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Nanoparticle Injection Technology for Remediating Leaks of CO_2 Storage Formation
(Extended Abstract)

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ABSTRACT

CO_2 is produced massively during multiple industrial activities, which contributes to environmental issues like the greenhouse effect. A common technique for carbon sequestration is to store liquefied waste CO_2 in deep underground reservoirs of depleted oil and gas wells. The integrity of the well formation is thus of vital importance for the proper function of the storage well. In this study, a nanoparticle injection technology is proposed and studied to reduce porosity and block micro-cracks in a cemented well, which can remediate leakage pathways for the CO_2. This technique uses an electrical field to drive the movement of charged nanoparticles through the cement sheath, while simultaneously driving out chloride ions which encourage corrosion. A desktop testing device is first adopted to verify the effectiveness of the method and for nanoparticle selection. Then, a full-size pressure vessel that can test well-cementing systems under elevated temperature and pressures is designed and built. Further experiments use cracked well cement samples made through the pressure vessel cured under high temperature and pressures. Various experimental results, including the conductivity profile, and permeability by water adsorption test show that the nanoparticle injection technique can help to reduce the permeability and seal micro-cracks of the well cement sheath to a certain extent. Some strategies to effectively remediate the leaked well are also proposed.

1. INTRODUCTION

Transporting natural resources, such as oil gas and CO_2, up to the ground and down into the underground reservoir has been successfully applied in the oil and gas industry in the past decades (Zhang et al., 2010). This process is known as geological carbon storage (GCS) technology. Currently, oil well cements have been widely used to seal the well for potential leakage of gas. The cement slurry is mixed above ground and transported underground through the steel pipe. Then, the cement is poured into the bottom of the well and pumped back up to the space between steel pipe and rock formation, shown in Fig. 1. Because of the harsh environment underground, the cement hydration process is different than that in aboveground environments and exhibits: early setting, modified viscosity, and high chemical shrinkage (Zhang et al., 2019, Zhang et al., 2020). After the long-time use of a wellbore system, the transportable gas has the potential to leak due to the unbalanced pressure generated from defects in the system (Nygaard and Lavoie, 2010, Crow 2006). As illustrated in Fig. 1, the gas may leak from the interface of different materials: the interface between steel casing and cement annulus, and the interface between the cement annulus and surrounding rock. Compared to the cement plug (cover of the steel casing), the cement sheath is thin due to the limited annular space (Němeček et al., 2017), and thus may become the path of gas leakage.

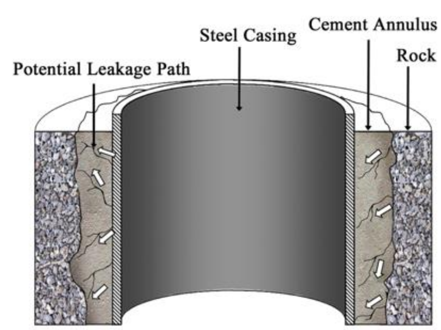

Figure 1. Possible leaking paths for gas

For an underground borehole system, the porous space is unreachable in deep wells. Therefore, the electro-migration method can be introduced in a borehole system to deliver nanoparticles for repairing leakage in the cement. This work is focused on sealing the leakage path and porous space in the hardened cement of oil borehole systems by using the electro-migration method. With the injected nanoparticles in the distressed cement, the repaired cement can become stronger and more stabilized. In this work, the injection performance of different types of nanoparticles have been proven.

Among all of them, nanosilica provided the best performance. The test was then conducted on the full-scale wellbore system with considering the real underground environment of high temperature and high pressure.

2. TESTING METHOD

The electro-migration method is an attractive technique for driving some beneficial particles into the cementitious material using an external current. It was recently developed based on the rapid chloride penetration test (RCPT) method (Behfarnia and Salemi, 2013). In this paper, the electro-migration method was used to drive nanoparticle solutions into the well cement to repair the potential cracks and leakages. In this method, nanoparticles are driven by the external current. The table-top testing apparatus is shown below in Fig. 2. As seen in the figure, there is a disc-shaped cement sample at the center of the apparatus. The cell includes two compartments which are connected through an external power source. Compartment 1 (left-hand side), is called the “upstream chamber”. The anions in the solution in the upstream chamber are injected into the cementitious material driven by the external current. In compartment 2 (right-hand side), the solution is sodium hydroxide. In accordance with the ASTM standard, the concentrations for the solutions are 3% sodium chloride and 0.3N sodium hydroxide by mass. The standard external voltage is 60V. Standard running time for the test is 6 hours. However, this standard test has obtained a lot of criticism, such as neglecting the temperature effect from high voltage, and the measurements are being done before a static state is achieved (Thomas and Jones, 1996). Thus, these parameters have been adjusted in this test with 20V and 12 hours of injection time. The selection of voltage is mainly to accommodate power-off protection mechanisms from the device used in this test (Germann Instruments RCPT). 20V is the maximum voltage which can be used to deliver a reasonable flow of current. In addition, the 12 hours of injection time can provide the most efficient injection of nanoparticles where the mesh electrode was mostly covered by the agglomerated particles.

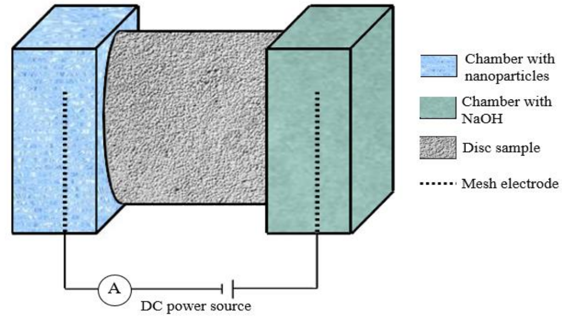

Figure 2. Electro-migration chamber used for ionic exchange test

3. FULL-SCALE WELLBORE TEST SYSTEM

To provide the underground environment in the lab, a literature review for the temperature and pressure range in the borehole environment was conducted firstly (Grandi et al., 2002, Kutchko et al., 2007). The temperature and the pressure underground depend on the depth, and the pore pressure of the layers drilled which may vary according to location. Usually, deep wells can be found with high pressure and shallow wells with low pressure. The same situation is true for the temperature. From the data collected, in 1 mile depth underground, the hydrostatic pressure is about 15 MPa and the temperature is around 80°C.

Based on the information provided above, this full-scale wellbore system has to provide two new features:

(1) A 100% scale steel casing and cement annulus. A section of a real borehole system is used as a sample, which can provide a realistic testing condition for the new injection technology, and boundary conditions between the well cement and steel, and between cement and rocks.

(2) Real size cement annulus that allows actual scale of injection devices to be installed on the cement samples, and thus the selected nanoparticle solutions can be used for testing.

The developed pressure vessel is shown in Fig. 3. The final design of the major vessel dimensions is 1.4 m in diameter and 3 m in height. The pressure vessel has been designed to comply with ASME Sec VIII, BPVC with safety factor of 3.5 to carry 14.2 MPa (2,060 psi) internal pressure and 90 °C (200 °F) temperature. Because of the safety concerns, the temperature and pressure were set up to 80 °C and 1200 psi, respectively.

Figure 3. Pressure vessel

In the next step, the concrete hollow cylinders were constructed to simulate the rock surrounding in a borehole system. A large (24" in diameter) concrete hollow cylinder was built as a model of the rock formations in a deep well. The cylinder was designed to fit in the pressure vessel (Fig. 4). The inner diameter (14") of the hollow cylinder was designed to fit the steel casing tube and cementing sheath using the real dimensions in a well. The average strength (according to the supplier) of the concrete was 7800 psi @ 30 days (=53 MPa). The compressive strength of a usual intact hard rock varies in the wide range of 30-400 Mpa (Bieniawski, 1984). Depending on the crack and slip systems in the rock, the effective strength of rocks is usually at the lower limits. Thus, the concrete strength of 50 MPa is a reasonable value to match the mechanics of the real rock confinement conditions.

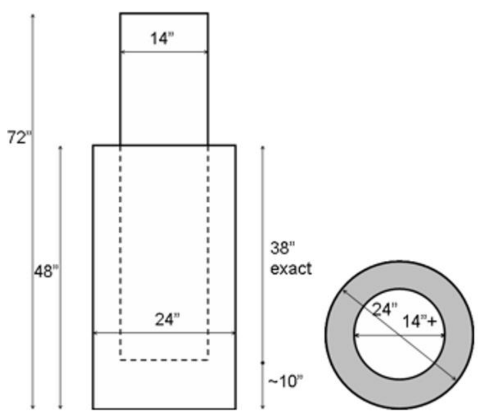

Figure 4. Casting hollow cylinders

4. MATERIALS

The Class G oil well cement was selected in this study according to the API Standard 10A and suggestions from the Society of Petroleum Engineers (SPE) (API 10A-11). Following the standard, the water to cement ratio used in this study is equal to 0.44. Two types of cement samples were prepared: the ‘intact’ sample and the ‘aged’ sample. The intact sample was cured in a water bath at 38°C and atmosphere pressure for 7 days. The aged sample was conducted under a temperature 90°C for 7 days immediately after 7 days of curing.

Nanoparticles have been treated as additives in cement slurries which can effectively enhance properties of the material, such as low electrical resistivity, self-cleaning, self-sensing capabilities, and high ductility (Sanchez and Soboley, 2010). In previous research, several nanoparticles have been shown to enhance the performance of the cement materials both physically and chemically, such as nano SiO_2, nano TiO_2, nano FeO, nano Al_2O_3, and nano $CaCO_3$, etc. (Li et al. 2004). In this study, three representative nanoparticles were selected for the tests using the newly-designed test system. The three nanoparticles are colloidal nanosilica solution (CNS), nanoalumina, and nanogel. The nanosilica and nanoalumina are commercial products and nanogel is lab-mixed. Both nanosilica and nanogel have negative surface charge and nanoalumina has positive surface charge.

5. RESULTS AND DISCUSSION

The test results from table-top testing apparatus are listed in the second and third columns of Table 1. From the Table, it can be concluded that all nanoparticles decrease the porosity of the samples after injection. The absolute value of porosity from the injected samples has an average value of 40.45% compared to 42% porosity of the noninjected samples. The highest porosity change was observed in CNS injected samples (4.59%). Therefore, the capability of sealing the pores is related to the charge passed during the test for most cases except for the Nanogel. Notably, the Nanogel showed the highest charge passed but with lowest porosity changes. This is because of the mechanism of expansion of Nanogel. With the injection of Nanogel, not only does the Nanogel seal the pores in the cement, it also generates cracking due to the particle expansion. This assumption was directly proved by submerging small pieces of Class G cement samples into the Nanogel solution for 24 hours. After the penetration of Nanogel into the pores, the Nanogel expanded, which imposes pressure on the inner surface of the cement pores and finally caused cracking of the cement.

Table 1. Results of porosity measurement and charge passed for respective treatment

Injected nanoparticles	δ_{intact} (%)	C_{intact} (Coulombs)	δ_{aged} (%)	C_{aged} (Coulombs)
CNS	4.59±0.9	6155±587	7.61±1.1	12233±877
AL	2.92±0.4	1384±646	N/A	N/A
Nanogel	2.79±0.7	7287±468	8.42±2.4	13768±1157

where δ_{intact} is the relative porosity change before and after the injection of nanoparticles for intact samples; C_{intact} is the charge passed during the injection of nanoparticles for intact samples; δ_{aged} is the relative porosity change before and after the injection of nanoparticles for aged samples; C_{aged} is the charge passed during the injection of nanoparticles for aged samples.

To prove the injection by an alternative way, the samples were cut into slices along the injection direction and conducted the BET test. The results collected from the BET method are described and compared in Fig. 5. From Fig. 5, the CNS injected samples show a decreased in surface area. The surface area of pores in the injected samples showed an average value of around 8 m^2/g rather than almost 12 m^2/g from the noninjected samples. This means most of the pore sizes have been decreased with the injection of nanoparticles. In addition, the surface area changes along the depth of the sample did not show consistency, a similar situation has been reported in the results of the saturate-drying method.

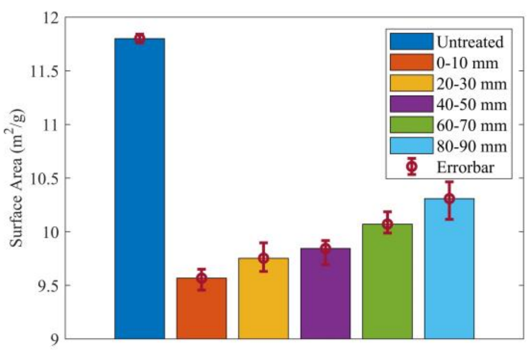

Figure 5. Surface area of pores of noninjected sample at different depths

Finally, from the test results of the lab-scale prototype test, the effectiveness of the injection process is confirmed again. The obvious decrease of the porosity from the injected samples compared with the non-injected samples can be captured. The nanosilica showed the best performance compared to the other two injected nanoparticles. In addition, the nanoparticle penetration depth was also recorded since the samples have been cut into several slices and measured the porosity individually, shown in Fig. 6. From the figure, at depths closer to the inject surface, the porosity is lower which means more nanoparticles have been injected. Among the three nanoparticles used, the CNS showed the best performance of changing the porosity compared with the nanoalumina and nanogel.

Table 2. Test results for samples from lab-scale prototype test

Injected nanoparticles	δ (%)	*C* (Coulombs)
CNS	8.19	2590
AL	5.84	756
Nanogel	6.37	11956

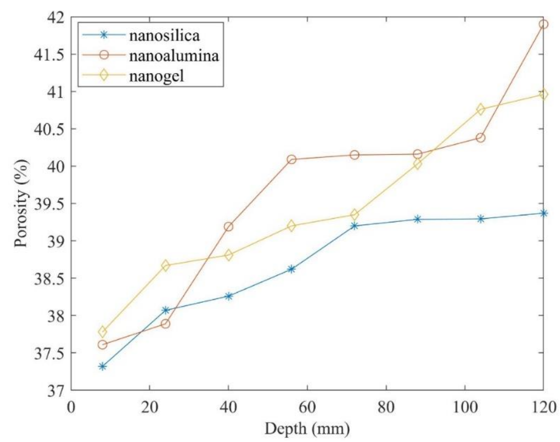

Figure 6. Porosity changes along the direction of injection

6. CONCLUSION

Three different types of nanoparticles have been successfully injected into the well cement by using a new electro-migration method. Different testing methods have been provided to prove the effectiveness of injection: saturate-drying method, and a BET method. The porosity decrease, the charge-passed increase during the injection, and the pore surface area decrease were more obviously captured from aged (cracked) samples.

The full-scale wellbore testing system was designed and developed to provide the underground environment and integrity of wellbore structure. Same three types of nanoparticles were further studied, and their effects on repair leakages of well cement were assessed and compared. The effectiveness of electro-migration method was evaluated under high temperature and high pressure environmental conditions.

REFERENCES

API 10A-11 Specification for cements and materials for well cementing, American Petroleum Institute Publishing Services, Washington DC, 2002.

K. Behfarnia, N. Salemi, The effects of nano-silica and nano-alumina on frost resistance of normal concrete, Constr. Build. Mater. 48 (2013) 580–584.

Z. Bieniawski, Rock Mechanics Design in Mining and Tunnelling, A.A. Balkema, Rotterdam, 1984: p. 272.

W. Crow, Studies on wellbore integrity, in: 2nd Wellbore Integr. Netw. Meet., Princeton, New Jersey, USA, 28-29 March, 2006.

S. Grandi, R. Rao, M.N. Toks, Geomechanical Modeling of In-Situ Stresses Around a Borehole, Massachusetts Institute of Technology, Earth Resources Laboratory, Cambridge, MA, USA, 2002.

B.G. Kutchko, B.R. Strazisar, D.A. Dzombak, G. V Lowry, N. Thaulow, Degradation of Well Cement by CO2 under Geologic Sequestration Conditions, Environ. Sci. Technol. 41 (2007) 4787–4792.

H. Li, H. Xiao, J. Yuan, J. Ou, Microstructure of cement mortar with nano-particles, Compos. Part B Eng. 35 (2004) 185–189.

J. Němeček, L. Li, Y. Xi, Electrokinetic nanoparticle injection for remediating leaks in oil well cement, Constr. Build. Mater. 156 (2017) 63–72.

R. Nygaard, R.G. Lavoie, well integrity and workover candidates for existing wells in the Wabamun Area CO2 sequestration project (WASP), in: Can. Unconv. Resour. Int. Pet. Conf., Society of Petroleum Engineers, Calgary, Alberta, Canada, 2010: p. 13.

F. Sanchez, K. Sobolev, Nanotechnology in concrete – a review, Constr. Build. Mater. 24 (2010) 2060–2071.

M.D.A. Thomas, M.R. Jones, A critical review of service life modelling of concretes exposed to chlorides, in: Concr. Serv. Mank. Radic. Concr. Technol., 1996: pp. 723–736.

J. Zhang, E.A. Weissinger, S. Peethamparan, G.W. Scherer, Early hydration and setting of oil well cement, Cem. Concr. Res. 40 (2010) 1023–1033.

Y. Zhang, C. Bouillon, N. Vlasopoulos, J.J. Chen, Measuring and modeling hydration kinetics of well cements under elevated temperature and pressure using chemical shrinkage test method, Cem. Concr. Res. 123 (2019) 105768.

Y. Zhang, L. Li, Y. Xi, M. Hubler, Experimental and theoretical study of the restrained shrinkage cracking of early age well cement, Constr. Build. Mater. 262 (2020) 120368.