THE EFFECT OF CELLULOSE NANOCRYSTAL (CNC) ON THE WATER PERMEABILITY OF EARLY AGED OIL WELL CEMENT

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Abstract
Well cementing is one of the most crucial steps in any well completion. Oil well cement paste is employed to fill the annulus between the casing string and the well bore. However, since the cementing process takes place at the end of the drilling process, a satisfying and acceptable job may not be performed. When pumped inside the annular space between the casing and the ground formation, oil well cement has to isolate and protect the casing from any kind of damage. Therefore, the durability of the cement paste utilized in oil well cementing is extremely important. In the absence of aggregates, concerns arise both in the short term performance including fluid loss (filtration) and flowability, and in the long term as in shrinkage cracking and permeability of the cementitious slurry. Nowadays, various commercial additives are produced and employed in oil well cements to address the durability issues. In this study, cellulose nanocrystal (CNC) is utilized as a replenishable and non-toxic additive to oil well cement paste, in order to reduce the permeability of the system. Early aged hollow cylindrical specimens dosed with CNC were tested by using a pressurized permeability cell. Furthermore, the water permeability of the specimens were evaluated using Darcy's law for laminar flow. The results were then compared to the water permeability of neat oil well cement paste with no additive.

Keywords:
Oil well cement paste; Permeability; Cellulose nanocrystal; Durability

1 INTRODUCTION

During the past few decades, oil consumption has increased significantly, especially from 1964 to 2008 [Yahaba 2010]. This is mainly due to the fact that today, modern technology and culture is very much dependent on oil and oil-related products, although alternative renewable energy sources have propagated their way into human lives. The limited amount of oil present on earth has gradually forced everyone to extract, place and consume it properly, with the least time, energy and money wasted on this path. Thus, a large amount of money has been used in the oil industry to introduce and invent appropriate, suitable and advanced technologies to the address this issue [Shahriar 2011].

In order to adequately design an oil well, different aspects, dimensions and parameters should be considered and addressed within the design. A poorly designed oil well might lead to incidents such as oil spill or other environmental disasters (due to toxic substances) [Shahriar 2011]. Well cementing is one of the most crucial and important steps in any well completion. However, since it takes place at the end of the drilling process, a satisfying and acceptable job is rarely done. Hence, a large and significant amount of time and energy is then spent in order to do the required corrections or retrofitting the well in some cases.

In the cementing process, cement is used to fill the annular space between the casing string and the ground formation within the drilled hole. The cement used in an oil well has exclusive functions to perform. These include restricting the movement of hydrocarbons and/or water in between the permeable zones, providing a suitable mechanical support for the casing string, protecting the casing from any sort of physical damage including corrosion, and supporting the well-bore walls in order to prevent collapse of formation. Note that the difference between construction cement and oil well cement is that there is no aggregate added to oil well cement and also a large volume of water is used in oil well cement, in order to make the slurry pump-able. A vast number of additives are nowadays available to meet and achieve any kind of desired characteristics.

Durability is one of the main concerns when dealing with any kind of cementitious material or specimen. In structural applications of cementitious materials, maximum load and strength limits are rarely witnessed, therefore durability of the concrete and the reinforcement within the concrete plays a significant role in the failure of structures. Stressed or unstressed, cracks will be observed on any cementitious member.

Transport and penetration of different types of harmful fluids into the cementitious member will eventually lead to the failure of the member. Therefore, permeability of any cementitious material, is one of the key factors affecting its durability. Permeability of a concrete or cementitious sample can be defined as the ease with which liquids, gases and other aggressive ions penetrate the sample. As mentioned by Zhang [Zhang 2011], a higher permeability leads to a greater penetration of aggressive fluids or even water into concrete, which will eventually cause damage and deterioration. Therefore, a concrete with a lower permeability is basically accepted as a more durable concrete.

While pumped inside the annular space between the casing and the ground formation, oil well cement has to isolate and protect the casing from any kind of damage. Therefore, the durability of the cement paste utilized in oil well cementing is extremely important to any individual involved in the oil industry. In the absence of aggregates, concerns arise both in the short term performance including fluid loss (filtration) and flowability, and in the long term as in shrinkage cracking and permeability of the cementitious slurry.

Nowadays, various commercial additives are produced and employed in oil well cements to address the durability issues. In this study, cellulose nanocrystal (CNC) is utilized as a novel and non-toxic additive to oil well cement pastes. This additive is widely used in different industrial applications.

2 MATERIALS AND PREPARATION

2.1 Materials

Oil well cement (Class G)

The cement in mind for this experimental study is class G cement, based on the American Petroleum Institute (API) classification, specification 10A for oil well cements [API 2010]. Class G cement is comparable to ASTM Type II or Type V Portland cement. It is recommended to use a water-to-cement ratio of 0.44 for this type of cement. Tables 1 and 2, describe the physical properties and chemical composition of this type of cement.

Tab. 1: Physical properties of Class G cement (prepared by Lafarge Canada, December 8th, 2015)

Physical Analysis	
Thickening Time (Schedule 5)	99 min.
Max. Consis. 15-30 min.	23 Bc
Fineness 45 μm sieve	93.9%
Blaine	311 m^2/kg
Free Fluid	4.4 %

Cellulose nanocrystal (CNC)

Cellulose nanocrystals are rod shaped nanoparticles derived from cellulose which may be referred to as cellulose whiskers. There has been a significant trend in employing and utilizing CNC in many research areas due to its unique strength, optical and surface properties. The applications of CNC varies from case to case. In some cases it has been used in drug industry whereas the construction industry has also had its share. There are different methods of producing and preparing cellulose nanocrystals nowadays. In their experimental work, Bondeson and colleagues prepared some rod shaped cellulose nanocrystals by acid hydrolysis of dissolving pulp or cotton with 65% concentrated sulfuric acid [Bondeson 2006]. The outcome of their experimental work was preparation and production of certain cellulose nanocrystals with a width of generally 5-10 nm and a length of 100-300 nm. In this study, the aspect ratio or the shape parameter (length/diameter) of the CNC particles are in between 10-60. Furthermore, it is understood that the rod shaped cellulose nanocrystal particles in aqueous solutions have negative electrical charges. This could be explained as a result of the formation of sulfate groups on their surface, as described by Boluk et al. [Boluk 2011]. Cellulose nanocrystals are also widely employed as reinforcing agents in nanocomposites, electro-optical materials, bio carrier, etc. due to their low cost, availability, inherent renewability, nanoscale dimension, unique morphology, light weight, sustainability and abundance. Note that basically, properties of cellulose nanocrystal is closely related to their structure, size and surface charge.

Tab. 2: Chemical composition of Class G cement (prepared by Lafarge Canada, December 8th, 2015)

Chemical Analysis	
Silica (SiO_2)	20.9%
Alumina (Al_2O_3)	3.8%
Iron Oxide (Fe_2O_3)	4.7%
Calcium Oxide, Total (TCaO)	62.9%
Magnesium Oxide (MgO)	4.5%
Sulphur Trioxide (SO_3)	2.6%
Loss on Ignition	0.66%
Insoluble Residue	0.13%
Equivalent Alkali (as Na_2O)	0.48%
C3S	57.9%
C2S	16.1%
C3A	2.0%
C4AF	14.3%
C4AF + 2X C3A	18.3%

Nowadays, mechanical high shear disintegration and high pressure homogenization are used to isolate nanofibrillated cellulose from raw commercial pulp and straw. Venere described cellulose nanocrystal as one of the most novel biomaterials that are employed and utilized in a wide range such as structural components of electronic sensors, water purification filters, and also the strengthening of construction materials [Venere 2013]. In order to have a better understanding of cellulose nanocrystals, one should know that a cellulose molecule has an extremely complex hydrogen-bonding network with multiple isotropic and anisotropic phases, as elaborated by Dufresne [Dufresne 2012]. The fibrils (substructure of cellulose) are orientated in the same direction in an isotropic phase where as in an anisotropic phase, there are several layers of isotropic phases stacked upon each other to form a fibril layer in different orientations [Habibi 2010]. This is mainly important because these isotropic and anisotropic phases impact and influence the physical properties of cellulose.

2.2 Preparation

Oil well cement paste

The paste was initially formulated based on a mixture of water and oil well cement (Class G). Furthermore, cellulose nanocrystal (CNC) particles were added in form of an aqueous solution. As described earlier, the water-to-cement ratio selected for this purpose was 0.44 based on the API specification 10A [API 2010]. For the mixing process, a high shear cement (concrete) mixer was utilized and the mixing took place in a noticeably high speed. In this process, first the amount of water was calculated based on the water-to-cement ratio. This amount was then used to evaluate the desired amount of CNC. Note that only a dosage of 1% w/v of water of CNC has been used in this experimental study. Furthermore, as described earlier, the CNC particles were mixed with an adequate amount of water (deducted from the total amount of water so that the water-to-cement ratio would not change). After mixing the cement powder with the remaining water (while the mixer is turned on), the CNC solution was added to the high shear mixer.

Fig. 1: Prepared cementitious slurry.

Note that is this experimental study, two different type of samples were designed and prepared in the form of hollow cylinders: (1) samples cast from cement and water only (referred to as C+W in this paper) and (2) samples cast from the combination of cement, water and CNC (referred to as C+W+CNC in this paper). The inside and outside diameter of these cylinders were 50 mm and 100 mm respectively, with a specimen height of 200 mm. Ultimately, the prepared specimens were cured in a humidity room for a period of 1 week prior to testing. Fig. 2 below demonstrates a prepared hollow cylindrical sample which has been demolded using a hydraulic jack and cured for a week and it is ready to be tested.

Fig. 2: Hollow cylindrical samples prepared.

3 MEASUREMENT PROCEDURE

3.1 Flow rate measurement

The specimens were tested by using a pressurized permeability cell developed by Hoseini et al. at the University of Alberta, which has been adapted from Biparva's apparatus [Hoseini 2009]. However, in this research, the permeability test was not executed under load and the specimens remained unstressed. The test setup is demonstrated below in Fig 3. By utilizing this permeability test setup, in this proposed method, pressurized water (approximately 100 psi ≈ 0.69 MPa) was introduced to the outer wall of the cylindrical specimens (inside the permeability cell). Note that the specimens were sealed (by using silicon) within the permeability cell, to prevent leakage. Consequently, the water permeated through the specimen and eventually the mass of the outflow was collected in a beaker which had been rested on top of a sensitive weighing scale. The scale was connected to a computer and real-time measurement and recording of the outflow mass was performed. Note that in this method, the flow was monitored until a steady-state condition was reached.

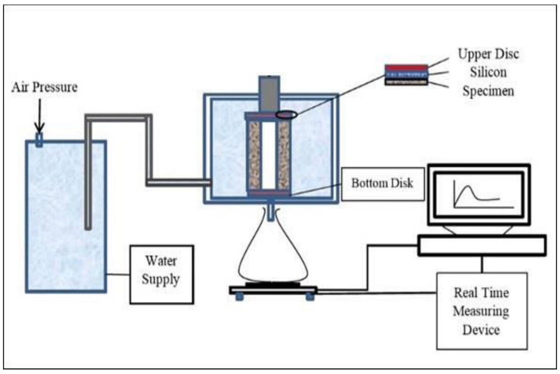

Fig. 3: Schematic diagram of the permeability test setup employed in this study [Hoseini 2009].

3.2 Permeability measurement

After reaching the steady state condition on each sample (usually about 2-3 hours after starting the test), the mass flow rate was evaluated and by utilizing Darcy's law for laminar flow, the water permeability of each cementitious sample was evaluated.

4 RESULTS AND DISCUSSION

4.1 Mass flow rate

After performing the experiment on the specimens with and without cellulose nanocrystals, the mass flow rate profile of the cementitious specimens were obtained as below. Figure 4-1 demonstrates the flow rate profile of the neat oil well cement paste, which has no additives and also contains no cellulose nanocrystals (CNC) where as in Figure 4-2 the flow rate profile of the cement paste including cellulose nanocrystals (CNC) is illustrated. Based on the curves and the results obtained, it was concluded that the oil well cement paste samples containing cellulose nanocrystals reached the steady state condition at a much lower flow rate compared to the neat oil well cement paste samples.

As observed in Fig. 4, the mass flow rate of the cementitious sample with CNC was significantly lower than the sample without CNC. Also, the sample with CNC reached the steady state condition faster.

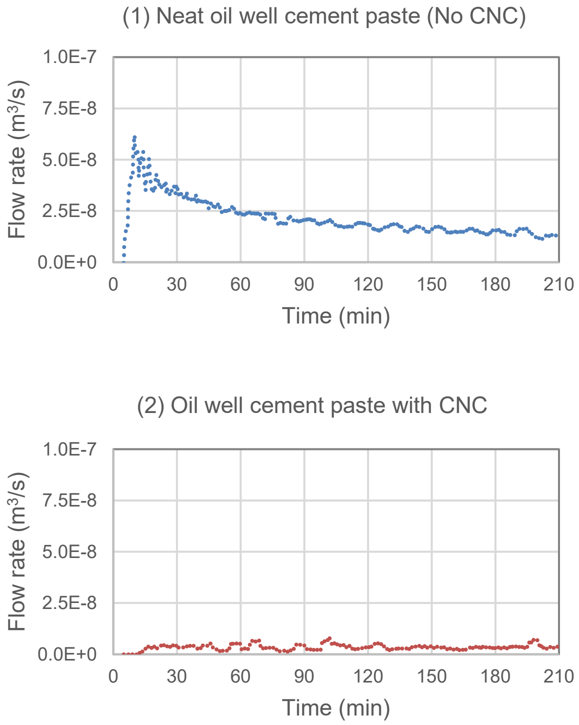

Fig. 4: Mass flow rate profile of oil well cement paste samples: (1) without CNC, (2) with CNC.

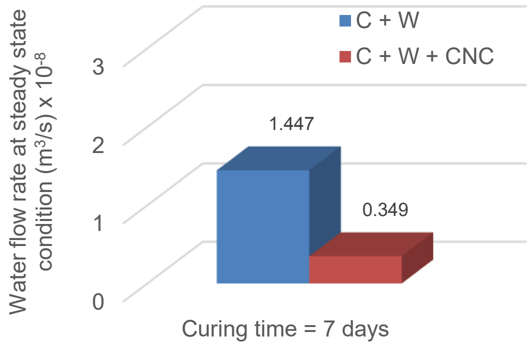

Fig. 5: Flow rate comparison between samples with and without CNC.

4.2 Water permeability

Furthermore, based on the flow rate (Q) obtained in the previous section, the water permeability coefficient of the specimens were calculated according to Darcy's law for laminar flow.

$$k_w = k_i \left(\frac{\rho . g}{\mu}\right) \quad (1)$$

$$ki = \left(\frac{Q.\mu.L}{A.\Delta P}\right) \quad (2)$$

Where:

k_w: water permeability coefficient (m/s);

k_i: intrinsic permeability (m^2);

ρ: density of water (kg/m^3);

g: gravitational acceleration (m/s^2);

μ: viscosity of water (kg/ms);

Q: rate of water flow (m^3/s);

L: specimen's thickness (m);

A: permeation area (m^2);

ΔP: pressure difference introduced (Pa – N/m^2)

Figure below demonstrates the comparison between the water permeability coefficient of samples with and without CNC.

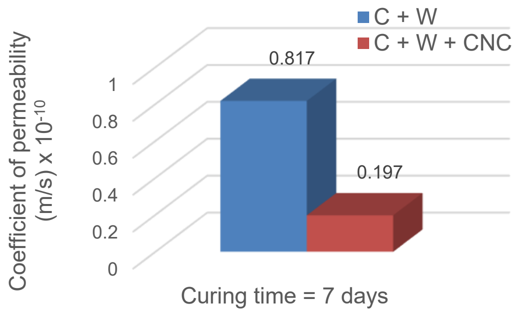

Fig. 6: Coefficient of water permeability (k_w) comparison.

Note that a decrease in the coefficient of water permeability (k_w) was observed by introducing cellulose nanocrystal (CNC) to the mix design. This could be due to the fact that CNC particles may have changed the pore structure and pore size distribution of the specimen. Also, previous studies show that the addition of CNC will increase the strength of the cementitious system [Cao 2015]. This increase in strength was also observed in this study whereas after 7 days of curing, the compressive strength of neat oil well cement (without CNC) samples was 19 MPa whereas the compressive strength of the samples with CNC was 26 MPa. Hence, the decrease in permeability could be related to this change of strength. CNC particles in the paste tend to host hydration and act as a seeding agent. This phenomenon is believed to lead towards an increase in hydration and also in strength development.

5 CONCLUSION

In this experimental study, the water permeability of oil well cement paste was investigated in order to understand the effect of cellulose nanocrystal (CNC) particles on it. Hollow cylindrical specimens were prepared from 2 different formulations, one excluding CNC and the other including the nanomaterial. The samples were cured for 7 days after demolding, prior to the permeability test. The following specific findings were observed:

- The addition of CNC particles led to a decrease in the flow rate of the cementitious system.
- Introducing CNC particles, significantly reduced the water permeability of the cementitious samples.
- This was clearly observed in all the samples tested, verifying the consistency of the results.

6 ACKNOWLEDGMENTS

The authors would like to express their gratitude to Alberta Innovates Technology Futures (AITF), Alberta Innovates Bio Solutions, Alberta Pacific Forest Industries (Alpac) and Lafarge Canada.

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