THE INFLUENCE OF CELLULOSE NANOCRYSTALS ON THE FRESH PROPERTIES OF OIL WELL CEMENT PASTE

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ABSTRACT
Cementing is one of the most important and crucial stages in any well completion, to fill the annulus between the casing string and the well bore. 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. Hence, the rheology of the oil-well cement slurry assumes great importance. This report is on a feasibility study, that examines the use of innovative cellulose-based nanomaterials on the flow properties of the resulting cementitious system. The cementitious slurry developed in this research is composed of water, class G oil well cement, bentonite and cellulose nanocrystals (CNC). The rheological behavior of different types of colloidal suspension was assessed first on a mixture of water, bentonite and CNC. The parameters assessed were the yield shear stress, flowability and the viscosity among others. Significant changes in viscosity and shear strain were observed due to the addition of the CNC. Subsequently, the results from the rheology testing on colloidal suspensions were utilized to anticipate and predict the behavior of cementitious systems with CNC. Thus, the workability of fresh cementitious systems developed based on these colloids was assessed. Based on the findings in this study, the addition of CNC to colloids leads to shear thinning which in turn results in lower slump for the cement based slurry.

Keywords: Oil Well Cement, Cellulose Nanocrystal (CNC), Rheology, Fresh Cement Paste, Yield Shear Stress, Flow Behaviour, Colloidal Suspensions

1. INTRODUCTION
1.1. General information
The cement used in an oil well has exclusive functions to perform. These include restricting the movement of the fluid 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. Cementing is one of the most crucial and important steps in well completion, but since it takes place at the end of drilling, a good 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. This cement is used to fill in the annulus between the casing string and the drilled hole. Following the functions listed above, the purpose of this (oil well cementing) could be summarized in three general points: a) zone isolation and segregation, b) corrosion control of the casing, and c) formation stability and pipe strength development. Note that the difference between construction cement and oil well cement is that there is no aggregate added to oil well cement and further a large volume of water is used in oil well cement, in order to make the slurry pump-able.

1.2. History of oil well cement

The cement slurry, which is pumped into the oil or gas wells, is a combination of Portland cement, special additives and water [1]. Note that these special additives are employed to control certain characteristics of the slurry, such as thickening time, compressive strength, density etc. Portland cement plays a key role in casting and producing oil well cement and, nine API classes of oil well cements are recognized based on the usage and the purpose of the well and all the influencing factors [2]. These influencing factors could be summarized as the depth of the well, the special properties required, resistance to sulfate attack, early age strength gain, pressure and temperature among many others. Aside from the nine API oil well cement classes available commercially, some other types of cement may also be used in this industry [2]. These cements do not fall into any specific category or classification. They are a combination of Portland cement and suitable additives.

1.3. Rheological behaviour of oil well cement

Fluid loss is an inevitable part of the cementing process during well completion. One will ideally not want a large amount of fluid loss, since the slurry becomes significantly viscous and difficult to pump. Neat cement paste (i.e. with no special additives) usually demonstrates a fluid loss rate of approximately 2000 cc/hour [3,4]) or higher. It has been demonstrated that almost 50% of this water loss is due to filtration, even though the presence of mud cake decreases the filtration [3,4]. In order to reduce the amount of filtration, some special additives are usually added to the cement slurry, such as bentonite or organic colloids like carboxymethyl hydroxyethyl cellulose (CMHEC). Generally, a cement slurry with a high density results in a higher filtration loss. Basically, in permeable sections or formations, the loss of cement filtrate will result in the dehydration of parts of the cement slurry. Eventually, this prevents the flow and influences it negatively. As a result, a decrease in the cement flow rate is observed and hence, the ability and capability of the cement in consideration will be partially damaged [3,4,5]. There could also be some circulating pressure restricting the annular space that could possibly break down the formation. Note that the presence of relatively thin mud cake reduces the filtration.

The rheology of the cement slurry is therefore an important element in its design. Based on existing data, one notes that oil well cement slurries have high viscosity and this significantly reduces the pumping rate. In order to tune the rheology, certain viscosity modifying admixtures are usually added to the cement slurry. Further, additives are used in oil well cementing in order to minimize cement dehydration in the annulus, reduce gas migration, improve bonding and also minimize the formation damage to some extent. Basically, fluid loss additives prevent leak-off of water into rock, maintain key characteristics such as thickening time, rheology, and strength development and, avoid build-up of cement filter cake. Some of the most common fluid loss additives are cellulose derivatives, synthetic polymers and latex. Generally, cement additives are divided in to two classifications based on their reaction type: chemical and nonchemical. Chemical additives alter the hydration (water intake) of the cement while the nonchemical additives influence the density of the cement or control its fluid loss. In the study reported here, the cellulose derivative (CNC and CMC) additives employed may be considered as chemical additives, since they deal with the hydration of the slurry by absorbing the water and releasing it gradually.
2. EXPERIMENTAL DETAILS

2.1. Materials

As stated earlier above, the cementitious slurry developed in this research is composed of water, class G oil well cement, Bentonite and Cellulose Nanocrystals (CNC). Information regarding each of these specific materials used in this system is presented below.

2.1.1. Oil well cement Type G

The cement used here was a Type G cement, based on the American Petroleum Institute (API) classification, specification 10A for oil well cements [2]. This cement was recommended to be used with a water/cement ratio of 0.44 and it was comparable to ASTM Type II or Type V Portland cement.

2.1.2. 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 [6]. 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 research, the aspect ratio or the shape parameter (length/diameter) of the CNC particles were 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. [7]. 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, nanoscaled 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. Nowadays, mechanical high shear disintegration and high pressure homogenization were used to isolatenanofibrillated cellulose from raw commercial pulp and straw.

Venere [8] 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. 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 in 2012 [9]. 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 [10]. This is mainly important because these isotropic and anisotropic phases impact and influence the physical properties of cellulose.
2.1.3. **Carboxymethyl cellulose (CMC)**

Carboxymethyl cellulose (CMC) is one of the organic additives with a molecular weight of generally 700 kBa which may improve the rheological properties of clay suspensions, thus there is a significant industrial interest in it [11]. Given that bentonite was used in suspensions examined here, the addition of carboxymethyl cellulose (CMC) was deemed suitable for modifying the viscosity of the suspension by controlling the mud flow loss and also maintaining adequate flow properties at high temperature and pressure [12]. It is also used in producing commonly used products such as creams, lotions and toothpastes since it influences and improves the binding, thickening and stabilizing properties of the product [12]. It is frequently employed in drilling fluid industries due to its suitable price to performance ratio.

2.1.4. **Bentonite**

Generally, clay minerals are used in industries such as ceramic production, drilling fluids, moulding sands, and cementing. An important reason is their ability to provide adequate particle dispersion in order to have a uniform and stable system [13]. In some cases, clay particles may become aggregated. This aggregation which may occur under some specific circumstances and varying conditions of pressure and temperature will eventually vary the flow behavior [14]. As mentioned above in this article, there are different types of additives usually added to bentonite in order to stabilize it and prevent any sort of aggregation. In this case CMC was added primarily, but since the bentonite provided already had some industrial additives, CMC was eventually removed from the mix design. Note that bentonite was obtained in the form of a gel (Wyoming gel) for this study and the latter is widely available. As for the flow behavior of any type of clay suspension, the relationship between the shear stress ($\tau$) and the shear rate ($\gamma$) is commonly analyzed. Based on the plot of shear stress and shear rate (consistency curve), four different types of flow exist: Newtonian, Pseudoplastic, Bingham Plastic and Dilatant. The aqueous clay suspensions are basically described in accordance to the Bingham theory of plastic flow [15]. There are many models to describe the rheological behavior of clay suspensions, however, it is understood that the Herschel-Bulkley equation is the most suitable model:

$$\tau = \tau_f + K\gamma^n$$

Where $K$ is a measure of the consistency of the fluid and $n$ is the flow behavior index that is obtained by measuring the decrease of the effective viscosity with respect to shear rate [16]. In this model, the suspension is considered to have an initial yield stress at some low shear rate and it will then demonstrate
a shear-thinning behavior at higher shear rates [14]. Note that based on the previous studies, water-bentonite dispersions at a concentration of more than 1% generally display a yield stress that is the stress above which the material flows like a viscous fluid [17].

2.2. Preparation

There were two stages for preparing the desired materials in this research. In the first stage, the colloidal suspensions were made on which the rheology tests were carried out. In the second stage, the cementitious slurry based on the previously prepared were produced for workability assessment.

2.2.1. Colloidal suspensions

At this stage of the experiment, the suspensions were mainly divided in to two groups in terms of the constituent materials: 1) suspension including CMC and 2) suspensions excluding CMC. The basic mix included water, bentonite and cellulose nanocrystals (CNC). Throughout this research program, the dosage of bentonite used was 3% (w/v of water) whereas the dosage of CNC and CMC (when used) were 1% and 0.25% respectively. At first, each one of these constituent materials was mixed with water by a high shear mixer and at the final stage of mixing, all of them were mixed together, in order to get a better dispersion and a more uniform system.

![Figure 2. Mixing process of the colloidal suspension (left) and the prepared samples (right)](image)

After preparing the required samples, they were stored inside the refrigerator until the time of testing. Rheological tests were performed on each sample for at least three times in order to achieve a more reliable result.

2.2.2. Cementitious system (slurry)

The second stage in the preparation of the specimens was to design and prepare the cementitious slurry mix. The paste was initially based on a mixture of water and oil well cement (class G). Furthermore, the bentonite and cellulose nanocrystals (CNC) were added in form of an aqueous solution. The water/cement ratio selected for this purpose was 0.44 based on the API specification 10A [2].
Note that CMC was excluded at this stage of the experiment, since the bentonite gel was deemed stable enough and also, it allowed the authors to investigate the influence of CNC solely. Adding bentonite is justified as follows: After the drilling process is finished, the cementing will begin but one cannot rule out the contamination by bentonite inside the well. Thus, the cement paste will eventually mix with the residual bentonite. As a result, nowadays, it is common to take the bentonite contamination into account while designing the oil well cement slurry.

Therefore, in this study it was decided to use a dosage of 3% (w/v of water) of bentonite in the mixes in mind, in order to take the contamination in practice, into account. For this mixing process, a high shear cement (concrete) mixer was utilized and the mixing process took place in a noticeably high speed. In this process, first the amount of water was calculated based on the water/cement ratio. This amount was then used to evaluate the desired amount of Bentonite and CNC. Note that only a dosage of 1% (w/v of water) CNC was used in this stage as well. Furthermore, as described earlier, the bentonite and CNC powders were individually mixed with an adequate amount of water (deducted from the total amount of water so that the water/cement ratio would not change), precisely in the same manner in which they were mixed originally as a colloidal suspension. Then, after mixing the cement powder with the remaining water, while the mixer was on, the bentonite and CNC solutions were added to the EIRICH mixer. At this stage of the experiment four different samples were designed and prepared: 1) cement and water only, 2) cement, water and bentonite, 3) cement, water and CNC and 4) cement, water, bentonite and CNC. Following the preparation of the cementitious samples, the fresh paste was then tested in the laboratory in order to investigate and understand its flow behavior.

![Figure 3. EIRICH high shear mixer (left) and the prepared cementitious slurry samples (right)](image)

### 2.3. Rheology testing of colloidal suspensions

A small amount of the desired sample was placed on the rheometer in order to perform the test. For this purpose, an AR G2 (TA Instrument) rheometer was utilized. The most important fact in this test was to select the appropriate geometry for the rheometer. Hence, in this scenario, a calibrated cone (SST) geometry was selected with a cone angle of 2 degrees and a diameter of 60 mm. In order to perform the test, the rheometer was turned on alongside with the water pump and air pipes attached to it.

Then the selected geometry which has to be clean is assembled to the machine in order to run the experiment. Prior to running the experiment, the instrument should be mapped and cleaned as well. The
specific amount of the prepared sample is then placed on the surface of the rheometer. After finalizing all the settings on the TA software (connecting the machine to the computer device in the laboratory), a temperature of 25 degrees Celsius is selected while choosing to perform the rheology test in normal pressure. Figure 4 demonstrates the cone and plate utilized in the rheometer while the rheology results for the designed samples are presented further in this article.

Figure 4. Schematic figure of the cone and plate utilized in AR G2 rheometer (TA instruments)

2.4. Testing of the fresh cementitious slurry (paste)

The second stage of testing was to investigate the flow behaviour and workability of the fresh cement paste developed. As stated earlier, four different types of samples were prepared in order to investigate. Two method of testing was considered to understand the flow behaviour of the samples. A mini slump test was performed initially. Furthermore, the flow table was utilized to measure the yield stress of the cementitious paste. These two experiments were conducted in order to understand the flow behavior of the paste under gravity and also applied load (number of blows for the flow table test). The methods are elaborated below.

2.4.1. Mini slump test

Immediately after the mixer was turned off, an adequate amount of paste was poured into the mini slump cylinder. Then, the cylinder was raised in order to measure the diameter of the cementitious paste. Each time, six diameter readings were taken from different point of views in order to have a more precise and reliable measure. Also, the height of the paste was also measured three times in each case, even though not significantly large, in order to have a better comparison. This test was performed to understand the yield stress of different cementitious systems and their flow behavior under gravity and no external load.

2.4.2. Flow table

The second experiment conducted on the fresh cementitious systems, was the flow table. This experiment was performed in order to understand the rheological and flow behavior of the fresh paste under applied load (not just gravity as before). Prior to starting the experiment, it was anticipated that the pastes will not withstand twenty-five blows on the flow table (as stated in the standards). Thus, while testing the first mix
(cement and water – no additives) the diameter of the paste on the flow table was measured when fully spread. This was just after a couple of blows, not the standard twenty-five. In this analysis the number of blows to spread the paste fully on the flow table was also taken into account in order to have a better comparison between the mixes. Therefore, in all four mixes, the diameter was measured once after just two blows, then after twenty-five if it could withstand it. Note that, in this experiment, the diameter has been measured in three different point of views to have a more reliable and precise measure. At the end, the height of the paste (elevation from top of the paste to the surface of the flow table) was also measured.

3. RESULTS AND DISCUSSIONS

3.1. Rheological behaviour of colloidal suspensions

Figures 5 and demonstrate a comparison between the rheological parameters as found for the samples under test.

![Figure 5. Comparison of different colloidal samples (1): shear stress vs. shear rate](image)
As seen above, the suspension with no cellulose nanocrystal (CNC) was not stable at low shear rates and an appropriate result for shear rates below 1 (1/s) was not generated for it. Hence, it is observed that the presence of CNC improves the stability of the suspension especially at lower shear rates. Note that the presence of CMC does not improve the stability of the suspension dramatically; however, the viscosity and the shear stress are increased significantly by adding CMC. This might be a disadvantage in the oil well cement industry. Therefore, here is another reason to exclude this material from the cementitious mix design and instead opt for a bentonite gel to ensure dispersion and uniform mixture for oil well application.

3.2. Flow behaviour of the fresh cementitious slurry

As described earlier in section 2.4, two different methods of flowability analysis were considered. The results corresponding to each method of testing is presented below.

3.2.1. Mini slump test results

This test was performed to understand the yield stress of different cementitious systems and their flow behavior under gravity with no external load. The results are presented below.

<table>
<thead>
<tr>
<th>Table 1. Mini slump test results (diameter in mm)</th>
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<tbody>
<tr>
<td>Mix Type</td>
</tr>
<tr>
<td>Reading Attempt 1</td>
</tr>
<tr>
<td>Reading Attempt 2</td>
</tr>
<tr>
<td>Reading Attempt 3</td>
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<tr>
<td>Reading Attempt 4</td>
</tr>
<tr>
<td>Reading Attempt 5</td>
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<tr>
<td>Reading Attempt 6</td>
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<tr>
<td></td>
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<tr>
<td>--------------------------</td>
</tr>
<tr>
<td>Standard Deviation</td>
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<tr>
<td>Average Diameter</td>
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</tbody>
</table>

**Table 2.** Mini slump test results (height in mm)

<table>
<thead>
<tr>
<th>Mix Type</th>
<th>Mix 1 (C+W)</th>
<th>Mix 2 (C+W+B)</th>
<th>Mix 3 (C+W+CNC)</th>
<th>Mix 4 (C+W+B+CNC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reading Attempt 1</td>
<td>14</td>
<td>16</td>
<td>29</td>
<td>35</td>
</tr>
<tr>
<td>Reading Attempt 2</td>
<td>13.5</td>
<td>16.5</td>
<td>30</td>
<td>33</td>
</tr>
<tr>
<td>Reading Attempt 3</td>
<td>13.5</td>
<td>15</td>
<td>30.5</td>
<td>35.5</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.29</td>
<td>0.76</td>
<td>0.76</td>
<td>1.32</td>
</tr>
<tr>
<td>Average Height</td>
<td>13.67 ± 0.29</td>
<td>15.83 ± 0.76</td>
<td>29.83 ± 0.76</td>
<td>34.50 ± 1.32</td>
</tr>
</tbody>
</table>

Note that in the Tables 1-2 above, the mixes are variously denoted C, W, B and CNC. These represent cement, water, centonite and cellulose nanocrystals, respectively. Also, the diameter of the paste (after removing the slump cone) decreased upon adding bentonite and cellulose nanocrystals to the mix. These measurements demonstrate the increase in yield stress of the mix as a result of the two additives. In order to have a better comparison, figure below illustrates the difference between the mixes.

**Figure 7.** Mini slump test results
It is clear from the figure above, that cellulose nanocrystals were more effective than the bentonite added to the conventional mix (consisting of cement and water) in terms of altering the yield stress and the flow behavior of the system. On the other hand, the presence of both, bentonite and cellulose nanocrystals provides the most satisfactory result.

3.2.2. Flow table results

The results for the flow table analysis are displayed in Tables 3-4 below. As shown in Table 4, mixes without CNC could not resist the twenty-five blows on the flow table, while on the other hand after the CNC was introduced to the cementitious system, not only was the diameter significantly lower after only 2 blows, but compared to the other mixes (Table 2), mixes with CNC were able also to withstand the complete twenty-five blow regime on the flow table. This means, the yield stress of the cementitious system with CNC is higher than the pastes with no CNC. Note that in this case as well, the combination of CNC and bentonite was the most desirable in that a higher yield stress is required to cause flow. The figure illustrated below demonstrates a comparison between all four types of mixes, in terms of their paste diameter and height after the flow table test.

<table>
<thead>
<tr>
<th>Table 3. Flow table diameters after 2 blows</th>
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<tbody>
<tr>
<td>Mix Type</td>
</tr>
<tr>
<td>Reading Attempt 1</td>
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<tr>
<td>Reading Attempt 2</td>
</tr>
<tr>
<td>Reading Attempt 3</td>
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<tr>
<td>Standard Deviation</td>
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<td>Average Diameter</td>
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<table>
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<tr>
<th>Table 4. Flow table diameters after 25 blows</th>
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<tbody>
<tr>
<td>Mix Type</td>
</tr>
<tr>
<td>Reading Attempt 1</td>
</tr>
<tr>
<td>Reading Attempt 2</td>
</tr>
<tr>
<td>Reading Attempt 3</td>
</tr>
<tr>
<td>Standard Deviation</td>
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<tr>
<td>Average Diameter</td>
</tr>
</tbody>
</table>

<table>
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<tr>
<th>Table 5. Flow table height of paste after 2 blows</th>
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</thead>
<tbody>
<tr>
<td>Mix Type</td>
</tr>
<tr>
<td>Height of Paste</td>
</tr>
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</table>
Note that, mixes 1 and 2 have a diameter of 255 mm after twenty-five blows (Figure 8). This means that the paste in both cases was fully spread on the flow table, which has a diameter of 255 mm. Therefore, there is no difference between their diameters at the end of this stage. However, after the cellulose nanocrystals were introduced, the paste withstood the twenty-five blow regime, especially when a combination of bentonite and CNC was utilized (Mix 4). Once again, this could be taken as another witness to the desired effect of CNC upon the yield stress of Type G cement based paste.

4. CONCLUDING REMARKS

The rheological behavior of different types of colloidal suspensions were assessed by to examine the effect of bentonite along with cellulose nanocrystals. Significant changes in viscosity and shear strain were observed due to the addition of the CNC. The trend seen with the rheology testing on colloidal suspensions were utilized to anticipate and predict the behavior of cementitious systems with CNC. The following specific findings were observed:

- The rheological parameters indicate that cellulosic nanocrystals increase the viscosity of bentonite suspensions. As well, CNC makes the suspension stable at low shear rates.
- All the suspensions examined here demonstrated a shear-thinning behaviour. This was more manifest in mixes containing CNC.
- Flow tests on cementitious slurry made with the colloidal suspensions and oil well cement illustrate that adding CNC makes for stable slurries that can survive the 25-blow regime. Whereas adding bentonite alone had very minor effect on the flow diameter and height, the addition of CNC significantly stiffened the mix as expected from the associated low shear rate.

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