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A review of the basic safety requirements of emerging infrastructures for Green Transition

Paolo Mocellin*, Chiara Vianello

Università degli Studi di Padova, Dipartimento di Ingegneria Industriale, Via Marzolo 9, 35131 Padova (Italia)
paolo.mocellin@unipd.it

The transition to a Climate-Neutral economy requires a reduction of energy-related carbon dioxide emissions and Carbon dioxide capture and geological storage (CCS) is a key technology that will contribute to mitigating climate change. Hazards and risks related to processing, transport, and storage of CO_2 are not new aspects, but peculiarities of CO_2 safety scenarios can lead to risk underestimation and misperception. Solid-phase occurrence and heavy gas dispersion, multiphase releases, leakages from wells and storage sites, and the integrity of equipment subjected to internal corrosion and cryogenic temperatures, are typical scenarios involved in CCS chains. These are often mentioned in technical standards and regulations and require proper advanced assessment. In this work, the main hazards and risk scenarios in CCS operations with a special focus on atypical instances that are peculiar to the case of CO_2 will be reviewed. Open issues concerning the modeling of consequences and specific risk-related topics are discussed.

1. The context of a safe Green Transition

The European Union is committed to becoming the first climate-neutral bloc in the world by 2050 (European Commission, 2019). Significant investments in the national public sector, as well as in the private context, are required to effectively contribute to the transition challenges to a Climate-Neutral and Circular Economy. The ambitious target is to transform the fossil-based global energy sector into a zero-carbon framework, via reducing energy-related CO_2 emissions and improving energy-efficient solutions to limit climate change. In this sense, the European Green Deal provides an action plan to boost the efficient use of resources by moving to a clean circular economy and this target requires actions on all sectors of the economy including: investing in environmentally-friendly innovative technologies, decarbonizing the energy sector, rolling out cleaner and cheaper transport forms and improving global environmental standards (IPCC, 2005).

In March 2020, the EU has adopted an industrial strategy that will support the green transformation to enhance the modernization and exploitation of new opportunities for decarbonization. This topic has been identified as crucial in the framework of envisaging global reduction of greenhouse gas emissions of 50 % by 2050. Within the Climate Change program, the Carbon dioxide capture and geological storage (CCS) is a bridging technology that will contribute to mitigating climate change, as stated by the EU Directive 2009/31/EC. It consists of the capture of carbon dioxide (CO_2) from energy-intensive industrial installations, its transport to a storage site, and its injection to a suitable underground geological formation for permanent storage (Raza et al., 2019). It emerges that 7 Mton of CO2 could be stored by 2020, and up to 160 Mton by 2030, that is the CO_2 emission avoided in 2030 via CCS could account for some 15 % of the reductions required in the EU (G.C. Institute, 2020). These targets are feasible if CCS proves to be even an environmentally safe technology, deployed in an environmentally safe way. The declared purpose is to eliminate as far as possible, or at least control and reduce, negative effects and any risk to the environment and human health related to the implementation of CCS solutions.

In this work, we reviewed and systematized the basic and crucial safety requirements that apply to the CCS technology, along with good practices. We discussed peculiarities related to risk assessment and management related to carbon sequestration infrastructures via a framework analysis of main operations, substances adopted, and operational issues.

2. Safety issues in CO2 capture and geological storage (CCS)

Like any other industrial technology, safety studies are indispensable in the sizing, operation, and dismission of CCS chains. In this way, adequate safety measures are identified and appropriately incorporated into design and operation, also representing an input to decision-making.

Each CCS step, namely capture, transport, and storage of CO_2 is affected by safety concerns that originate from a variety of causes mainly related to substances, equipment, and process operations (Table 1).

Table 1: Hazards related to CCS steps of CO_2 capture, transportation, and storage.

Step	Hazards
CO_2 capture	Substances (sorbents, fuels, range of amines, large inventories of oxygen, …) Equipment (amine absorption and separation columns, air separation units (ASUs) even cryogenic, …) Process operations (amine absorption and separation, acid gas removal, shift conversion, CO2 purification)
CO_2 (pipeline) transportation	Substances (high-pressure dense phase CO_2, hydrates, impurities) Equipment (booster stations, compressors, metering, high-pressure pipelines) Process operations (pumping, compression)
CO_2 storage	Substances (elevated CO2 concentrations, dissolved CO2, formation fluids) Equipment (injection operations, storage site closure, post-closure step) Process operations (injection rate, geological pathways, fluids mobilization, leakage)

The most abundant substance in CCS operations, namely the CO_2, has peculiar safety specificities that emerge in intrinsically and extrinsically risk scenarios and that are listed in Tables 2 and 3.

In a general framework, facilities and equipment dedicated for the corresponding capture, transportation, and storage technologies are designed and constructed according to applicable international, regional, and national standards, and also according to specific company standards (Energy Institute, 2010). Different standards and regulations can be applied in the case of CCS, e.g. ISO TR 27912:2016 (capture systems, technologies, and processes), BS ISO 27913:2016 (pipeline transportation systems), BS ISO 27914:2017 (geological storage), BS ISO 27916:2019 (CO_2-EOR). Recommended practice DNV-RP-J202 also deals with design and operation of CO_2 pipelines, with specific references to pipeline standards ISO 13623, DNV-OS-F101, and ASME B31.4 along with cross-links to other references, codes, and standard of API, ASME, CSA, IEC, NACE, NORSOK, and PHMSA. Also, primary instruction manuals and guidelines related to CCS are available (EPA Guidelines, DOE/NETL BPM series, CSA CCS international standardization, ENV Guidelines for applying offshore CO2 storage).

Table 2: Comparison between natural gas/oil and CO_2 properties critical for safety.

Feature	Natural gas	Oil	CO2
Colorless	Yes	No	Yes
Odorless	Yes	No	Yes
Transport in liquid form	Yes	Yes	Yes
Flammable	Yes	Yes	No
Toxic or asphyxiant	Yes	Yes	Yes
Heavier gas/vapor behavior	No	No	Yes

Table 3: CO_2 properties and related risk scenarios.

Property	Risk scenario
Asphyxiant, odorless	Harmful to human targets, oxygen displacing
Heavy gas	Accumulation in low-lying areas in the case of a release
Corrosion	Formation of corrosive acid solutions when mixed with water, degradation of sealing
Supercritical state	Almost zero viscosity and surface tension enhance sealing challenges

2.1 Carbon capture and hazardous substances

Safety issues related to the carbon sequestration chain vary according to the capture processes and chemicals involved in steps of Table 1 (IPCC, 2005). Some leading examples are related to ammonia, amine solutions, and nitrosamines that can cause injury and toxicity. The CO_2 itself has toxicity related to the asphyxiating feature increasing with concentration. For instance, the LTEL at TWA of 8 is 0.5 %, whereas the STEL at 15 min is 1.5 %. Specific safety measures should be put in place to ensure these limits are observed when operating a CO_2

capture and handling system (Engebo et al., 2013). Despite the non-flammability of CO_2, pure components of aqueous solutions of ammonia and amines used in the capture step have low boiling points and high auto-ignition temperatures. However, flammability-related risks are reduced or solved when aqueous solutions are used if the concentration level is kept below a certain level.

Specific equipment and behaviors of the CCS chain are believed to pose safety risks. This has been documented for pre-scrubbers for SO_2 abatement and amine absorbers where side degradation reactions may sustain the formation and accumulation of ammonia, aldehydes amines, and polymeric materials, along with acids and nitrosamines that can accumulate in the absorbents or accidentally emitted. When dealing with safety studies applied to CCS, different chemical substances should be subjected to safety considerations. For example, compounds that may be present in emissions from a capture unit with amines include amine-based solvents, amines, amides, aldehydes, alcohols, acids, nitrosamines. To these are added acid gases (SO_x, NO_x, CO_2), heavy metals, anhydrous ammonia, sulfuric acid. In the case of CO_2 compressors, large amounts of highly concentrated CO_2 can be released during normal operation or emergency shutdowns. Mechanical malfunctions or additional incidents can induce similar scenarios. Countermeasures need to be established in case high-pressure CO_2 is released since freezing and blockage can occur.

2.2 Transportation in CCS and CO_2 pipelines

According to actual best available techniques, pipelines are likely to be the primary means of transporting CO_2 from the point of capture to storage (Lu et al., 2020). In the case of handling CO_2, there is a general perception that transporting it via pipelines does not represent a significant barrier to implementing large-scale CCS projects. Nevertheless, there is significantly less industry experience than oil and gas services, and several issues need to be properly addressed and the associated risks effectively managed (Barrie et al., 2005). In dealing with CCS pipelines, there is still a lack of statistical data relevant to CO_2 pipelines, and different design and operational criteria may not accurately reflect the appropriate situation of CO_2 (e.g. criteria of natural gas pipelines). Failure statistics for both onshore and offshore facilities are considered separately and are generally based on historical incident data from other relevant pipeline systems. Within a safety philosophy applied to the design and operation of CO_2 pipelines, the main issues to be carefully included and quantified are:

- internal failure mechanisms related to corrosion, acid stream dew point and water content,
- pressure control and overpressure protection systems,
- flow assurance, avoiding multiphase flows,
- thermal insulation and leak detection,
- pipeline layout and routing, economic and risk-based optimization,
- accidental risk scenarios and context analysis (topography, population density).

The composition of CO_2 streams in pipelines depends on the CO_2 source and the capture technology, in general, several impurities may be present (O_2, H_2O, N_2, H_2, SO_X, NO_X, H_2S, HCN, COS, NH_3, amines, aldehydes). Impurities have impacts on the thermodynamic and transport properties of the CO_2 stream, which are usually hard to be correctly defined (Mocellin and Maschio, 2016). Besides, impurities act critically on corrosion mechanisms (Choi et al., 2010). Avoiding the formation of corrosive phases and solids in pipelines is essential for safe operation and safety studies should deal with such an occurrence (Mocellin et al., 2018). The same applies to the presence of components that enhance the formation of an aqueous phase since proper CO_2 dehydration is essential for corrosion control and to reduce the potential for hydrate formation. For carbon steel pipelines, internal corrosion is a significant risk for pipeline integrity, and free water combined with CO_2 may induce high corrosion rates, primarily due to the formation of carbonic acid (King, 1985).

2.3 Geological storage in CCS

According to EU Directive 2009/31/EC, an environmentally safe geological storage of CO_2 should be guaranteed with the prevention or the elimination, as far as possible, of negative effects and any risk to the environment and human health. Safety and security issues should be addressed in the selection, exploration, operation, closure, and post-closure of storage sites. In this sense, the context in which the geological storage system is inserted should be identified and characterized by a risk management plan. This includes the identification of threats and related risk scenarios, the assessment of resources that could be affected by CO_2 injection operations (biosphere, geological and economic context), the identification of interdependencies and cascading effects, and tailoring of novelties and specificities related to the specific storage project.

General applied criteria and issue for the identification of threats during CO_2 injection and storage are:

- assessment of sufficient capacity and injectivity of the geological site,
- analysis of the long-term containment, prevention of relevant leakages,
- seismic issues and earth deformation processes that may lead to adverse impacts,
- feasibility assessment of modeling and cost-effective monitoring, and criteria for the site closure,

- implementation and monitoring of operational safety and environmental protection procedures, avoiding impacts to health, safety, and the environment.

In this framework, the infrastructure design shall facilitate safe and effective CO_2 storage, and all injection site activities shall be performed in such a way as to minimize environmental impacts and to avoid groundwater contamination (Jiang, 2007). As an example, the website and the design of the well should be assessed according to different safety parameters to avoid damages to the infrastructure and the geological formation that may lead to CO_2 loss of containment and environmental contamination. Hazard characterization includes the consideration of potential leakage pathways, the magnitude of leakages, analysis of critical parameters that affect the leakage, and the assessment of secondary effects of storing CO_2. The monitoring activity, during injection operations and in the long-term horizon of the post-closure of the well, includes the follow-up of fugitive emissions, static and dynamic parameters of the wellheads, the composition of injected material, and reservoir temperature and pressure.

3. Specific aspects of modeling CO_2 risk scenarios and consequences

In the CCS framework, an overall safety objective should be established, planned, and implemented, covering all phases from conceptual development until post-closure and abandonment of a CCS project.

The risk assessment and management, as well as the HazId, MAHs (Major Accident Hazards) categorization, and risk reduction practices are usually referenced and provided by international standards, regional and national standards, also according to company standards. Despite CO_2 is listed as Category C fluid according to ISO 13623:2017, the CO_2 exhibits specific aspects related to safety assessment (IEA, 2010), including:

- human impact to acute inhalation of CO_2 and occupational exposure limits for CO2,
- health effects of CO_2 composition with other chemical components,
- accidental release of CO_2 and release rates,
- dispersion modeling, environmental impact.

Many references list several hazards and potential major accidents linked to parts of the CCS chain, including Top Events like losses of containment of CO_2, oxygen or toxics, explosions, and fires (Vianello et al., 2016). What emerges is that risk and safety studies are indispensable

A crucial issue in modeling risks of CCS chain concerns the modeling and validation of source terms and dispersion for potential major (controlled and uncontrolled) releases from CO_2 infrastructures, to inform layout and safeguards, and to demonstrate safety. Several projects have dealt with the formulation of good practices and guidelines like the EC FP7 CO2PipeHaz project specifically focused on CO_2 pipeline safety.

CO_2 differs from the decompression of hydrocarbons because the release can appear as a combination of different CO_2 aggregation states with the potential for phase changes within the flow expansion region. Typical of a CO_2 source term is the occurrence of a two-, even three-phase release driven by peculiarities in the thermodynamic behavior of CO_2 in which liquid, vaporous and solid CO_2 are formed. The triple point of CO_2 is (216.5 K, 5.11 atm) and the atmospheric sublimation point (solid-vapor equilibrium) is at 194 K. Estimated hazards ranges are very sensitive to source model assumptions and details, and the CO_2 case should also incorporate the sublimating bank scenario that may represent a secondary delayed source term under specific conditions (Vianello et al., 2014; Mocellin et al., 2015). In Fig. 1 an overview of the CO_2 source term is given, where the investigation for conditions of solid CO_2 occurrence is part of the process. This topic is also of interest for controlled pipeline depressurization whereas any solid components in the CO_2 inventory can impart erosive properties to the release stream (Mocellin et al., 2019). According to ISO 27913:2016, the thermo-hydraulic model applied to pipeline design should, as a minimum, accounts for two-phase single and multi-component fluid, and steady-state conditions. Heavy CO_2 gas dispersion should be carefully addressed whereas larger effects related to the solid phase appearance are expected in the case of large leaks and full-bore ruptures (Mocellin et al., 2016b). The effect related to the sublimation of cold vapor from the bank surface needs to be considered within the modeling if conditions are suitable for solid-phase appearance (Mocellin et al., 2016c).

A topical aspect of risk assessment is related to CO_2 stratification that is significantly influenced by ground topography, obstacles, and wind direction. In the case of CO_2, likewise, cryogenics and subcooled releases, detailed assessment studies based on advanced dispersion tools and computational fluid dynamics (CFD) may be required to give reliable estimations of exposure of people to the asphyxiant CO_2. Effects related to release inventory, environmental local conditions, surface roughness, and topography, and impurities should be considered when dealing with CO_2 dispersion. Many dispersion models that can be applied to the case of CO_2 still require further validation, especially in CCS large-scale applications (Kaufmann, 2011). It should be noted that a good dispersion study is crucial for emergency planning of CCS transportation infrastructures, which in turn is affected by model uncertainties related to the source term and consequences. The layout in CCS facilities and the routing of pipelines are key aspects to be considered (Knoope et al., 2013).

Also, releases from underground pipelines require a specific modeling approach given that the dispersion process is reduced, and hazardous distances increase.

Within the geological storage step, a safety and security plan according to ISO 27914:2017 should encompass scenarios resulting from CO_2 migration and releases that may have a role in both environmental and safety issues. A proper CO_2 dispersion and effect modeling is required for the analysis of gas-phase CO_2 concentrations above a storage complex and in near-surface environments to reliably need the impact on human and environmental safety.

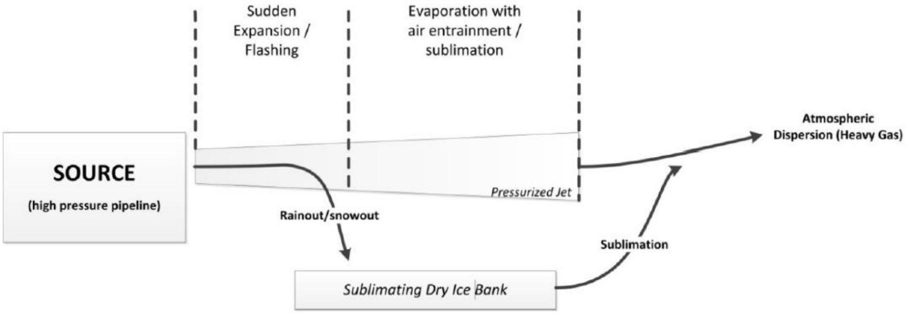

Figure 1: Typical source term components within a CO_2 release framework (adapted from Mocellin et al., 2016a).

4. Integrity and routing of CCS infrastructures

The integrity of equipment, transport infrastructure, and storage well are relevant aspects included even in the European directive that applies to the Carbon Sequestration. All relevant causes that may adversely affect the integrity have to be identified and treated. Many substances listed in section 2 may have an impact on the integrity of capture equipment, especially in the case of a high concentration of acidic gases. Acid gas removal and particular control are essential to maintain the integrity of fans, ducting, and other equipment. Low-temperature operations and corrosion alter the equipment integrity as well, especially in the oxyfuel capture method where high SO_2/SO_3 and moisture content increase the dew point temperature possibly leading to sulphuric acid condensation. Impurities can negatively affect pipeline integrity through local corrosive mechanisms and limitations on the maximum levels of impurities apply within the CO_2 stream. Safety and integrity implications are strictly correlated and an IMP (integrity management plan) is crucial in managing CO_2-specific threats and consequences. A successful IMP includes design parameters correlated to the peculiar CO2 behavior (phase envelope, corrosion allowances), residual water, manufacturing, and operational anomalies. Moreover, operational data like water and impurities content, hydraulic and thermal profiles of the CO_2 flow and depressurization history are synthesized are used to support the IMP.

Casing, tubing, and packer integrity are checked and treated concerning the geological storage. Reparations are operated once required according to detected CO2 loss of containment or unintended flows. Periodic inspections and integrity tests during injection operations are due to evaluate cement integrity, corrosion effects, and gas saturation in the well. The same procedure has to be performed also in the abandonment step to best manage the well overall integrity. Pipeline safety is an essential consideration in routing selection, alongside other aspects, such as the economy. Therefore a coupled safety and economic optimization may be required (d'Amore et al., 2018). The route is determined by the source and destination of CO_2 and sets the pipeline length, the operative conditions, and materials. The long-distance piping system crosses different areas and risk scenarios should be treated accordingly, especially in special areas. These include highly-populated and urban areas, land covered areas, sensitive areas, linear features (rivers, highways/railways), and deepwater (Serpa et al., 2011). The deterioration and loss of integrity of the CO_2 pipelines ascribable to impurities and failures are common causes of loss of containment scenarios. Safety concerns related to pipeline routing can be due also to phase changes that can occur at different times or locations along the pipeline route (and that depend on local conditions). Furthermore, some routine and unscheduled operations including the pipeline venting are critical and may sustain solid-phase occurrence, low-temperature effects, and the discharge of large inventories of CO_2.

5. Closing remarks

The purpose of this short review is to provide a systematization of available information, best practices, and open issues related to each of the main steps of a carbon sequestration chain. Safety concerns exist in the capture, transportation, and geological storage, due to inherent substances and operations. What emerges is that despite carbon sequestration is not a new development, different safety aspects are still debated and unsolved. Intrinsic issues are naturally related to processed substances and known, although underestimated, CO_2 peculiarities. CO_2 poses significant and peculiar risks once processed in controlled or even uncontrolled scenarios. Topical is the solid phase occurrence and the modeling of release sources including pure CO_2 and impure mixtures, besides conditions and mechanisms of corrosion in carbon sequestration equipment. These aspects should be adequately addressed in the analysis of preventive actions oriented to integrity preservation but also for consequences modeling. Future directions should include the formulation of modeling tools able to predict corrosive mechanisms in CO_2- rich operations, the implementation of coupled economic and risk-based algorithms to drive the best routing, and an inherently safe design of the entire chain as the experience with large-scale projects and future implementations grows. An independent knowledge mechanism of CO_2-related infrastructures is essential to overcome actual limitations that improperly pair many safety-related aspects of oil and gas handling infrastructures to those for carbon sequestration.

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