

Full Length Research Paper

Concept of complete CO₂ capture from natural gas inside exploration wells and its storage in rock reservoirs

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The innovative concept herein shown intends to present a new system of carbon capture and storage (CCS) from natural gas extracted on cement completions of gas wells by absorbent selective nanoporous materials, forming conducting channels on linked pores. CO₂ fluids will be transported upwards and then injected and stored in upper nonproductive oil and gas porous rock reservoirs by the removal-transport-injection system (RTIS), assuring also the mechanical safety of the wells. This innovative concept allows the treatment of natural gas in oil and gas wells on fields, through the extraction of carbon dioxide. The natural gas will be free of CO₂, the major responsible gas for green house effect and therefore its production will be environmentally friendly.

Key words: Carbone dioxide, carbon capture and storage (CCS), gas wells, completion, removal-transport-injection system (RTIS).

INTRODUCTION

Oil and Gas accounted close to 60% of primary energy consumption in 2017 and the gas quantity was higher than 20% (Dudley, 2019). The transition to a lower-carbon fuel mixture is ongoing, and will be guided by natural gas and renewables use towards 2040. The renewables will grow faster in the world energy system than any fuel before. Considering the rapid transition scenario (RT), the growth of the renewables will be the highest ever, with an increment between 1 and 10% in 15 years. In this scenario, oil and gas will account for almost 50% of primary energy consumption in 2040 and the gas quantity will be lower than 30%. The renewables will account only around 15% of consumption in spite of the prediction of its strong growth. The consumption of oil will

decrease and the use of gas will continue to increase, helped by the contribution of the growing use of carbon capture use and storage (CCUS) in the RT scenario. The quantity of natural gas use in 2040, in conjunction with CCUS, will be about 1/3 of the total consumption amount (Dudley, 2019).

The development of materials with high availability for CO₂ capture and storage (CCS), retention capacity and absorption selectivity it is a quest in science and technology nowadays. Many materials are being investigated in order to correspond to this major challenge, encompassing factors as: availability, environmental friendliness, non-toxicity, a low level of greenhouse gas emission during processing, material

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stability, production cost, energy of adsorption/desorption, sorbent regeneration, sorption kinetics and capacity per volume or per mass of host material (Cavalcanti et al., 2018).

Cavenati et al. (2004) stated that the adsorption is a main unit operation in the chemical and petrochemical industries in order to carry out separation and purification of gas mixtures, namely in the case of the methane-carbon dioxide. The carbon dioxide capture from a gas mixture flue can be done by selective efficient adsorbents as zeolites. They referred also the CO₂ and N₂ removal from natural gas streams through proper adsorbents by the Molecular Gate technology (Engelhard, USA).

Joos et al. (2015) reported that the exhaust gases with a residual heat at 400 K are sent into the atmosphere under a high-pressure stream after leaving the heat exchanger of a fossil fuel-fired power plant. In the context of CCS, on nanoporous materials, the CO₂ adsorption can be favored by the differences in the entropy and adsorption enthalpy for CO₂ and H₂O at high temperature, and H₂O absorption at low temperature. The adsorption of CO₂ is carried out at high temperature (400 K), and the release of CO₂ occurs at low temperature, being the absorbent saturated with H₂O.

Joos et al. (2015) also referred advantageous materials aside zeolites and zeolitic imidazolate frameworks (ZIFs), e.g. metal-organic frameworks (MOFs), and porous polymer networks (PPNs). Other authors reported procedures to carry out the carbon dioxide sequestration and separation from gas mixtures (Rolniak and Kobayashi, 1980; Sircar, 1988; Dong et al., 1998; Talu, 1998; Dreisbach et al., 1999; Murata and Kaneko, 2000; Siriwardane et al., 2001; Siperstein and Myers, 2001; Krooss et al., 2002; Murata et al., 2002; Ko et al., 2003; Olajossy et al., 2003). This paper aims to present the concept of an advanced innovation in Oil and Gas industry: the CO₂ capture from natural gas mixtures inside moderate and deep gas wells and its storage in upper nonproductive porous rock formations.

This innovative concept herein shown intends to avoid the extraction of carbon dioxide from gas wells and its lifting and transport to surface Oil and Gas facilities on fields. The natural gas will release carbon dioxide through well cement completions that will be injected and stored in upper nonproductive Oil and Gas porous rock reservoirs, assuring the mechanical safety of the wells.

MATERIALS AND METHODS

The Oil and Gas wells comprise near surface or intermediate or deep well bores with cement in annulus between rock walls, covered with mud support, and steel casings (API Spec 7-1/ISO 10424-1 (2004, 2007, 2009, 2011), TR 5C3/ISO 10400 (2007, 2015), ISO 10426-1 ANSI/API SPECIFICATION 10A (2009), API RP96 (2013)). A representative production steel casing is herein described with 9^{5/8} in. O.D., surrounded by a typical cement thickness of 1.5 in. on the referred annulus and encompassing an inner production tubing or liners. The communication between the rock reservoir and the well is carried out by casing perforating

explosives, blasted inside the well that allow the flow of natural gas from the reservoir to the production well.

According to Cavenati et al. (2004), the natural gas is composed mainly of methane, between circa 80 and 95%, with variable amounts of C₂₊ hydrocarbons and nitrogen, carbon dioxide as a minor component (around 1%). However, the effluent gas extracted from a well under a CO₂ flooding may contain 20 to 80% of CO₂.

CO₂ injection and storage in rock reservoirs is a common practice in Oil and Gas industry. The modeling studies required to increase its performance are very important (Salem and Shedid, 2013). Also, in order to prevent the equipment and pipeline corrosion, the carbon dioxide reduction has a major importance.

Carbon dioxide is supercritical in gas reservoirs generally at depths higher than 1 km and at temperatures higher than 35°C. According to Vargaftik (1975), the phase diagram shows the critical point at P = 73.8 bar (P = 7.4 MPa) and T = 31.0°C. Therefore, carbon dioxide has supercritical and gaseous states. Supercritical carbon dioxide is a fluid with hydrostatic gradient value of 0.091 bar/m approaching that value of water. However, pure carbon dioxide gas value of viscosity is circa 0.015 cP (1.5×10⁻⁵ Pa.s) at 61 bar and 40°C, higher than pure methane value of viscosity at same P and T that is about 0.011 cP, showing low viscosity. These values of viscosity increase around ten times at 101 bar and same temperature. Even supercritical carbon dioxide reveals high mobility.

Most demanded well cements are ISO/API classes C, D, G, H and are intended for use when conditions require high, early strength and are available in moderate sulphate-resistant (MSR) and high sulphate-resistant (HSR) grades, similar to ASTM C150, type III (ISO 10426-1 ANSI/API SPECIFICATION 10A (2009)).

According to ISO 10426-1 ANSI/API SPECIFICATION 10A (2009), the ground clinker generally consists of hydraulic calcium silicates, aluminates and usually contains one or more forms of calcium sulfate as an interground additive. During manufacture of class G and H well cements, aside calcium sulfate or water, or both, no additives are allowed to be intergrounded or blended with the clinker. The main standard chemical composition of these cements is the following: maximum value of 6% of magnesium oxide and 3-3.5% of sulfur trioxide (3.5% class C), tricalcium silicate varying between 48% and the extremes 58% (MSR) - 65% (HSR), tricalcium aluminate with the maximum values of 3% (HSR)-8% (MSR), tetracalcium aluminoferrite has the maximum value of 24% (HSR). The total alkali content expressed as sodium oxide equivalent has the maximum value of 0.75%.

The maximum values of the insoluble residue and the loss on ignition are 0.75 and 3%. The free-fluid content has the maximum of 5.9% on G and H and the mixture water values are the following: 56% on C, 38% on D, 44% on G, 38% on H.

The compressive strength tests are obtained after 8 h or after 24 h of curing time. These tests can be carried out, the both, under atmospheric pressure on C, G and H or 20.7 MPa (3000 psi) pressure on D. The compressive strength values obtained on C, G, H specimens are shown in Table 1. D specimens should have compressive strength values of 3.4 MPa (500 psi) and 13.8 MPa (2000 psi) after final curing times of 8 and 24 h at a temperature of 110°C (230°F). After a final curing time of 24 h at a temperature of 77°C (170°F), the compressive strength values on D specimens should be 6.9 MPa (1000 psi). The cement class G has a major use on completion works in moderate and deep wells constructed in the world. The porosity and permeability data of the cement class G are herein analyzed under degradation effect of carbon dioxide saturated water and supercritical carbon dioxide, based on an experimental simulation case of a completion inside a gas well.

Um et al. (2011) conducted an experiment on 14 mm diameter × 90 mm long samples of a class G cement with w/c = 0.33 (water/cement ratio). These specimens were tested under the temperature of 50°C and a pressure of 10 MPa in order to represent the CO₂ injection's temperature and pressure conditions

Table 1. Compressive strength values obtained on C, G, H API classes.

Values of compressive strength of API classes C, G, H (MPa)		
Curing time (hours)	8	
Curing temperature (°C)	38	60
Compressive strength (MPa)	2.1	10.3
Curing time (hours)	24	
Curing temperature (°C)	38	60
Compressive strength (MPa)		
C	13.8	No requirement
G and H	No requirement	No requirement

at 1 km of depth, a geothermal gradient of 30°C/km and a pressure gradient of 10.5 MPa/km. These samples shown a degradation depth of circa 1 mm after 1 month of testing and around 3.5 mm after 5 months, whereas the carbonated cement shown on the outer degraded zone increased the porosity and cracks occurrence, developing mainly nano-meter sized pores lower than 20 nm.

The air permeability of cement samples was predicted to increase, according to Ghabezloo et al. (2009) porosity-dependent equation, from 0.58 to 34.74 mD ($34.74 \times 10^{-15} \text{ m}^2$) after 1 month reaction with CO₂ saturated water at high P-T, as a result of porosity increment from 31 to 45%. The results obtained by Um et al. (2011) revealed that the degradation effect of CO₂ saturated groundwater was higher than the effect of cement exposure to supercritical CO₂, according to X-ray microtomography images carried out on deteriorated specimens.

Gasda et al. (2004) also referred the potential leakage of CO₂ occurrence on the interface between host rock and cement, cement and casing, cement plug and casing, or through the cement pore space and fracture.

THE INNOVATIVE CONCEPT

The cement material used by completion procedures should encompassing carbon dioxide selective absorbent nanoporous materials, capable of removing carbon dioxide from natural gas-rich methane mixtures flowing from reservoir rocks, under high pressures and temperatures inside the wells, after the curing time of 24 h, as super critical carbon dioxide. Then, this fluid is conducted through the main micro and nanopores channels of linked nanoporous materials on cements, physically and mechanically adequate for this purpose, towards less warm upper levels. The mechanical behavior of ISO/API cements improved by this construction procedure should be, aside compression resistance, both tensile resistant to inner circulation of carbon dioxide and ductile enough to accommodate variations of annulus deformation caused by rock walls displacements.

Several embedded and linked extraction micro devices will exert capillary forces and/or suction pressures responsible for this uplift phenomenon. These should be linked to compressor micro devices included on cement top levels that will receive and develop carbon dioxide deeper injections into upper non-productive porous rock

formations. This system of removal-transport-injection (RTIS) inside the wells completion should have proper nanosized sensors connected to a central unit and could be machine learning guided.

Open porosity values of circa 30% of cements inside representative wells' annular sections of about 158 cm² that is, 24.5 in.², trough 1 km wellbore-long, means a volume higher than $4.7 \times 10^6 \text{ cm}^3$ (4.7 m³) that is, circa 560 ft³ (cf). Considering a representative production of 5000 barrels of oil per day of 24 h (BOPD) and a GOR of 700 scf/bbl (Jacobsen et al., 1990), that is, 3.5×10^6 scf of natural gas per day. Assuming a composition of carbon dioxide of 1%, gives 3500 scf. This means, that in this case the RTIS will perform more than 6 travels of carbon dioxide upwards per day on cement completion, that is, a travel per less than 4 h or circa 7 cm/s (0.7 m/s or 2.75 in./s). Figure 1 illustrates the general working methodology of RTIS in a well gas. This innovative concept could also consider thinner vertical transport tubes, manufactured with e.g. shape metallic alloys, inside cement completion to carry out carbon dioxide but would require to tackle with expected corrosion problems that could occur caused by e.g. H₂S. This phenomenon will jeopardize the uplift of carbon dioxide, the physical and mechanical stability of completion and the support effect of casings in Oil and Gas wells.

DISCUSSION

Ghabezloo et al. (2009) shown based on permeability determined on 90°C-cured and saturated class G cement samples carried out inside triaxial tests chambers, the availability of inducing transient pulse from differential pressure applied on both ends of the specimens with 76 mm of length. The specimens were under an effective stress inside the pore space of the cement of circa 12 MPa, obtained from the difference between the value of 30 MPa of external confining oil's hydrostatic pressure and 18 MPa of the value of the internal pore pressure fluid. It took about two hours to reach the value of 7.5 Mpa from the initial pore pressure of circa 18 MPa, recorded between the two opposite ends of the 76 mm-long

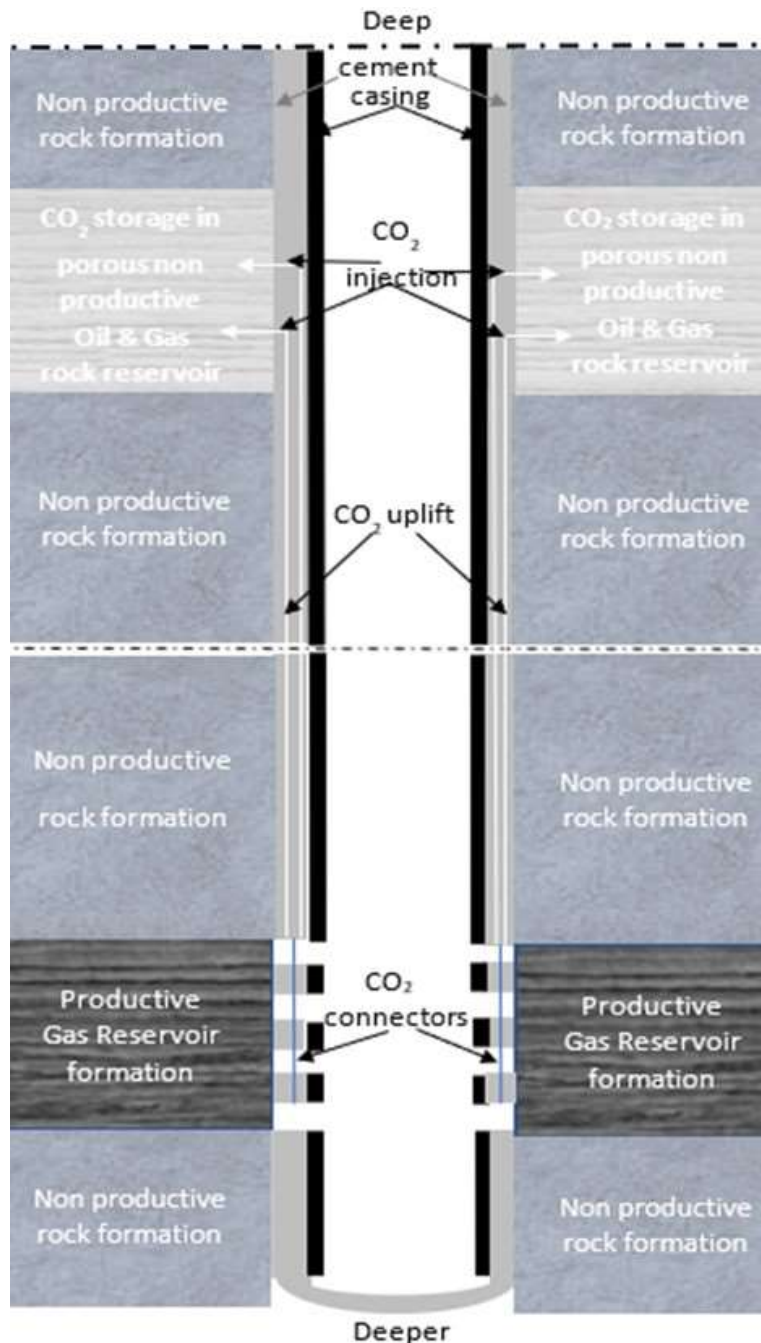


Figure 1. General working methodology of RTIS in a well gas.

specimens. The radial strain value obtained under the former pore pressure was circa 8×10^{-4} . The confining stress applied on the specimen was 22.5 MPa.

These data are an evidence of the availability of inducing supercritical fluid flow inside pores of cement materials at pressures similar to those that occur at more than 1 km depth without mechanical failure. However, the experimental evidence shown a significative difference between the referred velocity of travel of supercritical CO₂

of 0.7 m/s and the velocity value of 0.38 m/h obtained by Ghabezloo et al. (2009) on water transport. The viscosity of the supercritical CO₂ is circa ten times lower than the viscosity of water and contributes to the significant increment of the velocity of the travel of the former in the cement voids.

Hasan et al. (2013) studied microporous materials for sorbents capable of capturing and compressing atmospheric CO₂ with low cost and high purity and

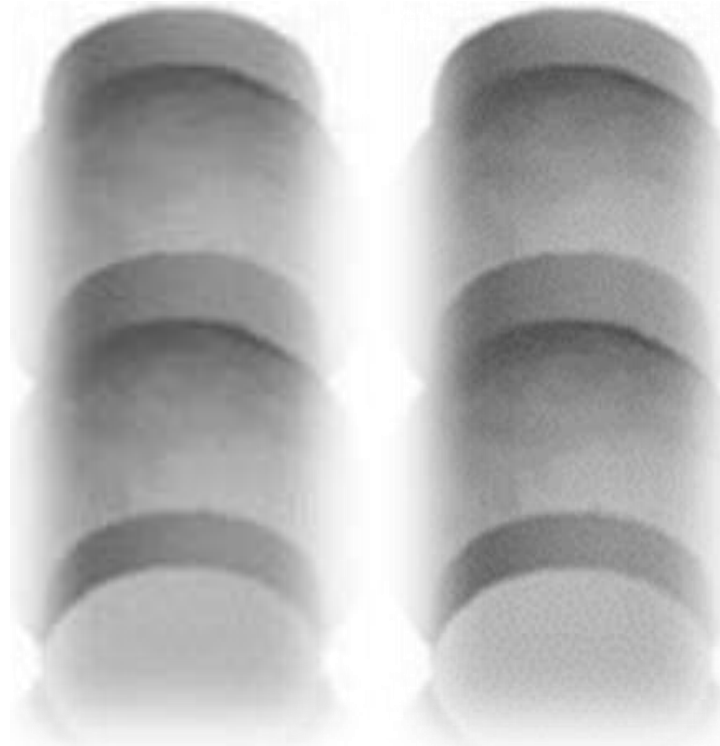


Figure 2. Model of columns of cylinders connected to spheres.

recovery, based on a computational screening approach that combines zeolites selection and process optimization. They considered a mixture-flue of 14% CO₂ and of 86% N₂ that went under adsorption in several zeolite's voids by two operational modes: pressure-swing adsorption (PSA) and vacuum-swing adsorption (VSA).

Considering the molecules of CO₂ and N₂ as hard spheres of diameter of respectively 3.4 Å and 3.1 Å, and the methane molecule with an effective length and diameter of 3.99 Å, the author of the RTIS concept selected as a valid example the case of AHT zeolites for capturing and compressing CO₂. The pore length diameter (PLD) and largest cavity diameter (LCD) of AHT zeolites are 3.4 Å and 4.6 Å. The PLD of AHT zeolites is lower than effective length diameter (ELD) of methane molecule and does not allow the former to enter inside zeolite voids. This zeolite has a purity of 90% and a recovery of 91.5%. Figure 2 shows the model of pore system distribution of AHT zeolites of columns of cylinders connected to spheres (caverns). The macro-system described by Hasan et al. (2013) has a compressor that pressurizes the dry feed gas in PSA mode. The CO₂ flow enters inside the column in VSA mode. The adsorbent zeolites are packed in multiple columns. Each column's length (L) is allowed to vary from 1 to 5 m, being the optimum length of about 1 m.

The CO₂ inside each column is affected by a cycle with the following four steps: (i) pressurization, (ii) adsorption,

(iii) forward blowdown, and (iv) reverse evacuation or desorption. Additional N₂ is purged by a vacuum pump during blowdown. CO₂ is extracted through a second vacuum pump, at the lowest pressure, during evacuation. After, it is compressed to 15 MPa through a compressor train with intercooling. The desorption curves of AHT zeolites under 1 MPa of pressure and T = 25-50°C show a loading of 2.5-2.75 mol of CO₂ per kg of AHT zeolite. The energy consumption per ton of captured CO₂ based on the AHT macro-system of Hasan et al. (2013) is 124 kWh and the cost per ton of CO₂ captured and compressed to 15 MPa, including dehydration, is 33.8 USD.

First et al. (2013) evaluated the market of purification of natural gas (separation between CO₂ and methane) in 97 billion USD. The RTIS concept applied on the gas production inside wells could have a major role on the industry of purification of the natural gas.

Hasan et al. (2013) described a macro-system that is another macro-evidence of the feasibility and reliability of the RTIS concept. An advantage of this concept is the following: the CO₂ extracted should be injected on rock voids under a pressure value of at least, half of the 15 MPa referred by Hasan et al. (2013), that is, 7.5 MPa. However, it will be needed to develop micro-devices e.g. micro-compressors, micro-vacuum pumps, nano-monitoring sensors operating through machine learning and micro-satellites' connections for the RTIS concept.

The assembly of km-long column's packs of zeolites inside cement's pore voids in Oil and Gas wells is also a challenging endeavor.

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CONFLICT OF INTERESTS

The author has not declared any conflict of interests.

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