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# Highly concentrated carbon nanotube admixture for nano-fiber reinforced cementitious materials

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ABSTRACT

The use of effectively dispersed multiwalled carbon nanotube (MWCNT)/aqueous/surfactant suspensions in cement based materials have been shown to substantially improve their mechanical properties. The produced MWCNT suspensions have a high aqueous content, which corresponds to the mixing water. In the present work, a method for preparing highly concentrated MWCNT suspensions is presented, thus reducing the volume of the resulting admixture that is required in cement based materials. A centrifugal process, that uses two different ultracentrifuge rotors, was employed to reduce the quantity of water in the suspensions. Optical absorbance spectroscopy shows that the ultracentrifugation process increases the concentration of the MWCNT suspensions by a factor of 5. Using the highly concentrated MWCNT suspensions following dilution results in nanocomposites with mechanical properties that are comparable to the performance of samples prepared using the non-concentrated suspensions. These results verify that the ultracentrifugation concentration method successfully preserves the solubility of the MWCNT suspensions without affecting the reinforcing properties of the admixture. In this manner, the ultracentrifugation concentration method may constitute an effective preparation step for large-scale implementation of MWCNT admixtures.



## 1. Introduction

The utilization of highly dispersed multi-walled carbon nanotubes (MWCNTs) in cementitious materials has shown to substantially improve the mechanical and other properties of the cementitious matrix. It was found that by adding a very low amount of MWCNTs or carbon nanofibers (CNFs), at concentrations of 0.025–0.08 wt.% of cement, the strength and stiffness of cement beams increases up to 50% and 70%, respectively [1–6]. The application of low concentration of MWCNTs and CNFs enables the control of matrix cracks at the nanoscale level [7]. Also, at such low concentrations of CNTs, the cost of CNT reinforced concrete is comparable to or even lower than that of fiber reinforced concrete, suggesting that of the use of CNTs in concrete is economically feasible. In addition to the benefits of reinforcement, autogenous shrinkage tests have demonstrated that MWCNTs can also have beneficial effects on the early age strain capacity of cementitious materials, which leads to an improved durability of the cement matrix [1].

The current preparation method of MWCNT suspensions for use in cementitious materials includes a simple one step technique, which involves the application of ultrasonic energy and the use of a commercially available surfactant [2,8]. The MWCNT suspensions prepared by this method have a high aqueous content of 98.68%, which corresponds to the mixing water. By concentrating the MWCNT suspensions, this high aqueous content is reduced, which decreases the volume and cost of the transportation and delivery of these admixtures in large-scale cement applications. Therefore, the development of a technique that will effectively concentrate the MWCNT suspensions, without compromising their performance in cementitious materials following subsequent aqueous dilution, is essential.

A number of solution-phase processes exist, where carbon nanomaterials, such as CNTs and graphene flakes, are concentrated by the removal of their solvent. This can be achieved by precipitation via addition of organic solvent and vacuum filtration [9], solvent exchange utilizing polymer–organic solvent [10] and sedimentation and decantation by ultracentrifugation [11]. Among these processes, the ultracentrifugation method is ideal for applications where the presence of organic solvents will become a hindrance. Ultracentrifugation process has been proven as a facile method to increase the concentration of CNTs in aqueous solutions

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prior to being used in a technique called density gradient ultracentrifugation (DGU) [12–16]. In DGU, a preparative ultracentrifugation process called pelleting, generally used to sediment solidified organic compounds out of solutions, has been adapted from biology [17,18] to maximize the yield of process. During this technique, nanomaterials in aqueous suspensions are presented under a centrifugal force inside a tube and travel towards the bottom at certain sedimentation rate, forming a highly concentrated region which can be recovered after decantation (Fig. 1).

The objective of this research is to develop a method to effectively concentrate MWCNT suspensions for cementitious materials. To accomplish this, the aforementioned ultracentrifugation method was adapted and employed to reduce the amount of water in the MWCNT/water/surfactant suspension, thus increasing the MWCNT concentration. The effect of two ultracentrifuge rotors, the swing bucket and the fixed angle rotor, on developing highly concentrated MWCNT suspensions was investigated. Optical absorbance spectroscopy was used to evaluate the concentration of the suspensions after ultracentrifugation. Cementitious nanocomposite samples were prepared using the highly concentrated MWCNT suspensions, after they were diluted in the mixing water. Dilution was conducted by simply adding water to the suspensions prior to mixing with cement. The mechanical properties, i.e. flexural strength and modulus of elasticity, of the nanocomposites produced with the highly concentrated/diluted MWCNT suspensions were evaluated and compared with the properties exhibited by the nanocomposites produced with the original, non-concentrated MWCNT suspensions.

## 2. Experimental study

### 2.1. Method of MWCNT concentration

Purified multiwalled carbon nanotubes (MWCNTs), produced by the chemical vapor deposition method (CVD), with a diameter of ∼20–40 nm, length of ∼10–30 μm and purity >95% were used as received. The suspensions were prepared using MWCNTs at a concentration of 0.26 wt.%. To homogeneously disperse the MWCNTs in the mixing water, they were added in an aqueous solution containing a surfactant to MWCNTs weight ratio of 4.0. The mixture was then ultrasonicated using a 500 W cup-horn high intensity ultrasonic processor with a 13 mm diameter tip, operating at 50% of its maximum amplitude delivering 1900–2100 J/min. Energy was applied in cycles of 20 s to prevent the suspensions from overheating.

#### 2.1.1. Laboratory scale concentration method for MWCNT suspension

Ultracentrifuges are typically available with a wide variety of rotors. The most widely used configurations of rotors are the swing bucket and the fixed angle. The swing bucket rotors allow the tubes to hang on hinges so that they reorient to the horizontal as the rotor initially accelerates [19]. During ultracentrifugation the material travels down the entire length of the centrifuge through the media within the tube [20]. Fixed angle rotors are made of a single block of metal and hold the tubes in cavities bored at a predetermined angle [19]. The materials are forced against the side of the centrifuge tube, and then slide down the wall of the tube [20].

In this study, following dispersion, the suspensions were concentrated by ultracentrifugation using both a swing bucket and a fixed angle rotor. Initially, sedimentation of the MWCNTs was explored using a swing bucket SW41 rotor (Beckman-Coulter) with ambient temperature at 22 °C and at 41,000 rpm using centrifuge tubes that can hold 12 ml of suspension. In the aforementioned DGU process, OptiPrep containing 60% (w/v) of iodixanol was used as the density medium for the concentration process to increase the viscosity of concentrated dispersion for the subsequent density gradient separations. However, since the MWCNTs used have a density of 2.1 g/ml which is higher than the density of OptiPrep (1.32 g/ml) and furthermore there is no need for their viscosity adjustment, the suspensions with uniform density were simply added to the centrifugation tubes. The sedimentation of the MWCNTs in the centrifugation tube was monitored at 30, 45 and 60 min. Fig. 2 shows a photograph of the centrifuged tubes for various durations of ultracentrifugation. At the durations of 30 and 45 min, it was observed that the nanotubes started to concentrate at the bottom of the tube. At 60 min, the suspension was fully sedimented at the bottom of the tube.

After centrifugation, the supernatant solution was decanted down to approximately 2 cm from the bottom of the tube, enabling retrieval of 2.5 ml of concentrated suspension, which corresponds to about 20% of the total volume of the suspension. MWCNT concentration in the solution before and after centrifugation was quantified using optical absorbance spectroscopy (OAS). It was observed that the absorption of the suspension after centrifugation was lower than the sample before centrifugation. A close observation of the samples revealed the formation of a solid pellet of MWCNTs at the bottom of the tube, which may be attributed to the agglomeration of the MWCNTs. Several researchers have reported that the presence of MWCNTs agglomerates causes a decrease in the absorption spectrum because the MWCNTs bundles do not optically absorb in the wavelength region between 200 and 1200 nm [21]. The formation of the pellet caused by the agglomeration of the MWCNs might therefore be a possible explanation for the observed reduction of the absorption.

In an optimized experiment, the MWCNT suspension was ultracentrifuged at 20,500 rpm and it was observed that the MWCNTs

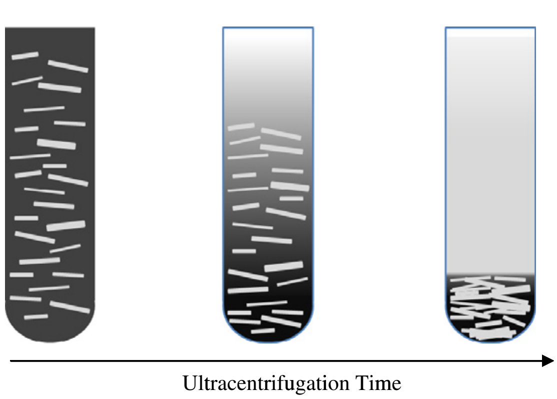


**Fig. 1.** Schematic figure showing the progression of sedimentation of nanomaterials inside a tube during ultracentrifugation.

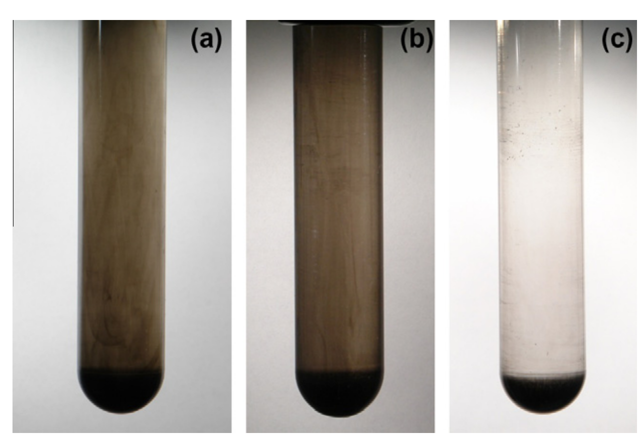


**Fig. 2.** MWCNTs suspensions ultracentrifuged for (a) 30 min, (b) 45 min and (c) 60 min.