per cent average ash content. Based on the economic viability, a few plants have switched over fully or partially to imported low-ash coal and high-sulphur low-ash petroleum coke sourced from within or outside the country. In terms of the heat value the proportion of substitute and waste fuels used is almost 15 per cent of the total fuel consumed.

2.3 Power Scenario

The specific power consumption is observed to be quite variable even for the same type and grade of cement as shown in Table 3. The average specific power consumption figures in the table are based on tentative data available at the author's disposal. The national grid that feeds power to the industry is largely fed by electricity generated by coal-based power plants. Further only 4% of captive power generation in the industry is based on renewable energy.

Table 3: Cement Varieties and Average Specific Power Consumption
(2004 - 05)

Type of Cement	Production x 10^6 t	Range of Specific Power Consumption kWh / tonne cement	Average Specific Power Consumption kWh / tonne cement
OPC (Both 43 & 53 grades)	55.97	85 – 110	90
PPC	60.23	75 – 105	85
PSC	10.73	75 – 105	80

3. Present Carbon Dioxide Emission Level at Production Stage

Using the year 2004-05 as the base, an attempt has been made to estimate the current carbon dioxide emission level on the basis of the following production and operating parameters of large plants:
- Clinker production of 110 million tonnes
- Corresponding cement production of 127 million tonnes
- Limestone –to–clinker conversion ratio: 1.46
- Average loss of ignition in limestone: 35 per cent

- National average specific heat consumption: 800 kcal/kg of clinker
- National average specific power consumption: 87 kWh/t of cement, which is significantly low due to extensive adoption of energy conservation measures.
- Average ash content in coal used: 35 per cent
- Average fixed carbon content in coal: 45 per cent
- Coal consumption norm for power generation: 650 kg per 1 MWh

The carbon dioxide generation in the production stage has been estimated for the following three steps:
   a) Decomposition of calcium carbonate from the raw mix (56 million tonnes).
   b) Carbon dioxide formation from coal fired in the pyroprocessing process (32 million tonnes)
   c) Carbon dioxide generated from coal estimatedly used in the generation of electricity consumed in both pyroprocessing and comminution process (12 million tonnes).

Thus, the total carbon dioxide emission at the given production level amounts to 100 million tonnes or 0.78 tonnes of carbon dioxide per tonne of cement produced. The reduction over the 2000 level is at about 17 per cent and has primarily happened due to increased production of blended cements, lower consumption of clinker in cements and overall energy conservation in the more recent and modern plants. The contribution of renewable energy sources as well as of alternative and waste-derived fuels has been negligible.

3.2. Status of CDM Projects

It may be relevant to indicate that the Indian cement industry has been quite active in undertaking CDM projects. As on 2 May, 2006 there were 28 CDM projects from 19 cement companies, which were in different stages of registration with the UNFCCC-EB. Of the above projects, 19 proposals were for blended cements, 5 for alternative fuels, 2 for energy efficiency, 1 for wind power generation and 1 for waste heat recovery. If fully implemented, these projects would generate an annual average carbon credit of 2.15 million tonnes equivalent.

3.3. Future Trends of Carbon Dioxide Emission

It is well understood that factors such as geography, climate, population density, resource endowment and economic structure influence energy use across countries. It appears from the trend analysis that the energy intensities in the developed and developing countries are showing reverse

pattern and the year 2015, as a result, is perceived as the cross-over point for the annual industrial emissions in the above countries (Fig. 2.) [2]. Taking the year 2015, therefore, as a near-future target, a tentative attempt has been made to forecast the carbon dioxide emission possibilities from the Indian cement industry in that year. The current and projected production details for this assessment are given in Table 4.
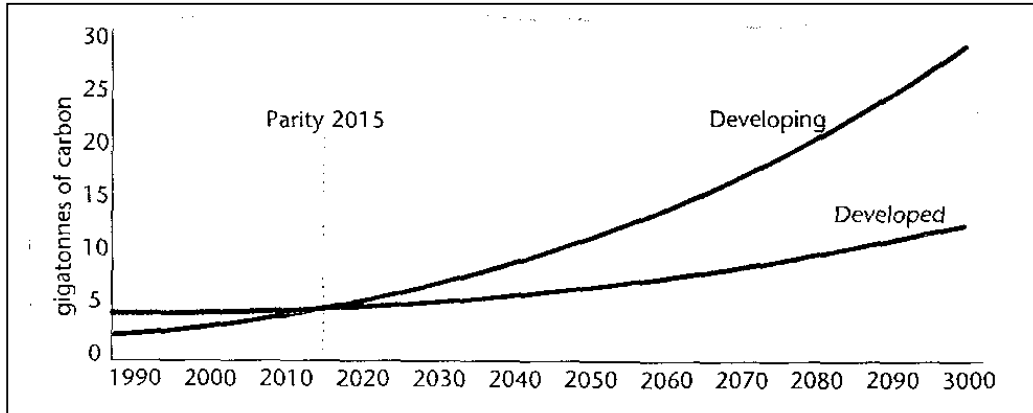

Figure 2. Annual Industrial emissions in industrialized and developing countries

In projecting the cement demand the actual production of 142 million tonnes in 2005-06 has been taken as the base and thereafter 8 per cent annual average growth has been assumed. For estimating the clinker-to-cement ratio the decreasing rate of increase in PPC production and the steady rate of production of PSC have been considered. So far as the energy efficiency figures are concerned, the trends of modern plants such as 80-85 KWh/t of cement and 690 Kcal/Kg of clinker have been given some weightage. However, in the absence of any reliable data base the future contribution of substitute fuels like petcoke, agro-industrial wastes and renewable energy usage could not be factored into the projection.

Broadly it appears that by 2015, although there could be about 16% further reduction in the specific emission of carbon dioxide, the absolute emission may increase by over 70 million tonnes. The impact of alternative fuels and energy resources as well as of further energy conservation measures is not expected to substantially alter the scenario. Under these circumstances certain other approaches outside the battery limit of cement plants may have to be considered. Some of these options are dealt with in the following sections.

4. Cogeneration of Chemicals Using Process Carbon Dioxide

One of the alternatives of reducing carbon dioxide emission is to capture it in the process and utilize subsequently for cogeneration of various other products and chemicals. The most common method to capture carbon

dioxide from the flue gas is the amine scrubbing; using monoethanolamine (MEA) as a solvent. The amine from the scrubber is heated by steam to release high purity carbon dioxide and the carbon dioxide free amine is then reused in the scrubber. However the major shortcomings for the application of MEA capture process are its energy intensive nature for solvent regeneration resulting in high capital and operating costs when applied to lean flue gas streams. Nevertheless, this is one of the proven industrial technologies for CO_2 capture. Other alternatives like use of ammonia as a solvent or the application of Pressure Swing Adsorption (or, Temperature Swing Adsorption or Electric Swing Adsorption), or adoption of membranes technology, etc have their limitations of application due to scale of operation or lean character of the flue gas.

Table 4 : Projected Parameters for 2015

Serial No.	Parameters	2004 - 05	2014 -15
1	Cement demand (million, tonnes).	127	263
2	Clinker – to – cement ratio.	1.28	1.38
3	Tentatively estimated national average specific heat consumption, kcal / kg.	800	750
4	Tentatively estimated national average specific power consumption, kWh / t of cement.	87	80
5	Total estimated emission of carbon dioxide, million tonnes.	100	171
6	National average specific emission, t/ t.	0.78	0.65

4.1 Process concept of Methanol Synthesis

The outline of the conceptual process is given in Fig.3 and is summarized as follows:
- CO_2 separation from flue gases using alkali/amine absorption and high temperature stripping.
- Generation of CO + H_2 mixture by coal gasification with steam.
- Production of methanol by catalytic hydrogenation of CO and/or CO_2
- Use of excess CO generated from gasification reaction as a raw material for other value added products or its recycle as a fuel.

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KILN  EXHAUST  GASES                              COAL  GASIFICATION  WITH  STEAM
CONTAINS  20-25%  CO2  V/V)                                    COAL

            │   PURIFICATION  AND  RECOVERY  OF  CO2              │

┌──────────────────────┐                            ┌──────────────────────┐
│C2H4OHNH2+H2O+CO2 ──▷ │   ABSORPTION  OF           │                      │    STEAM
│       MEA            │   CO2  IN  AMINE  SOLUTION  │  C + H2O ──▷ CO + H2 │    ◁──
│C2H4OHNH3+HCO3        │   (45°C-60°C)              │                      │
└──────────────────────┘                            └──────────────────────┘

            │
┌──────────────────────┐                                         │
│  STRIPPING  OF  CO2   │                             CO  +  H2
│  AT  120°C            │                                         │
└──────────────────────┘

            │  CO2                                                │

MEHTANOL  SYNTHESIS  VIA  CATALYTIC  HYDROGENATION  OF  CO  AND/OR  CO2
        ┌────────────────────────────────────────────────────────┐
        │   CO  + 2H2   ──▷    CH3OH        - 90.77  KJ/GM. MOLE   │
        │   CO2 +  H2   ──▷    CO + H2O     + 41.19  KJ/GM. MOLE   │
        │   ──────────────────────────────────────────────────    │
        │   CO2 + 3 H2  ──▷    CH3OH + H2O  - 49.58  KJ/GM. MOLE   │
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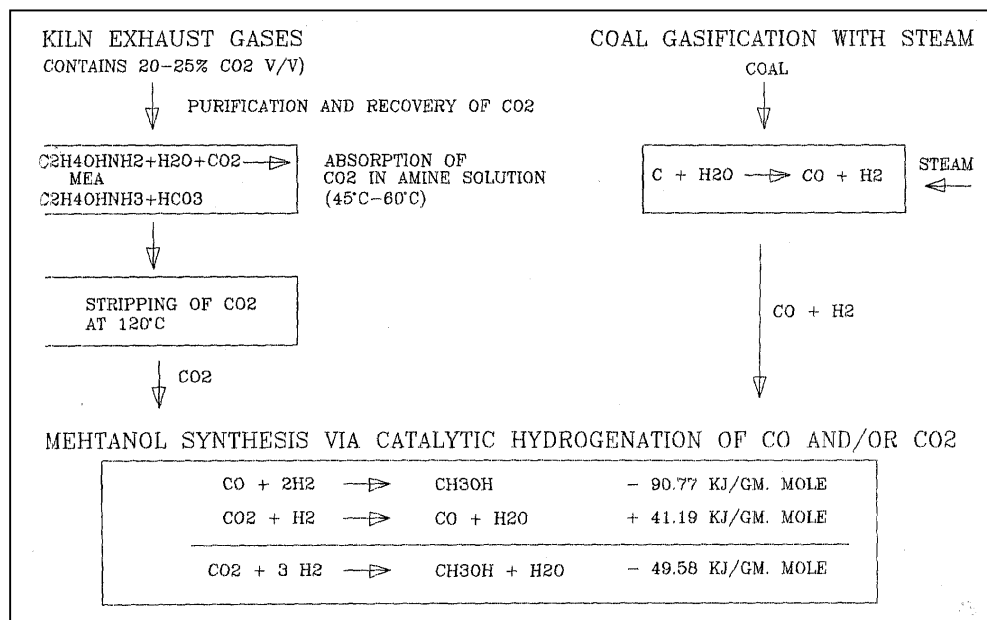
Figure 3. Conceptual process scheme for methanol synthesis

The stoichiometric estimation of the in-process chemicals are given in Table 5. One can also link up the synthesis of a whole series of chemicals with methanol, which is well known.

Table 5 : Stoichiometric Computations of the Reactions (Basis:3000 TPD Clinker Plants)

Parameter	kg Moles/ hr	TPD	kg/kg Cl
CO_2 generation potential @ 1.5 Nm^3 gas / kg Cl and 20% CO_2 level.	1674	1750	0.583
H_2 requirements	5025	241.2	0.08
Equivalent CO production.	5025	3376	1.125
Coal requirements @ 45% carbon in coal.	5025 of carbon	3216	1.07
Steam requirements.	5025	2171	0.723
Potential Methanol production.	5025	1286	0.429

It may also be borne in mind that CO_2 can as well be used as a feedstock for manufacture of ammonium sulphate and urea. There are many other known usages of CO_2 ranging from carbonization of beverages to making of dry ice to fumigation of grain silos, which have not been dealt with in this article as they do not promote bulk uses of CO_2. A few other emerging options for bulk storage, disposal and use are touched upon in the following sections.

5. Sequestration Options for Carbon Dioxide

A variety of means of artificially capturing and storing carbon, as well as of enhancing natural sequestration processes are being explored. The major natural carbon dioxide sinks are the oceans and growing vegetation which are not dealt within this article. One of the potential ways of artificial sequestration is seen to be in the form of carbonate minerals.
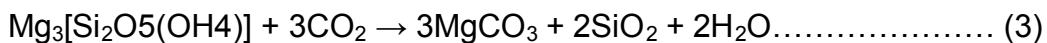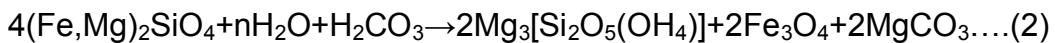
5.1 Mineral Sequestration

In nature it has been observed that carbon dioxide is often trapped in it's thermodynamically ground state. The formation of limestone is an example of this process, in which acids are used to convert mineral silicates to mineral carbonates. If the kinetics of these reactions can be speeded up the mineral sequestration of carbon dioxide may turn out to be feasible.

One plausible reaction is the interaction of dunite or serpentinite with carbon dioxide to form magnesite along with silica and magnetite, as proposed by Zeca Corporation for zero emission coal and carbon technologies for power sector [3]. The ideal reaction takes place only when extremely magnesia-rich olivine or serpentine is available as the reactant as shown below:

$$Mg_2SiO_4 + nH_2O + CO_2 \rightarrow Mg_3[Si_2O_5(OH_4)] + MgCO_3 + SiO_2 + H_2O \ldots(1)$$
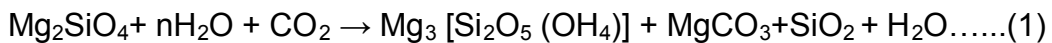
The presence of iron in the olivine or serpentine structure reduces the efficiency of the reaction steps which can be presented as follows:

$$4(Fe,Mg)_2SiO_4 + nH_2O + H_2CO_3 \rightarrow 2Mg_3[Si_2O_5(OH_4)] + 2Fe_3O_4 + 2MgCO_3 \ldots(2)$$

$$Mg_3[Si_2O5(OH4)] + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O \ldots\ldots\ldots\ldots (3)$$

Needless to emphasize, that the on-going research activities are aimed at speeding up these reactions. This approach is quite applicable for the Indian cement industry. The serpentinite occurrences in the east and south can be made use of for the respective clusters of cement plants.

5.2. Geologic Sequestration of Carbon Dioxide

The process of geosequestration or geological storage involves injecting carbon dioxide directly into underground geological formations. Declining oil fields, saline aquifers and unminable coal seams have often been suggested as storage sites (Fig. 6).
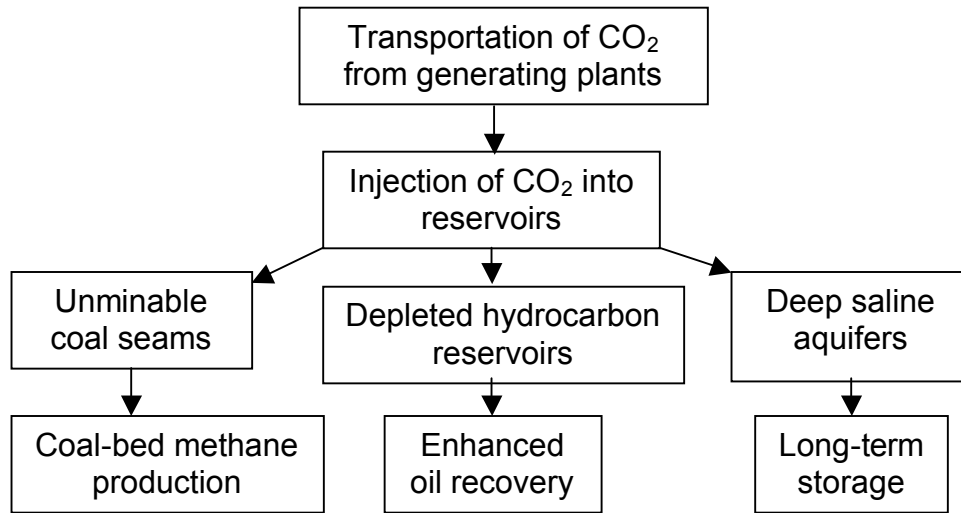
Figure 4. Options for geosequestration of carbon dioxide.

So far as India is concerned, the coal seam option appears interesting. Unmineable coal seams can be used to store CO_2 as it adsorbs to the coal surface ensuring safe long storage. In the process it releases methane that had previously adsorbed to the coal surface. This methane is recoverable. Again sale of this methane can be used to offset the cost of CO_2 storage.
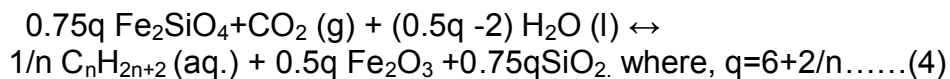
Government of India has taken appropriate steps to encourage and accelerate exploration and exploitation of coal bed methane (CBM) in the country as a promising new alternative energy source [4]. Based on the general information of geology and gas content of the seams of various coal fields of India the estimates of CBM are around 3 trillion cubic meters. India being the 5th largest holder of coal reserves (234 billion tonnes) in 42 different coal fields, the prospects of CO_2 sequestration for coal bed methane recovery is immense. What is important at this stage is to embark on a pilot project by selecting a storage site in proximity of a cement plant or a group of plants so as to minimize the transportation costs. Further, the process would turn out to be viable based on enhanced recovery, which will have to be assessed.

6. Reductive Sequestration and Recyclability of Carbon Dioxide

With a view to examining if carbon dioxide can be treated as a renewable resource, certain experimental studies have been reported on recyclability of carbon dioxide as fuel . The proposed process involves reductive capture of CO_2 in a two-part scheme related partially to the Fischer Tropsch process, and employing common minerals with sufficient reduction and/or photo reduction potential to convert CO_2 to formate

and/or methanol [5] and then to fuel–valued product. Thermo -chemical calculations show the overall scheme to be highly exothermic and thus self-sustaining with appropriate process design. The possibility of large–scale process level CO_2 reduction has appeared viable based on a report by McCollom [6] who reported experiments in hydrothermal media with dissolved CO_2 and the mineral olivine which showed that bicarbonate ion was immediately reduced to formate at 300^0C and 350 bar. The second account of a mineral-based conversion describes sunlight-driven production of formic acid from CO_2 at ambient temperatures. In this case Ohta et al [7] worked with a selection of common Fe [II] containing silicate rocks (amphibolite, granite, gneiss, shale) which were powdered and suspended in CO_2 saturated water. When the mixtures were irradiated by sunlight at ambient temperature, formic acid was formed at a rate of several μg / m^2 over 18h.

The practical features and commercial potential of obtaining fuel-valued products may be evaluated from the following fayalite-based equation:

$$0.75q\ Fe_2SiO_4 + CO_2\ (g) + (0.5q - 2)\ H_2O\ (l) \leftrightarrow$$
$$1/n\ C_nH_{2n+2}\ (aq.) + 0.5q\ Fe_2O_3 + 0.75qSiO_2 \text{ where, } q = 6 + 2/n \ldots\ldots(4)$$

Since there are indications that the above reactions do work and can be modified to produce varying proportions of C_1 and C_2 products, Mill and Ross [8] embarked on a project, the conceptual scheme is shown in Fig.5.

The core of the conversion is the central loop in which the CO_2 is reduced either thermally or through solar radiation to formic acid, possibly with conversion of Fe [II] in the mineral feed to Fe [III] magnetite as the corresponding oxidation state. The hydrogen source is water in the feed mixture. In the second step, vapour phase formic acid thermally disproportionates to fuel, which is passed back into the system and to CO_2 which is returned to the reduction cycle. The research programme had been designed to evaluate key kinetic and photochemical steps in such a manner that the database would be suitable for a sound appraisal of the conversion concept and an evaluation of the prospect of advancing to a process development study. India, endowed with Fe [II] bearing rocks and minerals base together with abundant sunlight has every reason to explore the new avenues of reductive sequestration of carbon dioxide. The focus of this experimental approach is to assess the balance between the fuel value provided by reduction of carbon dioxide and energy requirements for reduction. It must be recognized at this stage that this technology is at its concept proving stage but it has high potential to demand a close attention.
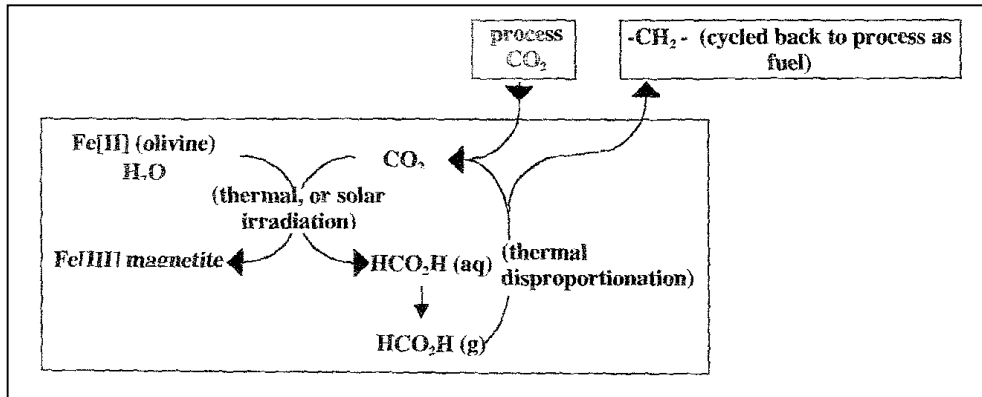
Figure 5. Proposed scheme for the conversion of captured process CO_2 back to fuel-valued products.

7. Conclusion

The combustion led production of carbon dioxide has evolved into a major environmental challenge that extends beyond national borders. The solutions that are known and those being investigated to minimize this problem are technologically quite demanding.

During the late nineties the contribution by the global cement industry to the total emission of carbon dioxide in the world was in the range of 5.5-6.4 percent. India, as the second largest producer of cement in the world, had specific emission of 0.94 kg CO_2 per kg of cement in 2000 which came down to 0.78 kg in 2004-05. Increased production of blended cements, lower consumption of clinker in such blended cements and overall energy conservation helped in achieving such reduction. India is also engaged in a large number of CDM projects that may generate an annual average carbon credit of 2.15 million tonnes equivalent.

However, the cement industry in India is still in its growth path. The tentative projections indicate that by 2014-15, the cement demand at the current growth rate would be of the order of 263 million tonnes and notwithstanding the maintenance of improved trends of energy conservation and production of blended cements, the estimated emission of carbon dioxide may be of the order of 170 million tonnes, Such a bulk quantity of carbon dioxide emission will be difficult to be sequestered unless newer technological approaches are explored. The newer technologies of high potential are the following: capture and co-generation of chemicals by adopting the available industrially proven technologies, mineral sequestration in the form of magnesite, geosequestration in coal seams, depleted oil reservoirs or saline aquifers. In India because of the present thrust on exploitation of coal bed methane, the feasibility of

geosequestration of carbon dioxide for enhanced coal bed methane recovery demands special attention.

A totally novel concept of treating carbon dioxide as a renewable energy source is emerging. The process involves reductive capture of carbon dioxide by thermal or solar irradiation by employing common mineral with sufficient reduction and/or photoreduction potential. Although this technology is in its concept proving stage, it has high potential to merit closer attention.

Acknowledgement

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