Polymer resins for remediation of leakages in CO_2 wells

CLIMIT Project- 256448

Background

CO_2 storage is one of several technologies that can contribute to significant reductions in global CO_2 emissions. One common solution for CO_2 storage is to re-use existing oil and gas wells or drill new ones into known reservoirs. To access such reservoirs, it is necessary to penetrate the cap rock and place an injection well. This means also creating a possible leakage path. If CO_2 is to be stored in a depleted hydrocarbon reservoir it must also be expected that a high number of abandoned oil/gas wells already penetrate the storage sites. The long-term safety of CO_2 storage is highly dependent on the integrity of all these wells.

Loss of well integrity has been identified as a major failure factor in CO_2 storage. It is stated in The Intergovernmental Panel on Climate Change (IPCC) special report on CCS that: "*injection wells and abandoned wells have been identified as one of the most probable leakage pathways for CO_2 storage projects*" (IPCC, 2005, p. 244). Thus, prevention and remediation options for any potential leakage through wells, play a crucial role in large scale implementation of CO_2 storage. Wattson and Bachu (2007) have statistically assessed the leakage potential for wells using a population of 316,500 abandoned wells in Alberta, Canada. The researchers looked at surface casing vent flows and gas migration from the well. They found that 4.6% of the wells had some sort of leakage. Further analysis showed that the major factors related to leakage were the geographic area of the well, the deviation of the well, the type of well (abandoned open hole or abandoned cased hole), the abandonment method, oil price and regulatory environment, and uncemented casing/hole annulus. Of the leaks that occurred 81% of them were above the top of the cement which indicates that the cement is a factor in preventing leaks and providing zonal isolation.

Many of the available oil & gas technologies and methods used to repair well leakages can also be applied to CO_2 storage applications. Squeeze cementing is the most commonly used remediation practice in the oil and gas industry for various well leakage scenarios. However, CO_2 can react with the different materials used to construct a well. When it reacts with cement, the cement's strength is reduced, and its permeability increased. CO_2 can also corrode steel, causing casing leaks. Due to the chemistry and the long-term effects associated with CO_2 storage, remediation methods will require modification for application in CO_2 wells.

Thermal activated polymer resins (e.g. ThermaSet® from Wellcem) have been widely used on the Norwegian Continental Shelf and in the Middle East oil fields. These resins are used to solve a variety of well integrity challenges such as casing leaks, channels behind the casing and plugging in general, as well as for leakage remediation. The resin formulation can be accurately designed for an application, adjusting density, viscosity, and curing time for optimum performance and placement. Thus, the resin remains in the liquid form during pumping or squeezing into a desired place. The curing of resin is activated when it reaches the target and the designed temperature. The resin offers common resin properties such as superior adhesion, chemical resistance, excellent mechanical properties, low viscosity in the liquid state and flexibility and toughness after curing. Thus, the requirement for the need and development of a laboratory qualification of resins and its long-term integrity in CO_2 wells has led to this project.

Objectives

The primary objective of the project was to evaluate the potential for thermal activated polymer resin systems as remediation materials to repair cement failure at laboratory scale and representative reservoir temperature. In this project, core flooding experiments have been performed in cement plugs with varying crack sizes to determine the ability of the polymer resin to be squeezed into designed leak paths of different sizes and lengths. The sealing ability of polymer resin as a remediation material in cement cracks of different sizes and lengths was also tested. The effect of CO_2 on the integrity of the resin materials under realistic downhole conditions was also investigated.

- Determine ability of polymer resin to be squeezed into designed leak paths of different sizes.
- Determine sealing ability of polymer resin in cement cracks.
- Determine the long-term integrity of resin material under CO_2 exposure at downhole conditions.
- Develop a more environmentally friendly polymer resin formulation with optimized fluid properties that enables use as remediation material.

Implementation

The project is co- financed by Wellcem and the Research Council of Norway (RCN). It was accomplished through close cooperation with Norwegian Research Centre (NORCE), University of Stavanger (UiS) and National Oilwell Varco (NOV).

Wellcem; its researchers have done numerous laboratory experiments and many hours in resin development. Wellcem performed all the work related to the design and measurement of the properties of the resin formula. The core plugs used in the core flooding experiments were prepared by Wellcem. The resin samples used in the long-term ageing experiments were also prepared by Wellcem.

NORCE; the core flooding experiments; permeability measurements and long-term ageing experiments were performed at NORCE.

UiS; the mechanical properties of resin materials were tested at University of Stavanger.

NOV; the marine toxicity tests of the developed environmentally friendly products were tested at NOV, Fjords Processing.

Results achieved

New products in the portfolio

- An environmentally friendly resin, EnvoSet®, has been developed and commercialized.
- A low toxic accelerator has been qualified to substitute the previous toxic chemical and already been used in the operations together with resin.
- An ultra-fine filler material has been qualified as weight agent and already been used in the operations together with resin. It is a green product that pose no hazard to the environment.

These products development has a positive environmental impact.

Determine the penetration and sealing ability of Resins

Laboratory core flooding tests have been performed to determine the squeeze and sealing ability of resin products in fractured cement plugs at realistic downhole conditions.

- Results show that ThermaSet® and EnvoSet® can be easily squeezed into large size cracks (500 μm), small size cracks (72 μm) and multiple size cracks (91-500 μm). The squeeze of resin proved to be successful for sealing the designed leak paths. Return permeability measurements showed zero permeability in the core sample. Resin formulation, such as viscosity and fillers are playing important roles.
- After a series of screening tests, the two resins ThermaSet® and EnvoSet® were selected and injected into artificial fractured cement cores. It has been shown that both resins are suitable as remediation materials and able to seal the fractures
- Laboratory CO_2-flooding tests were performed including simulation of CO_2 leakages after resin remediation by flowing supercritical CO_2 and then CO_2-brine through the core samples, to investigate the effect of CO_2 on the resin sealing performance over time. Fractured cores which were sealed with resin ThermaSet® and EnvoSet® were exposed to supercritical CO_2 for 38 days and then further exposed to CO_2-brine for 55 days, in both case at 75°C temperature and 100 bars pressure. The return permeability of cores remained at zero, showing the cores were still sealed after 93 days exposure to CO_2. This indicated resins in the fractured cores were unaffected by CO_2 exposure.

Determine the long-term integrity of Resins

The long-term integrity was evaluated by determining physical and mechanical properties at given time interval in an accelerated testing system with simulated downhole conditions: 100°C and 500 bars. The ageing tests have been performed with two resins ThermaSet® and EnvoSet®: before exposure (0 day), after 1 month, 3 months, 6 months and 12 months of CO_2-brine exposure and pure brine (as a reference) exposure.

- Experimental results showed reductions in the mechanical properties after long-term exposure to brine and CO_2-brine. These reductions levelled off after 1 – 6 months exposure and the strength remained high after the levelling off.
- Resins permeability to gas remained as low as initial, hence not measurable.
- In comparison with the reference brine, CO_2-brine creates an acidic environment (pH 3.1) thus has accelerated the resin – water interactions and resulted in faster changes to the resin samples. Such interactions reach equilibrium after some time and eventually resins have retained very similar level of mechanical properties either exposed to CO_2-staurated brine or pure brine.

As a final comment, it should be noted that due to the design of the experimental set-up and conditions, the reaction speed observed in these laboratory tests is considerably faster than what would occur in a real downhole situation. Therefore, 12 months exposure time in this experimental set-up will probably be comparable to hundreds or thousands of years of real downhole exposure.

Based on the laboratory core flooding experimental results and long-term CO_2 exposure study at realistic conditions, the evaluated thermal activated polymer resin systems were found to be suitable candidates for remediation of leakages in CO_2 wells. The results have also shown that the design of the polymer resin formulation is very important for the application.

Introduction of new/improved methods

Curing of resin is a polymerization process which is determined by the nature of the reactive groups in the resin formula and the specific conditions. The factors that can influence the curing of resin include additives, fillers, temperature, pressure, and contaminations. Wellcem has performed many research activities and gained much knowledge on the effect of these factors on the setting time and mechanical properties.

Wellcem has introduced a novel method – consistency under applied pressure test (CAPT) for the determination of curing of resin under downhole conditions. CAPT could allow a more accurate prediction of the curing process, thus enhance the value to the applications of resins in Oil & Gas wells.

New business opportunities

Wellcem sees interesting business opportunities in prevention and remediation for any potential leakage in CO_2 wells.

As CO_2 capture is implemented, storing CO_2 underground is considered the most effective way for long-term safe and low-cost CO_2 sequestration. Wellcem will be strongly positioned in this market. We can see the inception of such a market on the Norwegian Continental Shelf, and to an even larger extent in the US. For example, Equinor AS, recently drilled an exploration well licence 001 southwest of Troll A (Cook and Johannes formation) in the northern part of the North Sea. The objective of the well was to investigate whether reservoir rocks in the Lower Jurassic are suitable for storage of carbon dioxide (CO_2) (NPD website, 2018).

In Europe, there is a widespread preoccupation about CO_2 leakages in regard to CO_2 sequestration. Thus, prevention and remediation for any potential leakage in CO_2 wells, will play a crucial role in large scale implementation of CO_2 storage. In this scenario, a product that creates safer wells, will add distinct value.

The results achieved in this project are very encouraging. We believe it can promote the use of resin in the CO_2 wells, thus open up a new business market.