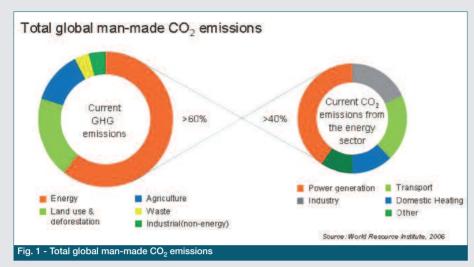
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Mario Marchionna eni spa mario.vito.marchionnani@eni.it

CCS TECHNOLOGY IN THE OIL&GAS INDUSTRY

The need to satisfy growing energy demand goes together with the need to tackle the risks to the climate related to increased CO_2 production. One of the solutions is the CO_2 Capture and Storage (CCS) technology, used to geologically sequester CO_2 generated by fossil fuels, especially from large-point source emitters.

ossil fuels (oil, gas and coal) are the most widely used energy sources today, accounting for more than 80% of worldwide energy consumption. Their undisputed leadership is however related to the issue of carbon dioxide (CO₂) emissions into the atmosphere, regarded as one of the main causes for climate change. Sixty per cent of the CO₂ produced by mankind originates from combustion of fossil fuels, which consequently is not the only activity that produces CO₂ (Fig. 1). Thus the need to satisfy growing world demand for energy, among the emerging economies in particular, goes hand in hand with the need to tackle the risks to the climate stemming from increased production of CO2. The first solution, and the most immediately practicable approach in the short term, is energy efficiency: i.e., measures, attitudes and technologies that help reduce consumption. Another possible solution is to use alternative energy sources, which play a relatively modest role so far. Biomass and related materials (woody substances, various types of waste) cover about 10% of our total energy requirement, a percentage that will remain about steady. This situation seems similar in nuclear energy, which, together with hydroelectric power, covers about 8% of the total requirement. Use of other renewable energy sources (wind and solar energy) is increasing a lot, but currently satisfies about 1-2% of the earth's energy requirement. In other words, fossil fuels will continue to dominate the world energy sector for decades to come. Thus, in order to achieve a signif-

icant reduction in $\rm CO_2$ emissions just over the long term direct action must be taken also on the use of these sources.

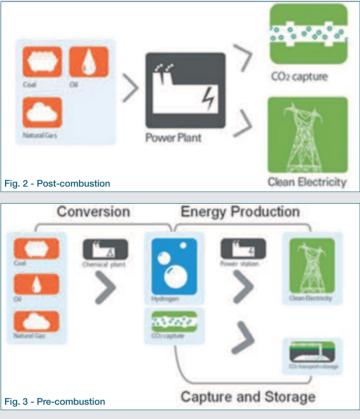
A switch between coal/oil and gas could be beneficial to reduce CO_2 emissions, at least as regards power generation; the presence of abundant reserves of natural gas, also unconventional as in the case of shale and tight gas, makes the use of gas really elective in the near-medium term as clean energy source. In the long term, a further alternative can be represented by CO_2 Capture and Storage (CCS) technology, used to sequester CO_2 generated by fossil fuels, thereby reducing emissions into the atmosphere.

The geological storage of carbon dioxide may enable real progress in the global effort to make meaningful reductions in CO_2 emissions especially from large-point source emitters such as power plants, refineries, cement plants and steel mills. Of course, CCS is not a panacea, there are several issues that need to be addressed before it can achieve a widespread application, but it does offer a tangible mean to deal with large volumes of gas emissions by using technologies already in-hand, and improving them.

CCS Technology

Typically, CCS is defined as the integrated process of gas separation at industrial plants (capture), transportation to storage sites and injection into subsurface formations.





Capture

The CCS process starts by capturing the CO_2 generated by power stations and large industrial processes (like cement factories, steel works and oil refineries) both before, during or after burning fossil fuels. These technological processes are already widely used to provide CO_2 for a variety of industries including the fertilizer and food and beverage industries. In general, capture technology can cut the CO_2 emissions by up to 95% offering huge CO_2 mitigation potential.

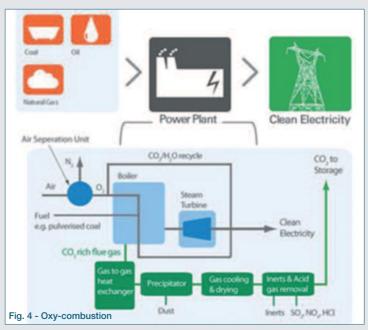
There are three main approaches to CO_2 capture that can be applied to a variety of industrial processes:

- *Post-combustion* (Fig. 2): separating the CO₂ from flue (exhaust) gases produced after burning fossil fuels in the air. The small volume of CO₂ in the flue gas (ranging from 3-15% by volume) is captured by dissolving the CO₂ into a liquid solvent such as amines, a class of organic chemical compounds. This technique is already applied to provide the CO₂ used in the food and beverage industry (for lemonade, beer and food preservation) and as a feedstock for fertilizer manufacturing, and can be retrofitted to existing power plants and industrial processes such as cement production, as well as integrated into new built facilities;
- Pre-combustion: separating fossil fuels into hydrogen and carbon dioxide before they are burnt. For instance for coal, the process involves converting coal into a synthetic gas comprising carbon monoxide and hydrogen. This gasification process was invented in 1794 and was used to make the "town-gas" used to light cities before natural gas was discovered and electricity became preferred.

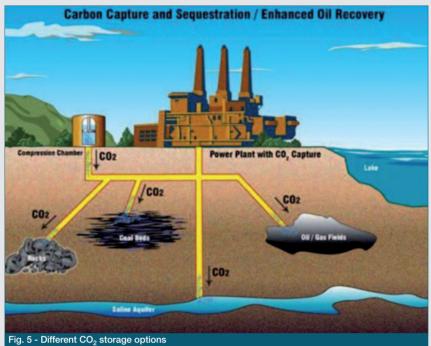
This "syngas" can be reacted again with steam to produce a mix of CO_2 and hydrogen - passing the mixed gas through a catalytic reactor under high pressure - in a process called "water-gas shifting". This process produces high concentrations of CO_2 (35-45%) that can then be captured. The resulting hydrogen can then become the energy source used to generate CO_2 -free electricity because when burnt, it produces only heat and water vapor. Pre-combustion capture technology is well established in the fertilizer industry and natural gas reforming, which uses similar technology, has been widely applied in the refining and chemicals industries. This approach, while more complex and consequently more expensive than those involved in post-combustion, are proved and effective at scale and could be cost-effectively used to make large amounts of clean hydrogen for the power industry as well as in refineries and other chemical plants (Fig. 3):

- Oxy-fuel combustion: burning the fossil fuel in oxygen instead of air results in an exhaust gas consisting only of concentrated CO₂ and water vapor. The CO₂ - typically greater than 80% by volume - is then far more easily captured when the water vapor is removed by cooling and compressing the gas stream. Oxy-fuel combustion systems have already been commercially applied in the glass furnace industry, while application to CO₂ capture is now approaching the demonstration stage. They show interesting possibilities for boilers and gas turbines systems and would largely be applied in the power industry (Fig. 4).

All of the three approaches to CO_2 capture in industrial processes rely on gas separation technologies. There are three basic methods of separating gases from each - solvent/sorbents (roll-over), membranes (roll-over) and cryogenic distillation (roll-over) - which can be applied as technologically appropriate to the above three capture approaches. Each of the three approaches to capture the CO_2 produced from the use of fossil fuels as well as the gas separation technologies are fea-



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sible, safe and well understood in terms of the fundamental science and the expertise needed to carry it out. The challenge lies primarily in developing and deploying these processes cost-effectively on a sufficiently large scale. At this time, undertaking power generation with CO_2 capture is necessarily more expensive than traditional systems the often-described "energy penalty" of 10-40%, resulting in higher electricity prices although the specifics vary depending on the plant type (size, age, fuel-type, existing efficiency rates etc).

Transportation

Among the several ways to transport carbon dioxide existing or proposed:

- trucks;
- rail cars;
- pipeline transportation;
- ships.

The only option able to assure a continuous, 24-hours/365-days service, without any storage, flow from the production site to the final sequestration appears to be the pipeline link. It also copes with reduced environmental footprint.

Storage

When CO_2 is stored, it is injected into the pore space of rocks deep in the earth's subsurface (at depths typically greater than 1,000 meters) and carefully designed operational protocols are observed to provide for safe operations. Once the CO_2 is safely injected in the ground, it is expected to remain there for a geological period of time.

Depleted hydrocarbon fields and saline aquifers (deep layers of waterbearing materials with an enormous CO_2 absorption capacity) are suitable deposits for permanent geological sequestration of carbon dioxide. In depleted oil or gas fields, the CO₂ penetrates the pores in which the hydrocarbons were trapped; if significant amounts of hydrocarbons are still present, injection of CO₂ may actually assist oil and gas production (Enhanced Oil Recovery and Enhanced Gas Recovery processes - EOR and EGR) (Fig. 5).

Eventually, CCS may be implemented at power generation facilities that use waste biomass feedstock. This scenario offers the prospect of generating power and taking net CO₂ out of the air at the same time. Large commercial-scale CCS projects are rare today because the basic business fundamentals are lacking. In most jurisdictions, it is not yet legal to carry out CCS, with the exception of EOR operations (where CCS processes have been used for years). However, several jurisdictions around the world are on the way to assemble the required legal and regulatory frameworks to enable CCS by amending existing regulations and creating new ones. Industry already has the technology, skills and capabilities to execute industrial-scale CCS projects, and the commercial reason to deploy the technology

looks next to materialize (especially when the CO_2 price will eventually increase). Along with the role of CCS as a long-term option to improve the sustainability of energy production in terms of impact on the climate and the environment, *eni* considers at the same time the development of CO_2 injection activities in hydrocarbon fields as an important option to enhance the Oil & Gas recovery rate (where the formation of the field permits this). In this case, too, the most of the CO_2 remains permanently stored in the reservoir. Actually, CCS is an enabling technology to increase oil production via EOR, natural gas production through EGR or monetization of CO_2 -rich Natural Gas assets. Also in the case of natural gas storage, the use of CO_2 as "cushion gas" could be attractive to allow an increased gas usage.

eni's activities

In the following, the main activities of eni will be briefly described.

The CO₂ Capture Project (CCP)

Since 2001, *eni* has been member of the international CCP consortium (www.co2captureproject.org), together with most of the oil majors. The CCP is a unique collaborative technology development program initiated in 2000 with participants from corporations, academia, governments, research institutions, policy makers and individual contractors who have come together to advance development of new approaches to capture and store CO_2 and improve efficiencies of existing technologies. The overall objectives are to deliver major cost reductions for carbon capture and demonstrate geological storage is safe, measurable, and verifiable. Phase 3 of the CO_2 Capture Project began in 2009 and is continuing support of R&D work for capture and storage technologies at multiple levels of development, from exploratory research to demonstration [1]. Different scenarios for application have been selected by the Phase 3 member companies:

- steam production for extraction of heavy oils / tar sands;
- Natural Gas Combined Cycle for power production;
- oil refinery (capture from process heaters, fluid catalytic cracking, hydrogen plants).

New scenarios for cost analyses are being developed (post-combustion and, where applicable, pre-combustion and oxy-firing) and will serve as the basis for comparison of the capture technologies under development. As example, demonstration of the next generation technologies being developed by CCP is a key aspect of the project and at least two technologies are planned for demonstration in the Phase 3 timeframe [2]:

- the regenerator of a large pilot Fluid Catalytic Cracking (FCC) unit in a Brazilian refinery run by Petrobras has been retrofit to oxy-firing with CO₂ recycle. The demonstration was carried out with success through the second half 2011 and the first half 2012 [3];
- the retrofit to oxy-firing of a commercial Once Through Steam Generator used in tar sands extraction operations in Canada is scheduled for 2013.

As regards storage technology, CCP3's Storage Monitoring and Verification (SMV) program is focusing on key assurance issues and field trialing of monitoring technologies.

The eni/Enel Alliance

In October 2008, *eni* and Enel signed a Strategic Cooperation Agreement to increase knowledge for CO_2 capture, transport and geological sequestration technologies and to accelerate the deployment of CCS. The main goals of the cooperation program are:

- to realize the first integrated pilot project in Italy, combining Enel's CO₂ post-combustion capture pilot plant at the Brindisi coal fired power station and the *eni*'s pilot CO₂ injection project in an exhausted gas field at Cortemaggiore;
- to carry out a feasibility study for the realization of a large scale integrated CCS demo plant for an Enel's clean coal power station;

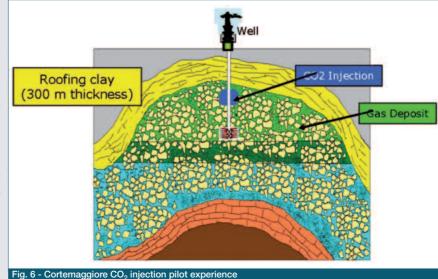
- to jointly evaluate the CO₂ storage potential in Italy. As regards the integrated pilot project, the CO₂ comes from the Enel's post-combustion capture pilot plant in Brindisi (10,000 m³/h flue gases) who separates about 5,000 ton CO₂/y; the pilot plant is in operation since the beginning of 2011, a CO₂ liquefaction and cryogenic storage system is being realized in Brindisi treating the CO₂ produced by the pilot capture plant, then the carbon dioxide will be transported to the Cortemaggiore injection site via trucks where it will be injected together with some other CO₂ acquired directly from the market.

The Cortemaggiore CO_2 injection project The CO_2 injection project in Cortemaggiore, a depleted natural gas storage field, represents the very first pilot project in Italy, aimed to verify on the field the behaviour and interaction of carbon dioxide with all the components of the injection system: reservoir, cap rock, wells and downhole equipment (Fig. 6).

The project consists in the injection of 24,000 tons CO_2 for maximum throughout 3 years, in a sand level at 1,500 m depth, used for natural gas storage since more than 40 years and therefore considered suitable and safe to confine CO_2 .

The specific objectives of the test are a field test verification of the forecasted behaviour of injected CO_2 (e.g. plume evolution, pressure changes, injectivity), the definition of a methodology (both technical and authorization issues) for CO_2 injection and the exploration of the opportunity of CO_2 as substitute of "cushion gas" as a long term option. A lot of internal studies outline the possibility to perform the pilot test under very safe conditions, ensuring the integrity of the reservoir/well/surface plant system, of the environment and of the anthropic system. With the aim to guarantee all these conditions, a monitoring plan has been provided before, during and after the realisation of the project. Baseline monitoring was already initiated since 2010.

Given the strategic relevance of the project, the authorization process has been joined with an information campaign, both at local and regional level, with the aim of obtaining that "public acceptance" necessary to avoid territorial contrasts and opposition to the project. Public meetings also with town halls, provincial and regional technicians have been useful to reach a more positive "climate" with local administrations and provided all the elements to clean out the major doubts related to the safety of the plant, to the integrity of the reservoir and to possible accident risks, during both transport and the injection phase. The project, after achieving positive opinion by the Ministry of Economic Development, obtained in 2011 the authorization of environmental impact by the Ministries of Environment and Cultural Heritage and last April an agreement was reached with all the local parties involved (municipalities, province, Emilia Romagna region...): first CO_2 injection should be forecast for the end of 2013.



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eni transportation activities

As CO_2 transportation is a mature technology, *eni*'s approach is mostly aimed to get a large acceptance from authorities/regulators and achieve fine tuning on existing know how. As a result, *eni* is participating in a few consortia, focusing on specific issues, i.e. addressing the risks of large CO_2 releases and other specific issues as the effect of CO_2 impurities on pipeline integrity.

Otherwise, in the frame of the *eni/*Enel cooperation, the two companies have also completed a feasibility study to evaluate the realization of a pilot pipeline loop to study a few selected and specific experimental issues regarding CO_2 transportation, as the validation of design models (both stationary and dynamic) and the optimization of operating conditions.

eni demo activities

Finally, *eni* has carried out advanced feasibility studies to develop demo industrial experience. Two real cases are under development: the former is related to a CO_2 -rich gas field asset where enhanced gas production can be achieved through CO_2 capture and re-injection; the latter has been recently initiated and is related to an EOR experience on heavy oil fields, in the area of Gela, Sicily, where 70,000 t/y of CO_2 captured from the refinery emissions of Gela's refinery will be transported to the site, far only about 15 km from the refinery, and injected to increase oil production and at the same time definitely stored.

In conclusion, *eni* is progressing in a solid technical program to exploit CCS technology in different scenarios of interest.

We believe that, towards an industrial application, pilot and demo projects are strongly needed to mature experience and demonstrate cost reduction potential (especially on the capture technology). At the same time, "public acceptance" issues and a sound authorization and regulatory framework will be key ingredients of the overall figure.

For sure, especially in this period of economic crisis, EOR/EGR activities may play an auxiliary role in helping to bring to scale the CCS technology.

References

- M. Crombie, S. Imbus, I. Miracca, *Energy Procedia*, 2009, 1(1), 55.
- [2] I. Miracca, Hydrocarbon World, 2011, 6(2), 6.

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[3] Petroleum Review, July 2011, 32.

La tecnologia CCS nell'industria Oil&Gas

La tecnologia CCS (CO₂ Capture and Storage) è una delle soluzioni per cercare di risolvere il problema di coniugare maggiori consumi di energia senza influire eccessivamente sul clima tramite accresciute emissioni di CO₂. La CO₂, generata da fonti fossili, viene geologicamente sequestrata nel sottosuolo dopo essere stata catturata da impianti di grande scala.

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- D.W. Breck, Zeolite Molecular Sieves, J. Wiley, New York, 1974, 320.
- [2] R.D. Shannon, Acta Crystallogr., 1976, **32**, 751.
- [3] U.S. Pat. 4.410.501, 1983.
- [4] Chemical Marketing Reporter, Schnell Publ. Co. Inc. (Ed.), June 15, 1992.
- [5] G. Perego *et al.*, Proceedings of 7th Int. Conf. on Zeolites, Tokyo, 1986, Tonk Kodansha, Elsevier, Amsterdam, 129.

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