FINAL REPORT

Project Title: **PROGRAMMABLE SEALANT-LOADED MESOPOROUS NANOPARTICLESS FOR GAS/LIQUID LEAKAGE MITIGATION**

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EXECUTIVE SUMMARY:

Along with substantial benefits and promises of carbon capture and storage (CCS) technologies, significant challenges exist in developing advanced materials and methods for mitigating and/or preventing wellbore leaks. The overarching objective of this project was developing a new sealant product and technology that significantly mitigate CO_2 leakage and increase reservoir storage efficiency for various wellbore conditions and chemical environments. The objective of Phase I of this project was to develop and fine-tune a prototypal cement-based porous nanoparticles (CPNPs) to offer the best solution to CO_2 leakage in environments with a variety of extreme conditions including high temperature, and high acidity. The objective of Phase 2 was testing and refinement of the product's CO_2 barrier efficiency and performance, following by product validation (meeting API recommended practices), and scale-up. The project objectives were designed to specifically obtain a final product and technology that addresses a main goal of the DOE's CCS programs, i.e. develop and validate technologies to ensure maximal storage permanence.

The project developed a new protocol integrating a collection of advanced synthesis and characterization techniques, a thorough combination of lab-simulation, scale-up analysis and cost-benefit analysis, thereby providing a *system approach* to achieve a beneficial and cost effective CO_2 barrier technology. The core synthesis strategy was based on a bottom-up approach to apply and further develop the vast knowledge on nanoparticles and nanocomposites towards a new CPNP-sealant product. Characterizations and testings comprised of a myriad of probes and techniques including advanced electron microscopies, spectroscopies, permeability measurements, mechanical analysis, and scale-up.

The following value propositions were obtained as a result of this project:

1) A completely new phase space that provides a revolutionary new paradigm for material design and engineering to mitigate wellbore leakage in existing wells and improve reservoir efficiency,
2) A CPNP-sealant material that is able to be pre-programmed with a range of ingredients that best fit various complicated well/reservoir environments under a variety of temperatures, pressures and chemical conditions, and
3) A final CPNP-sealant (matrix) product that will be easily integrated with existing remedial technologies to efficiently mitigate CO_2 leakage toward the goal of maximal storage permanence.

This project can not only mitigate wellbore leaks but can open up a whole new toolbox of multifunctional materials and composites for numerous analogous applications including applications to various gases, liquids, and as a carrier for nanomaterials. The following sections exhibits only the publicly available project information.

1. Introduction

As the world's population grows, so does its need for energy and resources. Often the extraction of these resources comes with a substantial cost, specifically the emission of carbon dioxide (CO_2) and other greenhouse gases (methane, nitrous oxide, etc.) into the atmosphere. The overwhelming majority of today's scientist agree that these greenhouse gases are a primary cause of global warming, an increase in the Earth's overall average temperature leading to potentially devastating effects on the world's population, food and water supply, etc. Of the anthropogenic greenhouse gases, carbon dioxide is proposed to be the principal cause of climate change and global warming[2]. In the United States, it is estimated that over 40% of CO_2 emissions are generated by electric power generation[3] and, thus, there has been a strong focus on reducing the emission from these power plants. The carbon capture and sequestration (CCS) program was designed to help mitigate the detrimental effects of CO_2 emissions while maintaining the country's ability to supply its energy needs (reuse of captured carbon for Enhanced Oil and Natural Gas Recovery, etc). To do this, the development of subsurface carbon storage systems with over 99% storage permanence is desired for both safety and efficiency concerns. And because some of the potential storage systems contain old or abandoned wells, a primary challenge is CO_2 leakage into natural aquifers or back into the atmosphere by way of these abandoned wellbores and their encasements (cement/concrete).

2. State of the Art

The operation period of carbon dioxide sequestration and storage projects is between 10-50 years while the post-operation period is intended to last from 100 to nearly 10,000 years[4]. Thus it is crucial that storage sites with previous well systems be able to remove the threat of CO_2 leakage for very long periods of time. The problem with old and abandoned well systems is that many times these wells were not designed for future long-term CO_2 storage and lack the necessary requirements to resist sustained pressure, temperature fluctuations, and chemical attacks. These extreme conditions can cause corrosion of the casing, cracks that develop in either well plugs or the cement sheath in the annulus (microannuli), and separations between the cement sheath and the formation or casing: all leading to the creation of gas and liquid escape pathways up wellbore.

In an effort to reduce the need of well repair and corrosion against CO_2 attack, many new well cements have been developed including Pozzolanic Portland cements, micro-fine cements, expanding cements, and latex cements[5]. Most of these cements are really just broken up or refined ordinary cement. Other types of preventative products are some of the 'self-healing' cements that are intended to reduce leakage pathways autonomously through reaction with hydrocarbons. These products lack multi-faceted functionality and cannot be programmed to perform in multiple environments with different conditions as our proposed product could. Although these relatively new products can offer improvements over conventional cements, each one has its drawbacks and permeable pathways continue to occur and exist in wells.

There are a number of ways that try to control and manage gas/liquid flow from CO_2 migration up the well bore. Some of these methods focus on decreasing the actual pressure of the storage formation at the bottom of the well[6], promoting trapping and dissolution of buoyant CO_2[7], and removing excess pressure by reduction of some of the injected CO_2. These and similar methods can help at preventing migration along both wellbores and natural escape routes but are unlikely to prevent all possible CO_2 migration as well as involve unnecessary steps if the wellbore could be properly sealed. Thus, repairing an oil well can prevent unnecessary procedures that, upon successful sealing, should reduce the overall remediation costs. However, well repair methods that are currently in use are not sufficient and/or lack the effectiveness mandated by CO_2 sequestration and storage.

2.1 Industry

In the sealing or plugging of leakage pathways (remediation) throughout a wellbore there are different methods that address the many types of leaks that may materialize. However, the general methods of remediation is squeeze cementing or (expandable) liner repair in the case of casing breaches.

Squeeze Cementing: This method has been employed by oil and energy companies for many years and involves the injection of cement, polymers (geopolymers), sealants, or mixtures thereof under pressure into the leakage zone. There are many current types of remediation "cements" which are specialized for the specific well conditions. There are also various types of squeeze techniques such as a running squeeze, hesitation squeeze, retainer squeeze, Bradenhead squeeze, and low and high pressure squeeze. The type of squeeze and the material used are very important in the overall success of the job. Although reports vary, in general, the average success rate of remedial applications is around 50% as often these jobs lead to formation breakdown instead of penetrating into the fluid escape pathways. Thus, it is clear that a better product is needed.

(Expandable) Liner/Tubular Repair: Liners/tubulars, expandable or not, can be used when steel casing have been corroded or when perforations in the sides of casings show leakage. This type of remediation is focused on leakage from the formation or cement sheath to the inside of the casing and does not intend to fix the casing but provide another new barrier that lines the inside of the casing. Standard liners/tubulars have been used in the industry but reduce the inner diameter of the oil well and thus are not desirable.

There are also numerous patents regarding mitigation of wellbore leaks which provide insight into importance of wellbore remediation. Patents such as US5377757 A[8], an epoxy system for squeeze repair assigned to Mobil Oil Corporation, US 8163679 B2, a cement composition and method for plugging perforations in the well assigned to Cemblend Systems, Inc.[9], and US 5238064 A[10] and US 5127473 A[11], cementing mixtures of different compositions and viscosity for squeeze repair assigned to Halliburton Company provide descriptions of different materials that could be used for remediation and leak repair jobs. However, none of these patents or the commercial products mentioned above are similar to our technology.

2.2.Academia/Other

Alongside industry, there are a number of academic studies and research being performed in order to advance the forefront of remediation technologies. There have been a number of experimental simulation and approaches that focus on injection of compounds that react with CO_2 or supercritical CO_2 in an effort to form some sort of blocking agent. In these instances, methods such as solid precipitation may be used to form precipitates such as calcium carbonate or magnesium carbonate, gel formation could be used by employment of time/pH dependent gelling polymer or sodium/colloidal silica, or even microbial biofilms could be used but with the probability of success being quite low[4]. Nanotechnology is providing new insight and possible solutions for preventing unwanted CO_2 leakage. Some have proposed injection of the nanoparticles alongside the CO_2 in an effort to decrease the difference in resident brine and CO_2-rich brine[12] or even as a nanoparticle-stabilized supercritical CO_2 foam[12].

3. Project Objectives

The first objective of our project was to develop and tune prototypal CPNPs to offer the best solution to CO_2 leakage in environments with a variety of extreme conditions including high temperature, and high acidity. This objective contained numerous synthesis optimization procedures and advanced characterization to allow for an effective product targeted at mitigating leakage in a wide range of conditions. It also focused on synthesizing a product that is programmable: tunable pore sizes to accommodate various sealants and/or gases. This objective also ascertained the best final product for surface adhesion and stability.

The second objective was testing of the actual barrier efficiency and performance. This objective also involved the testing and incorporation of our product into a carrier matrix such as water and cement to offer conceivable performance enhancements and cost reductions.

The third objective was meeting relevant API recommended practices, scale-up, and potential integration with current methods and equipment used for wellbore remediation or with minimal modification.

4. Key Project Achievements:

Our project was designed with the focus on the prevention and sealing/plugging of wellbore leaks and potential pathways. Our product can provide a novel and completely revolutionary product that can be applied directly to CO_2 leakage channels with none or minimal modification to current downhole remediation procedures. Investigation on both the materials and methods for preventing CO_2 escape in carbon sequestration and storage systems, as discussed in the previous sections, has shown that there are no commercial products or ongoing research related to our innovative idea. There have been attempts at implementing polymer, epoxy resins, refined cement (fine particles, etc), and composites thereof but we are developing a completely new way of looking at remediation. Our system can be viewed as a programmable material that can be used to seal cracks in the wellbore casing, surrounding cement sheath, or even the surrounding rock formation.

Our product consists of specialized cement-based porous nanoparticles (CPNPs) that will be loaded with job and condition-specific sealants which can stimulated to release upon exposure to various conditions including contact with CO_2 saturated brine, changes in pH, and increase in temperature. Our particles have a number of benefits:

(1) they are size-tunable spherical CPNPs which allow them to easily flow into even the smallest cracks which cannot be achieved by even the current micro-cements as they are usually still micron-sized,

(2) they are spherical and monodisperse in size allowing for maximum packing density (leading to low permeability and high strength),

(3) they can release loaded sealant into any remaining surrounding voids forming an impermeable barrier,

(4) they can effectively seal a wide range of materials including steel, rock, and cement,

(5) they are based on calcium-silicate material providing a strengthening effect as well as allows them to, upon exposure to heat, pressure, and/or water, bond to resident cement (if that is where the crack is located),

(6) they can be pumped into the CO_2 leakage pathways with only pressurized air which should allow maximum penetration contrary to conventional cements which usually only penetrate a few inches into the leakage zone.

Our product, due to its stability and resistance to temperature, pressure, and chemical attacks, will remain an effective barrier against CO_2 migration over the lifetime of the CO_2 sequestration storage site, thus, reducing the overall cost of further repair jobs. The CPNPs is easily dispersible in water (due to internal loading of sealant) which is something not usually available to some current polymer and epoxy technologies. Figure 1 shows a schematic of our technology.

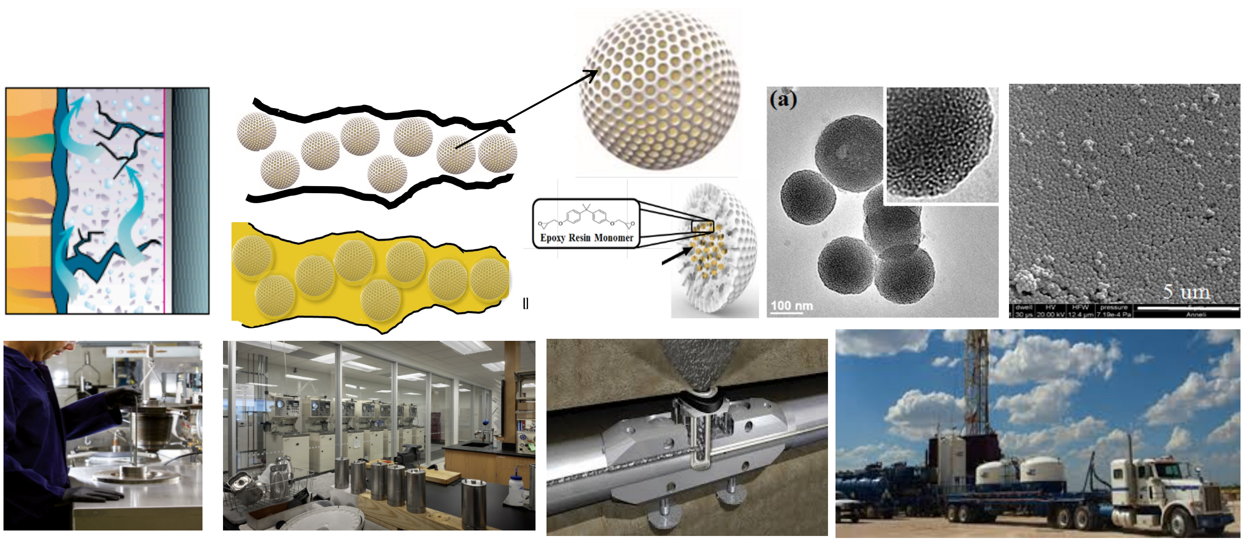

Figure 1. Schematic of our technology

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