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CARBON DIOXIDE SEQUESTRATION DURING SHALE GAS RECOVERY

Andrzej ROGALA, Katarzyna KSIEZNIAK, Jan KRZYSIEK, Jan HUPKA

Chemical Technology Department, Chemical Faculty, Gdansk University of Technology, Gdansk, Poland, andr.rogala@gmail.com

Abstract: This paper presents literature on theoretical and practical aspects of gas production from shale using carbon dioxide fracturing. Development of technical and environmental aspects of carbon dioxide fracturing technologies is also considered. Patents applicable to carbon dioxide fracturing are reviewed. In this work experiments were also conducted to verify possibility of carbon dioxide sequestration in the shale gas reservoirs. Carbon dioxide and methane (CH_4) storage capacity was measured as Langmuir volumes. The adsorption capacities depend on content of organic matter in the shale rocks and pressure. The obtained results indicate that developing of carbon dioxide fracturing is reasonable.

Keywords: *shale gas, fracturing, unconventional gas resources,* CO_2 *fracturing*

Introduction

Hydraulic fracturing (HF) is the main method of shale gas recovery. It is based on pumping fracturing fluid into a borehole under very high pressure to create fractures and stimulate reservoir for gas production (Howard, 1970). The fracturing fluid consists mainly of water and proppant (99.5%) and chemical additives (0.5%). Proppant is a material which prevents fractures from closing. Usually it is sand, sometimes ceramic material or resin coated sand (Mader, 1989). Chemicals are used to stimulate a reservoir and have various tasks in the fracturing fluids, they are: friction reducers, acids, corrosion inhibitors, biocides, iron control agent, gelling agent, cross-linker, breaker, KCl, NaCl. The hydraulic fracturing technologies, despite many years of use and numerous improvements, still have many problems. These are compatibility between fracturing fluid and reservoir rock and oil (Lal, 1999), water and waste water management, environmental costs, investment costs, risk of ground and surface water contamination, methane emission to atmosphere (USEPA, 2011), and wide social perception influenced by media. A continuous technology

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improvement is a natural trend in many research activities and introduction to the oil and gas field.

Table 1. Cation exchange capacity of clay minerals
(Eslinger and Pevear, 1988; Martin and Dacy, 2004)

Mineral	CEC [meq/100 g]
Smectite	80–150
Illite	10–40
Kaolinite	10–100
Chlorite	< 10
Hydrous Mica	10–40

A fracturing industry has identified a problem of compatibility between fracturing fluid and reservoir, especially containing water sensitive shales with smectite and illite. These minerals have tendency to bond high amount of water and swell/expansion. This phenomenon results in propped fractures reduced frac flow capacity and decrease of gas or oil flow in consequence. In Table 1 it can be found that smectite has much greater cation exchange capacity CEC than illite. Both of them have higher CEC than kaolinite and chlorite. CEC is closely connected with ability of a mineral (especially clay) to bind water. A greater value of CEC means that more water can be trapped in a clay structure and swell more intensively. The mechanism and understanding the water capillary forces is the subject of research worldwide. This is particularly important for Polish gas-bearing shale, which contains significant amount of smectite and illite. First fracturing works done in Poland showed that swelling clays significantly impede HF operations (PAP, 2013). The consequence of these problems is to develop wide range of technologies alternative to water based HF of shale oil and gas reservoirs that are water sensitive. The fracturing technology development is focused on water either reduction or elimination in the fracturing fluid. The application of shale inhibitors in water-based fracturing fluids is very expensive and due to shale anisotropy is not very well predictable. The best known technologies are: liquid carbon dioxide fracturing, nitrogen fracturing, carbon dioxide/nitrogen-based foam fracturing, gelled methanol fracturing and liquefied propane fracturing (Rogala, 2013). All these methods are designed to maintain compatibility between fracturing fluid and clay minerals containing expanding smectite and swelling illite (Ahn and Peacor, 1986). This approach allows to eliminate potential fracture closing by smectite and illite, which decides about the fracturing quality and overall frac conductivity.

Carbon dioxide fracturing

A widespread interest in the use of carbon dioxide (CO_2) in shale gas recovery is associated with the low price, general accessibility and its specific properties. Moreover, the United Nation policy of imposing money penalties for exceeding the limits of CO_2 emission to the atmosphere, further stimulates the use of this gas in the industry. As it is shown in Fig. 1, critical parameters of CO_2 are relatively small. Due to very high gaseous CO_2 injection pressure during fracturing and temperature in the reservoir about 80 °C, CO_2 becomes supercritical at the depth of 800 m and fluid, having much higher viscosity and density than gas. Supercritical CO_2 is completely compatible with the reservoir rock and reservoir fluid. In addition, CO_2 after contact with formation water, forms acidic species, leading to lowering pH. This property prevents creation of iron hydroxides, presence of which may plug slippage and reduce the frac conductivity (Economides et al., 2000). The same parameters of operation are not possible by using nitrogen, the gas that was also tested on wells. It has not only higher values of critical parameters, but also requires the use of high pressure equipment operating under higher pressure causing greater problems than in the case of CO_2.

The first carbon dioxide fracturing technology was patented in 1982 (Bullen and Lillies, 1982). This method is well-established and has been repeatedly modified. It is commonly used for dry fracturing in water sensitive formations. It involves injecting sand with liquid CO_2 as a carrier fluid for a proppant being mixed in a pressurized blender without the addition of water or other auxiliary compounds, except gelling additive. The proppants are synthetic or natural particles such as sand, resin coated sand or sintered bauxite ceramics, used in oil and gas industry to keep fractures opened. CO_2 on the surface is liquefied at a pressure of 1.4 MPa and a temperature of –34.5 °C. The proppant is added directly to a liquid CO_2 under these conditions on the surface using specialised equipment. The liquid CO_2 viscosity is about 5 cP and therefore, allows to increase viscosity to carry the proppant in propagated fracture. After stabilization of temperature and pressure, CO_2 partly dissolves in residual water and liquid hydrocarbon deposits.

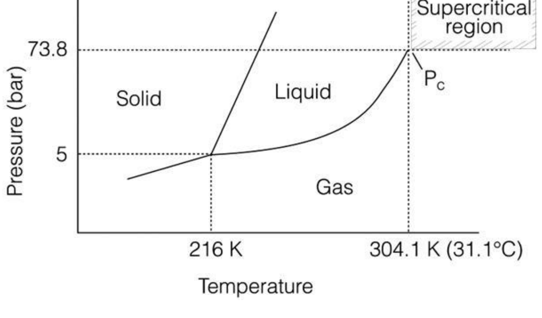

Fig. 1. Phase diagram of carbon dioxide (Ginty et al., 2005)

One of the most important advantage of liquid CO_2 fracturing is elimination of conditional formation damage normally related with the fracturing fluids. Another one is rapidly clean-up process and evaluation of the well following fracturing (Lilliesand King, 1982).

In Canada, only up to late 1990', there were more than 1200 tests, accomplished with success (Wright, 1998). The technology was also used in the USA for Devonian shale in East Kentucky and West Pennsylvania, Texas and Colorado (Arnold, 1998). It was observed that the average gas production in some wells was as much as five-fold greater than in the case of production using conventional HF treatments.

The main problem related with carbon dioxide fracturing (also using nitrogen or CO_2/N_2 mixture) is its transport in the liquid state and storage in pressurized tanks. In particular, the loss of CO_2 to the atmosphere should be avoided because of eventual impact on global warming. CO_2 fracturing keeps clays (smectite and illite) stabilized and prevents metal leaching and chemical interactions between fracturing fluid and reservoirs. The greatest successes in the CO_2 fracturing were recorded in Canada and in the former Soviet Union in late eighties (Luk and Grisdale, 1994).

Technologies of shale gas recovery based on carbon dioxide

Since the first carbon dioxide fracturing technology was developed, there were many attempts to use carbon dioxide in shale gas recovery. The following are the most promising solutions of problems associated with classical liquid carbon dioxide fracturing.

In 1987 a new composition of liquid CO_2 fracturing fluid was described by Canadian Fracmaster (Bullen et al., 1987). Alkene oxide additive was used (preferably propylene oxide) in the presence of a catalyst, producing in the reservoir random copolymer having a molecular weight of 20000 – 150000 and similar in structure to the polycarbonate (IR spectrum showed interleaved carbonate bond). The presence of this compound in an amount of 1.5–3.5% (wt) of the fracturing fluid significantly increased the viscosity and improved fracturing parameters. In addition, it was decomposed at normal temperature and pressure at the time from 24 to 48 hours and much faster under reservoir conditions, so that did not leave any undesirable chemical compounds in the shale formations.

At the end of 1980', a method of fracturing low permeability fields with a mixture of liquid hydrocarbons and CO_2 was developed (Mzik, 1989). The idea was the result of the observation that an oil viscosity increased more rapidly with increasing temperature than the mixtures of any suitable polymer, and additionally was miscible with liquid carbon dioxide. A mixture of hydrocarbons for the preparation of the proposed fracturing fluid was obtained by mixing petroleum products from the light and medium distillates and aromatic compounds. A mixture of hydrocarbons should have the following properties: average molecular weight of less than 200, content of at least 70% of the C5–C14 fraction, at least 8% by weight, aromatics solidification temperature below –40 °C, and density from 0.77 to 0.85 g/cm^3 at 15 °C. The fracturing fluid should consist of 95 to 15% liquid CO_2 and 5–85% of hydrocarbons. The proposed fracturing fluid is very simple, safe in use, and it can be injected using a conventional equipment for fracturing, also with the addition of proppant. The use of such a fluid, resulting in fractures with larger width than in case of use only liquid CO_2,also greatly facilitates the purification of the hole. In addition, the well clean-up is much faster.

A common problem connected with the liquid CO_2 is the presence of ice during the fracturing operation. If the wellhead pressure rapidly drops, CO_2 in such conditions may result in ice formation in a form of hydraulic head and pipes, which eventually restricts the gas flow. Therefore, it was decided to optimize the process by adding nitrogen to the CO_2 gas, which not only prevents ice build-up but also reduces the cost of operating the well (Gupta et al., 1998). A little different solution of this problem was proposed by Tudor (1999). He described a fluid consisting of 100% liquid carbon dioxide, 100% gaseous nitrogen and proppant. Contrary to expectations, the new method of liquid CO_2/N_2 treatments resulted in actual lowering the surface treatment pressures at equivalent volumetric rates, which reduced pumping costs and yield-improved leak-off characteristics.

One of the most important factor during shale gas recovery is concentration of proppant in the fracturing fluid. Nowadays, it should be about 0.48 kilograms per cubic decimeter and there is a problem to reach this value using non-aqueous fracturing technologies. Therefore Luk and Grisdale (1996) proposed to connect hydraulic/alcohol/hydrocarbon fracturing with carbon dioxide fracturing. They made two phase fracturing fluids able to have enough the maximum proppant concentration. A part of the proppant volume is added to liquid carbon dioxide and rest to water alcohol or hydrocarbon. Then, two systems are mixed together. The resulting fluid is much more compatible with reservoir than the classical fracturing fluids, especially with water sensitive shales. A high concentration of the proppant provides a high gas flow through the fractures.

US Patent 6729409 (2004) describes a method of using two-phase fracturing fluid in which the liquid phase is carbon dioxide and gaseous phase is nitrogen. In the liquid phase a nonfunctional non-ionic fluorochemical stabilizer was used. This technology can be used to stimulate unconventional hydrocarbon reservoirs of both oil and gas-bearing. The main advantage is a greater increase of fracturing fluid viscosity than in fluids of similar methods. It has positive impact on the maximum proppant concentration in fracturing fluid and gas flow through fractures.

In 2010 a new method of stimulation of shale formations using the carbon dioxide-based fracturing fluid, having viscosity below 10 mPa·s and share rate about 100/s,was invented (Kubala, 2010). The treatment fluid is injected into a borehole under a pressure higher than the reservoir pressure. The concentration of carbon dioxide is from 70% by mass to near 100%. There can be also used some surfactant, especially fluoropolymeric. Fracturing fluid can be aqueous, almost non-aqueousor non-aqueous. This technology leads to better fracturing parameters, fracturing fluid is more compatible with reservoir, the concentration of proppant can be higher than in other methods, as a result, the gas flow is also higher.

Mack (1999) proposed a shale gas fracturing technology, which is a modification of the hydraulic fracturing and carbon dioxide fracturing. A part of classical fracturing fluid is replaced by a mixture of nitrogen and carbon dioxide in a volume ratio from 1:5 to 1:4. Carbon dioxide is supplied as a liquid, whereas nitrogen is supplied as a gas. The proppant is added to the fracturing fluid together with a mixture of CO_2 and N_2. The surfactants and foam stabilizers are also added to the mixture. When the fluid is at the bottom of the borehole, carbon dioxide achieves the supercritical state because of a high temperature in the reservoir. Then, the foam is formed and intensifies the process of fracturing. The resulting fracturing fluid has much lower flow resistance in the reservoir, enabling lower power consumption by the pumps used for fracturing. Moreover, there is a compatibility between fracturing fluid and reservoir.

Comparison of liquid carbon dioxide fracturing and hydraulic fracturing

Table 2 shows the most important factors pertaining to shale gas recovery. The comparison between water-based hydraulic fracturing and liquid carbon dioxide fracturing was made.

Table 2. A comparison of hydraulic fracturing with CO_2 fracturing technology. N and Y mean no and yes, respectively. *Average data from field applied technology by Jan Krzysiek (unpublished)

Consideration	Hydraulic Fracturing	Liquid CO_2 Fracturing
environmentally friendly	N	N
fluid availability	?	Y
fluid recycling	Y	possible or useless
chemicals used	Y	reduced or eliminated
reservoir compatibility	biggest problem	Y
fracture creation	Y	Y
proppant carrying	Y	Y
recovery to pipeline	N	N
heavy metals flowback	Y	N
frac cost	1	>> 1*
fluid left in formation	Y	N
well clean up	Y	Y
frac geometry predictability	N	N
tilting stress development	Y	Y
zone water in flux risk	1	> 1*
fracture length	1	> 1*
fraced well performance	1	<< 1*
local road damage risk	Y	Y
environmental risk	Y	Y
NO_x and CO_2 in pumping	Y	Y
return on investment	1	< 1*

As shown in Table 2, carbon dioxide fracturing seems to be a method allowing elimination of water-based hydraulic fracturing which is not the most optimal. The main problems with this technology are economic and technological, that is the very long return on investment time and fact that expanding in reservoir carbon dioxide is extremely difficult to control. Presently, this method cannot be used in the deep wells, which occur in Poland.

Sequestration of carbon dioxide in shale gas reservoirs

One of the latest proposed solution is the conjugated hydrocarbon gas recovery and simultaneous storage of CO_2 in horizontal small diametrical wells made in a single horizontal well. The team, led by Niezgoda (WAT, 2012) proposed a method based on the stimulation of the reservoir using liquid carbon dioxide with the addition of proppant. The fracturing is achieved by pressure from supercritical CO_2 caused by reservoir temperature. Return on investment (ROI) as a prime target of investors is questionable. The inventors claimed that the efficiency of borehole can increase about 60 - 80% compared to 15% in the case of hydraulic fracturing. Unfortunately, negligible information about innovative solutions does not allow objectively evaluate possibility of carbon dioxide sequestration during the shale gas recovery. Nevertheless, the idea of the technology seems to be one of the best possible alternatives to hydraulic fracturing. Carbon dioxide sequestration during shale gas recovery could significantly change the importance of carbon dioxide place in the unconventional hydrocarbons resources market. This kind of technology is also supported by the Kyoto Protocol about reduction of global CO_2 concentration in the atmosphere (UNFCCC, 1997). Especially due to the prolongation of its duration until 2020 (UNFCCC, 2012). The results of these documents are EU actions to promote sequestration of CO_2. Therefore, there were conducted tests to evaluate possibility of carbon dioxide sequestration in the shale gas reservoirs.

Experimental

In this work experiments were conducted to verify possibility of carbon dioxide sequestration in the shale gas reservoirs. The carbon dioxide and methane (CH_4) storage capacities were measured as Langmuir volumes. Adsorption analyses were performed using the high-pressure volumetric adsorption. Isotherms were measured on a custom-made apparatus based on Boyle's law. Langmuir coefficients were determined using specialized computer software. To find the relationship between the gases storage capacity and content of organic matter in the shale reservoirs, the total organic carbon TOC analysis was also conducted.

The research was based on shale rock samples derived from the Ordovician (O1 and O2) and Lower Silurian (S1) period. The shale is a source rock for unconventional hydrocarbon fields in the Baltic Basin. The determined TOC values of shale rock samples and Langmuir coefficients for carbon dioxide and methane adsorption are shown in Table 3.

Table 3. Gas storage capacity and total organic carbon for collected samples

Sample	Formation	Langmuir Coefficients		Langmuir Coefficients		TOC [%]
		CH_4 [m^3_s/1000kg]	CH_4 [MPa]	CO_2 [m^3_s/1000kg]	CO_2 [MPa]	
O1	Ordovician	0.1412	1.216	0.9711	1.750	1.58
O2	Ordovician	0.9812	3.041	1.9113	2.211	2.92
S1	Lower Silurian	2.1401	7.122	4.0443	6.421	3.70

m^3_s – standard cubic meter

The shale rock adsorption capacity measured by means of the Langmuir volumes ranges from 0.97 to 4.04 standard cubic meters of CO_2 per 1000 kg of shale rock at the Langmuir pressures ranging from 1.75 to 6.42 MPa. The Langmuir volumes for CO_2 are much higher than for CH_4 which ranged from 0.14 to 2.14 standard cubic meters of CH_4 per 1000 kg of shale rock at the Langmuir pressures ranging from 1.22 to 7.12 MPa. The TOC values of tested samples ranged from 1.60 to 3.70%, sample O1 has the lowest TOC value and also the lowest Langmuir volumes, in particular pressures, whereas sample S1 has the highest TOC value, it also has the highest Langmuir volumes. To properly compare the adsorption capacity data, three pressure conditions were selected: 1.4, 2.8, and 4.2 MPa. The data are presented in Table 4.

Table 4. Summary of CO_2 and CH_4 adsorption capacity
in standard cubic meter per 1000 kg at selected pressures

Sample	Formation	Adsorbed substance	Absolute Pressure [MPa]		
			1.4	2.8	4.2
O1	Ordovician	CH_4	0.0852	0.1172	0.1450
		CO_2	0.3996	0.5881	0.7014
O2	Ordovician	CH_4	0.2721	0.4341	0.5298
		CO_2	0.9772	1.2975	1.4181
S1	Lower Silurian	CH_4	0.3186	0.5695	0.7753
		CO_2	1.4190	2.5233	3.3884

At a constant pressure of 1.4 MPa, the measured CO_2 adsorption capacity ranged from 0.40 to 1.42 m^3/1000 kg whereas methane adsorption capacity ranges from 0.09 to 0.32 m^3/1000 kg. At 2.8 MPa, the CO_2 adsorption capacity ranges from 0.59 to 2.52 m^3/1000kg and methane from 0.12 to 0.57 m^3/1000 kg. At 4.2 MPa for CO_2 it ranges from 0.70 to 3.39 m^3/1000 kg, while for CH_4 from 0.15 to 0.78 m^3/1000 kg. The adsorption capacities of CO_2 for the tested samples at the selected pressures are presented in Fig. 2. Figure 2 shows that, the higher absolute pressure during absorption, the higher adsorption capacity. Taking into account the fact that the fracturing pressure is about 100 MPa or higher, it may be assumed that the CO_2 adsorption capacity during shale gas recovery is much higher than in the presented results.

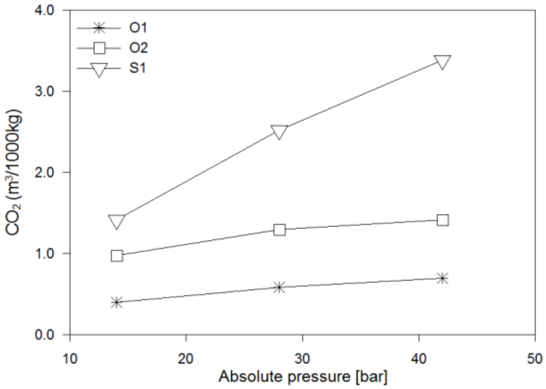

Fig. 2. Adsorption capacities of shale samples at selected pressures (1 bar = 0.1 MPa)

Conclusions

Considering economic, environmental and safety reasons, liquid carbon dioxide fracturing seems to be the most promising alternative to the hydraulic fracturing method. This may be warranted by the properties of this substance, which is non-toxic, non-flammable and it can be easily converted into a liquid state. Over the years carbon dioxide was used in foam fracturing, fracturing using mixtures of carbon dioxide with nitrogen or hydrocarbons as well as liquid carbon dioxide. All these fracturing fluids contained the proppant. There are major advantages of carbon dioxide fracturing:

- elimination of potential formation damage normally associated with fracturing fluids,
- the gas can be removed easily and the clean-up process is fast,
- CO_2 fracturing keeps clays (smectite and illite) stabilized and prevents metal leaching and chemical interactions,
- possibility of elimination of chemical additives,
- possibility of CO_2 sequestration (green technology),

and also disadvantages:

- a very expensive equipment,
- the ice presence in the hydraulic head and pipes, what eventually results in clogging gas flow,

- problems with transport in liquid state and stored in pressurized containers,
- possible loss of CO_2 – eventual impact on the global warming,
- a very long time of return on investment.

The following conclusions from the research of carbon dioxide sequestration in shale reservoirs can be drawn.

1. Langmuir volumes of carbon dioxide are much higher than volumes of methane under given conditions. It suggests that the volume of carbon dioxide possible to be sequestrated should be greater than adsorbed (not total) methane.
2. For maximum tested constant pressure of 4.2 MPa, CO_2 the adsorption capacity ranges from 0.70 to 3.39 m^3/1000 kg. This capacity should be much higher during carbon dioxide fracturing because of higher injection pressure. Thus, the sequestration should occur with a higher efficiency.
3. The TOC values of tested samples range from 1.60 to 3.70%
4. The adsorption capacities of CO_2 and CH_4 depend on content of organic matter in the shale rocks. The shale rocks with higher TOC values can absorb much more CO_2 and reservoirs can be more capacious for carbon dioxide sequestration.
5. To properly evaluate the possibility of carbon dioxide sequestration during carbon dioxide fracturing, further research is necessary. Precise estimates of geological deposits and detailed economic analysis are also required.

Taking into account the financial implications of not observing the limits of CO_2 emissions, cost-effectiveness of carbon dioxide can significantly increase in future. The Kyoto protocol and the European Union policies cause that the development of carbon dioxide fracturing can be very important. However, a long-term study and improvements of this technology are necessary.

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