



Electrokinetic nanoparticle injection for remediating leaks in oil well cement



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HIGHLIGHTS

- Novel electro-kinetic injection of nanoparticles into hardened cement is used for remediation of leaks in oil well cement for the first time.
- The oil well cement is characterized with high porosity and severe damage in operation. Both is taken into account in the paper.
- Novel nanoparticles including anionic (nanosilica), cationic (nanoalumina) and hybrid (nanoalumina coated nanosilica) particles are tested in the paper.
- The mechanisms of agglomeration of nanoparticles in well cement were examined.
- Results are verified by combination of experimental techniques (SEM, BET, electrical measurements).

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ABSTRACT

This paper presents experimental results on injecting nanoparticles into a hardened oil well cement with electromigration technique. Oil well cement is a special cement type used in underground constructions to protect steel casing of oil wells, CO₂ storage wells or oil and gas platforms. Due to the technological reasons, the hardened cement is characterized with a high initial porosity. Further distressing and fracturing occurs in the hardened cement originating from the harsh underground environment which includes elevated pressure and temperature. This leads to severe leakages of the stored media and puts the steel casing to the risk of corrosion.

The paper proposes to use a non-destructive remediation technique for the cement repair based on the electrokinetic injection of nanoparticles into the pore and crack space in the material. It shows the efficiency of the technique and presents results from injections with a variety of differently sized nanosilica, microsilica and nanoalumina particles. Characterization of the treated samples was based on microscopy observations, electrical measurements, the change in their open porosity and nanopore surface area assessed by the BET technique. It was found that the electrokinetic process and driving of particles in samples is very efficient and reduces the sample porosity by about 4–7% with respect to the initial porosity of intact specimens and 5–8% on aged samples. The BET analysis confirmed reduction of the inner pore surface area in the treated samples. Increasing level of agglomeration of particles on the surface as well as in the inner pores was observed during electrokinetic treatment and documented with the electric current measurements.

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1. Introduction

Many engineering structures such as underground wells in oil and CO₂ sequestration industries use cement shielding along with primary steel casing of the well. The cement shielding is often

exposed to harsh environment (e.g. increased temperature and pressure) leading to severe cracking and leaking from the well or surrounding geological formations. There are multiple mechanisms for the leaks to occur. Leaks from the well and ingress of underground waters and brines both endanger the steel casing and are potential risks leading to the well failure. Successful remediation technique must decrease the cement porosity, seal the cracks and decrease the permeability of the shielding. Besides enhancing cement grouts themselves, the research is focusing on remediation technologies for existing shields. The effectiveness of so far used

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injection technologies is very much dependent on the crack geometry and dimensions and not all pores can be blocked against further leaks. Therefore, the search for novel remediation technologies is ongoing.

This paper is focused on the remediation of leaks in the hardened cement of existing CO_2 sequestration wells using electrokinetic nanoparticle injection technique. Nanoparticles are very small in nature and they have an advantage of possible blockage of very small pores in cement which is especially critical for the CO_2 application. Since a wide variety of nanoparticles is potentially useful for the treatment, our aim was to investigate the efficiency of differently sized nanosilica and nanoalumina particles used for the purpose as well as other larger sized micro-particles such as silica fume. Intact samples as well as aged samples were investigated to mimic severely cracked and distressed cement shielding.

1.1. Well cementing

In the last 20 years, more than 100 projects have successfully transported the CO_2 into the reservoir underground [1]. After the injection, the CO_2 gas is potentially moved upwards or sideways because of pressure difference and buoyancy [2]. In the oil and CO_2 well cementing, the cement slurry is pumped to the bottom of the well through the primary steel casing and goes up into the gap between the casing and a rock formation. The primary cementing consists of placing of the cement into the annular space in order to provide the zonal isolation, i.e. restrict fluid movements between oil and gas formations and support the casing [3]. In the presence of high pressure and temperature the cement hydration is characterized by early setting and higher chemical shrinkage, modified viscosity. A variety of hydration retarders and viscosity modifier can be used [4].

After finishing the well, CO_2 may leak from interfaces, such as the interface of rock and cement, the interface of steel casing and cement, to cement voids and cracks or to cracks in the steel casing [2] (Fig. 1). The cement shielding outside the steel casing is relatively thin (a few inches) due to the limited space in the annulus and is therefore vulnerable to carbonation and other microstructural changes leading also to changes of the overall permeability and mechanical properties [5].

Depending on conditions of potential use, the oil well cement can be categorized into six classes according to the API 10A Standard [6]: A, B, C, D, G and H. Each class can also be divided into three grades: ordinary (O), moderate sulfate-resistant (MSR), and high sulfate-resistant (HSR). The A, B and C classes have to meet requirements of ASTM C465 [7] (similarly to types I, II, and III cements in ASTM C150 [8]). The Class D cement is used for

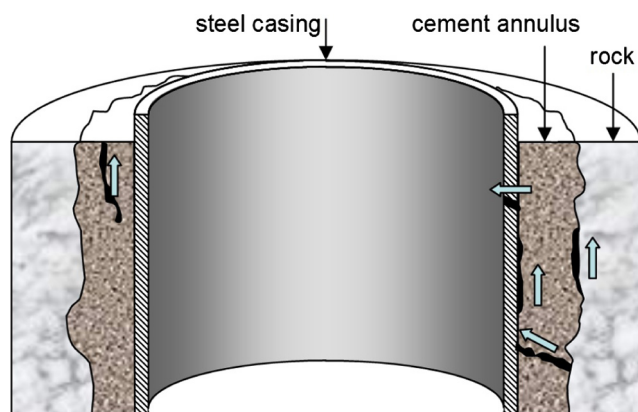


Fig. 1. Possible leaking paths (shown by arrows) for CO_2 from a well (after [2]).

moderately high temperatures and pressures under MSR and HSR grades. Class G and H cements are defined in the same manner by the API standard [6]. The particle size of Class G cement is finer than Class H. Both of them can be used as a basic well cement with MSR and HSR grades. According to the data from Society of Petroleum Engineers (SPE), approximately 80% of projects is adopting Class H and G cement in the U.S. and more than 95% of projects is using Class G cement in the rest of the world since Class G and H are designed to deliver better performance under high temperature and high pressure conditions. Other special (or proprietary) cements were used for oil well cementing in the past, although they are not very common, such as pozzolanic-portland Cement, gypsum cement, microfine cement, expanding cement, calcium aluminate cement, latex cement, resin or plastic cements, Sorel cement, ThermaLock™, EverCRETE™ and others.

The work in this paper is focused on class G well cement grade O.

1.2. Nanoparticles

Nowadays, nanoparticles are commonly used not only in science but also in many industries to deliver enhanced properties of composites, electronics or biosystems. Application of the nanotechnology in the construction sector started just recently, about a ten years ago. Since that time, a lot of research was dedicated to the application of nanoparticles or nanofibers into cementitious systems leading to improving cement matrix elasticity, strength, ductility, electrical conductivity, self-cleaning or self-sensing capabilities [9].

Development of nanomechanical tools such as nanoindenters and atomic force microscopes allowed characterization of many unique nanoscale properties of cement hydration products [10–13] including supplementary materials [14] or high performance concretes [15]. From the mechanical point of view, nanoparticles can either form nuclei for cement phases' hydration, form hydration products and integrate into them, or can serve as fillers to fill voids inside the microstructure leading to reduced porosity [16,17].

From the previous researches, different types of nanoparticles have been used for improving the properties of cementitious materials, such as nanosilica [18], nano-titanium oxide [19], nanoiron [20], nanoalumina [21], nano-calcium carbonate [22] and others. Utilization of carbon nanotubes also raised large attention, e.g. [23]. Nano- TiO_2 was widely reported to be able to deliver self-cleaning (catalytic) property to the concrete, e.g. [19]. Nano Fe_2O_3 reduces electrical resistance of concrete which is further altered by the mechanical load. It enables to develop a self-sensing capability of concrete [24]. Nano- Al_2O_3 is chemically very close to the raw cement phases. It was found to increase frost resistance of concretes [25]. The reactivity of nano-alumina is very high and the early stage cement hydration can be altered with its addition [26]. Enhanced early stage C-S-H nucleation and strength development was found with nano- CaCO_3 addition to cement [27]. Another particle-like structure, the nano-clay, has been utilized in cementitious systems mainly in order to control fresh concrete workability, improve mechanical performance, reduce shrinkage and permeability [28–30].

But the most frequent type of the nanoparticles used in the literature practical studies is the nanosilica due to its chemical compatibility with cement hydration products and due to its beneficial role on enhancing many mechanical, transport and durability properties [18]. Nanosilica was found to increase the resistance of water penetration and control the calcium leaching [31], to increase compressive and flexural strengths [32,9]. Up to 3% cement replacement with nanosilica was proved to decrease water

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