# THE SIGNIFICANCE OF INDUSTRIAL USES OF $CO_2$ (PROCESSES, PRODUCTS AND GOODS) AS INSTRUMENT FOR THE ATTENUATION OF THE GREENHOUSE EFFECT AND FOR THE OBTAINING OF ECONOMIC VALUES

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## Abstract

It is widely believed that climate change on the planet largely depends on discharges of $CO_2$ due to human activities.

This is the reason why many countries, including China, have committed themselves, with the Kyoto Protocol, to reducing their discharge of $CO_2$ into the atmosphere.

Reducing the discharge of $CO_2$ has therefore become a common objective of the international community, to be pursued primarily through a series of actions aimed at increasing the sustainability of industrial processes.

There are various types of actions that have been proposed: they range from reducing the use of fossil fuels, the separation of $CO_2$ prior to its release into the atmosphere, its capture and storage in the oceans or underground, to an increase in the use of renewable energy sources, nuclear energy, etc.

The paper, however, pays particular attention to the contribution that $CO_2$ is able to provide both in industrial processes and as a raw material employed in production processes, to obtain products and goods, and ultimately, to the way in which, from a waste product with a high environmental impact (like $CO_2$) it is possible to create economic value.

The authors quantify this possibility.

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**Riassunto**

E' opinione diffusa che il cambiamento climatico del pianeta dipende in gran parte dalle emissioni di $CO_2$ dovute alle attività umane. Questo è il motivo per cui molti paesi, compresa la Cina, con il protocollo di Kyoto si sono impegnati a ridurre le proprie emissioni di $CO_2$ in atmosfera.

La riduzione delle emissioni atmosferiche di $CO_2$ è pertanto divenuto un obiettivo comune della comunità internazionale, da perseguire prioritariamente mediante una serie di azioni rivolte ad accrescere la sostenibilità dei processi industriali.

Ci sono vari tipi di azioni che sono state proposte: esse vanno dalla riduzione dell'uso dei combustibili fossili, alla separazione della $CO_2$ prima della sua emissione in atmosfera, alla cattura e allo stoccaggio negli oceani e nel sottosuolo ad un aumento dell'uso di fonti rinnovabili di energia, di energia nucleare ecc.

Il lavoro, tuttavia, pone particolare attenzione al contributo che la $CO_2$ è in grado di dare sia nei processi industriali sia come materia prima impiegata nei processi produttivi per ottenere prodotti e merci, in ultima analisi al modo in cui da un refluo di elevato impatto ambientale ($CO_2$) è possibile ottenere valore economico.

Gli autori quantificano tale possibilità.

**Keywords**: Climate change, $CO_2$ discharge, $CO_2$ uses, Industrial processes, products and goods incorporating $CO_2$

## Introduction

As is known, the need to increase energy consumption in order to improve the quality of life, especially for the numerous population of the PVS (1), is closely connected with another need, that of contrasting the global environmental risks deriving in particular from the discharge of $CO_2$ from the burning of fossil resources (coal, oil and methane) which contributes 80% of greenhouse gases.

Some of the measures which favour this reduction can already be implemented in the short term: the war against waste, energy saving, the adoption of measures related to an increase in energy efficiency (2).

Other strategies of the short and medium term involve the use of renewable energy sources, such as the sun, the wind, geothermal energy, etc., or else the use of traditional renewable sources, such as the kinetic energy of waterways and waterfalls.

One of the medium-term technologies that aim to increase, or substitute the energy offer without increasing the discharge of $CO_2$, is nuclear fission, whereas nuclear fusion is still too far away to foresee its use.

However, considering the above-mentioned need for a rapid development of the PVS, it has been shown that in the year 2025, worldwide energy consumption will have to rise to 18.1 Gtep, compared with the present 11.4 (3).

According to the IEA (4), we will still have to rely for a long time on fossil sources for a very large percentage. Overall, these will probably contribute a quota of 84% of the increase in future energy consumption, and coal, by itself, should account for 73% of this increase (2030 compared with 2005) (5).

It would therefore seem to be obvious, on the basis of these prospects that the future trend will be a further increase in the production of $CO_2$. There is therefore a deeply felt need of incisive, rigorous industrial policies, aiming to adopt integrated technological systems involving the capture, transport and storage of $CO_2$ (CCS: Carbon Capture and Storage) (6). At present, $CO_2$ is usually removed in plants for the treatment of natural gases and the production of ammonia, although their purpose is not to favour the environment: in these cases, no provision is made for the storage of $CO_2$.

As regards its capture, as is known, this can be achieved, under present conditions, by means of three main approaches.

These approaches can be followed in large centres of discharge, as in the case of thermal power stations, industries for the production of steel, cement, or ammonia, or, as mentioned, in natural gas sweetening.
The three systems may be briefly described:
1 – post-combustion[1]
2 – pre-combustion[2]

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[1] DePost-combustion capture consists of the separation of $CO_2$ from fumes generated by combustion, preventively purified by means of the present treatment systems. This separation takes place using a solvent that absorbs $CO_2$ from fumes at a low temperature, and subsequently releases it for heating, thus generating a practically pure stream of $CO_2$.

[2] In pre-combustion capture, $CO_2$ is removed before combustion. The gasification of the fossil fuel with oxygen and the subsequent treatment of the gas generated produces a stream composed of hydrogen and $CO_2$; the $CO_2$ is separated, and the hydrogen is used for the generation of electricity in a combined cycle, or for other uses, as an energy carrier.

3 – oxy-fuel combustion[3].

In the first case, the energy cost of $CO_2$ capture can be quantified, in terms of loss of efficiency, as 8% - 10%. Process estimates indicate an energy penalization in the second case of a cycle based on coal, equal to 9% - 11%. In the third system the loss of efficiency linked with the capture process is estimated to be 9% - 10% (6).

Although oxy-fuel combustion technologies are in use in the aluminium, iron and steel and glass melting industries today, oxy-fuel technologies for $CO_2$ capture have yet to be deployed on a commercial scale.

Again with reference to these CCS systems, apart from the technical and economic problems to be solved, the $CO_2$, once captured and compressed at the various sources of discharge in the territories, has to be transported (by means of pipelines, or, liquefied, by ships or other means of transport), so as to be injected at high pressure in the depths of oceans, forming lakes of $CO_2$ at bathymetries greater than 3 km, in suitable stockpile sites of the subsoil (1 km deep).

In this case, the $CO_2$ needs to be injected at higher pressures, so as to permit the reaching of a "supercritical" behaviour, that is to say, a state assimilable to gas, in its capacity to spread rapidly in the porous spaces of the geological formation, and similar to liquid in terms of density, and thus storable. In exhausted fields of oil or gas, $CO_2$ goes to occupy the pores where the hydrocarbons were trapped (7). In cases where significant quantities of hydrocarbons are still present in the field at the moment of injection of $CO_2$, this favours the extra production of oil or gas, which may range from 7% to 23% (average 13.2%) (8-9).

The storage capacity in the subsoil of exhausted hydrocarbon fields is estimated by the IPCC (6) to be at least 2 thousand Gton of $CO_2$, and that of saline aquifers is decidedly higher.

The $CO_2$ storage systems also include the carbonation of siliceous minerals (serpentine, olivine and wollastonite) (10).

As described below, it is necessary, even in a short period, for carbonation technology to be applied in synergy with the protection of human health in cases of the reclamation of sites or materials to be decontaminated.

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[3] The fossil fuel in the burner is fed with oxygen, instead of air, thus generating a gas stream composed mainly of $CO_2$ and steam, which is partly recycled to the burner in order to make the combustion complete.
The steam is separated by condensation and the stream of concentrated $CO_2$ can be compressed and stored. In the oxy-fuel combustion capture system, the $CO_2$ efficiency is 100%.

However, as the storage technologies mentioned do not appear to be capable of making any contributions in the short term, due to numerous circumstances[4], it appeared to be important to pause, and analyse other $CO_2$ storage systems in order to evaluate their significance.

These consist of the industrial use of the gas, which thus remains stored in the products obtained, or in the processes used to obtain them, as happens in the solicitation of oil fields to add pressure and increase the quantity of oil recoverable.

The advantage is that of considering and making $CO_2$ a useful raw material which makes it possible, while delaying, or reducing, its effect on the environment (cancelling it), to create economic value.

## $CO_2$ discharge of anthropic origin and environmental problems

It is believed that since the industrial revolution, the $CO_2$ in the atmosphere has passed from 280 ppm to the present figure of 370 ppm (11). This is a concentration which is indicated by the analysis of glacial core samples to be the highest for about half a million years.

If each of the tanks in which $CO_2$ is naturally concentrated (oceans 38.400 × 109 t; biosphere and soil 2.180 × 109 t; atmosphere 725 × 109 t) had been able (and could) absorb a quantity of $CO_2$ proportional to its dimensions, the increase in the concentration of $CO_2$ in the atmosphere would be insignificant.

Unfortunately, however, of the approximately 25 Gton of carbon released by man every year, only about one half is absorbed through the "carbon cycle" (mainly by the oceans), while the remainder stays in the atmosphere (4).

Thus, unless suitable action is taken, its concentration in the atmosphere is destined to increase even further in the coming years.

The scenario that foresees that the concentration of greenhouse gases will double (from 370 ppm to 740 ppm) (11), which might already occur in 2060, in the absence of suitable measures, would lead to an

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[4] a)- high economic and energetic costs, with the possibility that the balance of $CO_2$, in the integrated CCS system may be negative; b)- the need for more detailed experimentation for certain systems of capture and storage; c)- the need to identify the most appropriate sites for the storage of $CO_2$; d)- $CO_2$ transport costs which are not always certain; e)- the existence of a park of efficient rigs, not yet amortised; f)- costs of updating obsolete equipment which are not always certain; g)- the presence of extra working costs.

increase in the average world temperature of 2 – 2.5 °C . The consequences would be the melting of the polar caps and icebergs, a rise in the level of the sea, the disappearance of entire areas and territories, the intensification of catastrophic events in the climate, a reduction in water resources, desertification, the extinction of animal and vegetable species, poverty and famine. Thus the need to control combustion is an objective to be pursued with determination.

For this reason, the political desire to reduce the discharge of greenhouse gases, and in particular $CO_2$, was demonstrated in 1997, in the Kyoto protocol (12).

## The production of goods as a system to reduce $CO_2$

Carbon dioxide is a precious industrial gas with a great number of uses, which include the production of chemical substances (e.g. urea, methanol, polymers such as polyurethanes and polycarbonates (13-14)), refrigeration systems (dry ice), an inert agent in food packages, the production of fizzy drinks, welding systems, fire extinguishers, processes for the treatment of waters, horticulture, calcium carbonate for the paper industry and several other applications.

In particular, there are a number of possible innovative process routes for the production of chemicals and polymers to be considered, in which $CO_2$ is used as a substitute for other chlorine buildings blocks, such as carbon monoxide, methane and methanol. The use of $CO_2$ requires the development of efficient catalytic systems, and in general the use of additional energy for $CO_2$ chemical reduction.

On the one hand, the use of $CO_2$ makes it possible to save non-renewable sources, and in particular to abandon antiquated industrial processes, substituting them with innovative processes which, unlike their predecessors, do not use toxic products like CFCs, phosgene and ethylenic glycol, as reaction blocks in the classic synthetic process of polymers, such as polyurethanes, polycarbonates and polyurea elastomers.

Table 1 summarises these applications, indicating the physical state and the degree of purity that is required from carbon dioxide during the production phase.

Obviously, each application uses appropriate technologies, which are a part of the specificity of the process, and of the product to be realised.

TABLE 1

**LIST OF THE MAIN USES AND INDUSTRIAL APPLICATIONS OF $CO_2$**

| **Products / Processes** | **Purity $CO_2$** | **State** |
|---|---|---|
| Production of urea | > 99.7%. | Gas |
| Production of methanol in processes where CO is not used | > 99.7%. | Gas |
| Production of polymers: polycarbonates, polyurethanes and polyureas) | >99 % | Gas |
| Production of Soda | | |
| (Solvay process) | >99.7% | Gas |
| Production of carbonates and hydrocarbonates of NH4, K and Ba | >99.7% | Gas |
| Increase in production of fuel oil in oil wells: it increases the pressure and favours extraction | < 90 % | Gas |
| Neutralisation of alkaline waste waters | >99% | Gas |
| Carbonation of waters for industrial use: hinders calcareous deposits | >99% | Gas |
| Cleaning of pipes containing inflammable gases | >95% | Gas |
| Movement of liquids that are inflammable or degradable | >99% | Gas |
| Stabilisation and 'inertisation' of stockpiles or freight containing dangerous fluids | >95% | Gas |
| Control of reaction temperature as an intermediate means of removal of heat, in particular in nuclear reactors, seeing that it does not become significantly radioactive | >99.99% | Gas |
| Refrigerating fluid in general | >95% | Liquid |
| Rubber finishing operations: hardening and removal by breaking of possible burrs | >95% | Liquid/ Solid |
| Maintenance of an inert atmosphere during electrical welding (MIG/MAG) | 90% and mixture | |
| He + N | Gas | |
| Hardening of fusion moulds and shapes in smelting processes | >99.7% | Gas |
| Tempering of certain alloys of Al and nickel steels | >99.7% | Gas |
| Cooling of mechanical pieces in the metallurgical industry | 99% | Solid |
| Gas lasers | Pure | Gas |
| Fire-fighting fluid in fire extinguishers | >96% | Gas |
| Refrigeration of food and drinks | >99% | Solid |
| Preservation of foodstuffs | >99.99% | Gas |
| Production of fizzy drinks | >99.7% | Gas |
| Increasing stability in pressurised containers | >96% | Gas |
| Carbonation with magnesium carbonate and serpentine | >90% | Gas |
| Production of vegetable biomasses in greenhouses (horticulture, floriculture, etc.) | >95 % | Gas |
| Production of microalgae in photobioreactors | >95 % | Gas |

Table 1 substantially indicates two kinds of use, as mentioned above: traditional and innovative.

Among the uses of the first kind, $CO_2$ has long been used in controlled-atmosphere packages for the preservation of food products, for the production of dry ice, to obtain decaffeinated coffee and decaffeinated tea, etc. In the drinks industry, it is used in the production of fizzy drinks and aerated mineral water, as well as in the purification of sugary juices and the production of sugar, in wine-making, in the production of fermenting agents and in the transformation of foodstuffs.

Other uses regards the filling of fire extinguishers, the preparation of urea for the production of nitrogenous fertilisers, Solvay soda and baking soda, and the preparation of several intermediate chemical products used to obtain the active principles of drugs, such as salicylic oxide.

In the laser industry, $CO_2$ is used in gas lasers, and in the iron and steel industry, it is used for the production of special steels and in welding; in mining, it is used to improve safety in mines, to remove methane from coal beds, and prevent explosions in mines.

Lastly, the natural systems of capture and storage include the processes of photosynthesis and carbonation of minerals, which have represented extremely significant stages of the $CO_2$ cycle on earth for millions of years.

In these cases, man's intervention adopts suitable actions that increase the speed of these processes to obtain products that are commercially useful, and improve the quantitative efficiency of $CO_2$ storage in biomasses (herbaceous and woody) and in siliceous minerals.

However, although these uses are interesting and may rapidly be introduced, they concern modest quantities compared with the overall anthropic discharge of $CO_2$.

In more recent times, the civilisation of knowledge has added to these uses innovative techniques that include the use of $CO_2$ as a source of carbon in various sectors of the chemical industry.

Particularly important is the substitution of phosgene (a highly toxic gas, used in the past also in wartime) which is used in various industrial processes, such as: the production of dyes, pharmaceutical compounds, perfumery, the synthesis of organic compounds and the production of polymers, such as polyurethane, polycarbonate and polyurea. Besides recycling $CO_2$ and making the chemical reactions less toxic, and safer, this substitution makes it possible to immobilise the gas for several years.

Another industrial possibility is that of obtaining methane and methanol, by means of the reaction of $CO_2$ and hydrogen, with the use of catalysts. In this way, we not only have a useful way of employing carbon dioxide, producing "alternative fuels" which can be used with consolidated technologies, but we also obtain (in the case of methanol) the result of converting hydrogen into a liquid fuel that can easily be transported.

As Table 1 shows, $CO_2$ can also be used to obtain raw materials.

The mineralogical fixation of $CO_2$ (carbonation) represents a storage technique of great potential, proposed for the first time in 1990 (15), but unfortunately little considered so far (16), in spite of the problem of the need to proceed, at the worldwide level, to a decontamination of mining areas, industrial sites, and materials deriving from asbestos products $(Mg,Fe)_7Si_8O_{22}(OH)$.

In this case, the advantages of carbonation are twofold, and they are extremely clear, in view of the danger of the dispersion of asbestos in the environment for man's health.

This technology consists of inducing an exothermic alteration in silicate minerals, which are abundantly present in the earth's crust, e.g.: olivine ($Mg_2SiO_4$), serpentine ($Mg_3Si_2O_5(OH)_4$), wollastonite ($CaSiO_3$). In the presence of a fluid rich in $CO_2$, these minerals are transformed into perfectly stable carbonate minerals, compatible with the environment, such as magnesite ($MgCO_3$), dolomite ($CaMg(CO_3)_2$, calcite ($CaCO_3$), siderite ($FeCO_3$), and dawsonite ($NaAl(CO_3)(OH)_2$.

It may be observed that this carbonation reaction requires low temperatures, and takes place spontaneously in nature, even if it requires long reaction times. However, the use of higher temperatures than those of the environment (150-180 °C) and the use of suitable catalysts at speeds up the reactions. To appreciate the prospects offered by this technology, it may be recalled, for example, that one tonne of olivine can store a quantity of $CO_2$ 65% greater than its own weight, indefinitely.

The products obtained by the sequestration of $CO_2$ are used as raw materials in certain industries, including mainly those of pottery, bricks and cement.

Furthermore, among the uses of $CO_2$ in the process of photosynthesis, it is important to underline the use that can be made of it in agricultural production in greenhouses or in aquaculture, to increase the yield of photosynthesis and the production of biomasses. This is particularly important, above all in industrialised countries, where it is possible to create a synergy between certain industrial processes and agricultural activities (horticulture, nursery gardens, etc.).

Inside photobioreactors, $CO_2$ accelerates the production of microalgae (*Spirulina, Skeletonema, Chlorella, Dunaliella, Isocrisis, etc.*) from which molecules and principles are obtained which have an important economic value: antibiotics, biopesticides, antioxidants, fatty acids, proteins with a high biological value, biopolymers, fertilisers, etc.

It may further be observed that the time for which $CO_2$ remains stored in the products or process is extremely important for environmental purposes. It varies, depending on the life cycle of the products obtained, or the use that is made of them in the industrial process (17).

In this connection, the production of carbon-based liquid fuels deriving from $CO_2$ obviously reduces the discharge of carbon dioxide only if the underlying energy infrastructures do not use fossil energy.

For example, by using hydrogen and $CO_2$ as raw materials for the production of methanol or petrol, we could continue to use these fuels (methanol and petrol) in the transport sector, rather than converting them to hydrogen, pending the success of the relative economy.

In this perspective, hydrogen would be produced from water, using the energy obtained from renewable sources, excluding biomasses, and from nuclear energy, while $CO_2$ would be used as a molecule in the production process of synthetic fuels.

In order to evaluate the effectiveness of storage, it may be helpful to recall the criteria that must be satisfied, so that significant results can be achieved, in line with the requirements of sustainability outlined by the Kyoto Protocol:

a) The industrial use of $CO_2$ must not simply substitute another source of $CO_2$, otherwise there would be no change in $CO_2$ discharge. One particularly qualified example, which involves a permanent storage in the subsoil, is the use of industrial emissions of this gas for introduction into oil fields, so as to increase the recovery of oil.

b) The compounds obtained with $CO_2$ must have a long lifespan before the $CO_2$ is released due to the effects of degradation.

c) Furthermore, for the industrial use of $CO_2$ to be environmentally effective, it is necessary to evaluate the entire process, in terms of $CO_2$. This means determining the effective "net" quantity of $CO_2$ not released into the atmosphere. This happens, for example, when the water source is used instead of fuels or other sources that do not develop $CO_2$.

## The balance between discharge of $CO_2$ and $CO_2$ storage

Table 2 shows the actual duration of the storage of $CO_2$ from the various industrial processes involved. It offers an immediate evaluation of the contributions made by each of the uses proposed to the solution of the environmental problems linked with the greenhouse effect.

Besides indicating the duration of productive cycles and the lifespan of products, which vary from months to centuries (column 5), the table also supplies data regarding the quantitative dimensions of markets and the quantities of $CO_2$ stored in the relative productions, together with the type of source of $CO_2$ used, which may obviously also be natural.

TABLE 2

**PERIOD OF FIXATION OF CO2 BY CLASSES OF PRODUCTS AND INDUSTRIAL APPLICATIONS (18)**

| **Class of chemical products or application** | **Annual market (Mt/year)** | **$CO_2$ used in chemical products or applications (Mt $CO_2$)** | **Source of $CO_2$ used (a)** | **Average lifespan of products of $CO_2$ storage (b)** |
|---|---|---|---|---|
| Urea | 90 | 65 | Industrial | 6 months |
| Methanol | | | | |
| ($CO_2$+ CO) | 24 | < 8 | Industrial | 6 months |
| Inorganic Carbonates | 8 | 3 | Industrial-Natural | From decades to centuries |
| Polyurethanes | | | | |
| Polycarbonates Elastomers | 10 | < 10 | Industrial-Natural | From decades to centuries |
| Technological | 10 | 10 | Industrial-Natural | From decades to centuries |
| Alimentary | 8 | 8 | Industrial-Natural | From months to years |
| | | | | |

(a) – The natural origins include both geological sources and fermentations
(b) – Period of time in which the $CO_2$ fraction is used, until its complete release

As mentioned above (in §2), the quantity of $CO_2$ from anthropic sources corresponds to about 25 Gton/year, whereas natural cycles absorb only about one half; consequently, based on the present storage quantities connected with the different industrial uses (table 2), the storage is in the order of 0.5% of these 25 Gton/year, that is to say, about 1% of the portion not absorbed naturally. Obviously, this percentage may vary annually, upwards or downwards, depending on the situations imposed by the market.

## Conclusions

This is a modest quantity. However, this industrial use of $CO_2$ must not be underestimated, since it not only creates economic value (processes, products and goods), but can also be united in synergy with other measures, such as recourse to a greater energetic efficiency of anthropic processes, the energy saving of fossil fuels, the use of inorganic renewable sources, nuclear energy, etc. It may further be observed, for the purposes of a greater recovery of $CO_2$, that the present scenario of global economic crisis is particularly favourable, because it imposes the adoption of measures to reorganise the industrial system, in the light of the need to contrast the discharge of greenhouse gases, as required internationally by the Kyoto protocol. Obviously, the possibilities described depend on the energy policies and industrial policies that Governments, especially of industrialized countries, choose to pursue.

Taking advantage of the opportunity offered by the worldwide economic crisis that we are going through means exploiting the chance to reconvert and innovate industrial processes that are obsolete, or at least no longer in line with the needs of sustainability which humanity is increasingly interested in pursuing.

The above structural changes to industrial processes would offer advantages for enterprises, for the environment and for society as a whole, already in the short-medium term.

All this would especially be true if the use of $CO_2$ allowed the elimination of toxic waste products, the reclamation of territories where contaminating materials are present (for example, asbestos products) and the substitution of dangerous processes (for example, the substitution of phosgene). This would favour the possibility of reorganising the chemical industry from the point of view of $CO_2$.

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