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FRACTURE PROPERTIES OF CEMENTITIOUS COMPOSITES REINFORCED WITH CARBON NANOFIBERS/NANOTUBES

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Abstract: *The main objective of this work is to determine the mechanical properties of a new cementitious nano-composite material. Carbon nanotubes/nanofibers were synthesized directly on the particle surfaces (Portland cement, fly ash, sand). Mixing these carbon-modified particles with ordinary Portland cement creates a cementitious binder, where the carbon nanofibers are perfectly dispersed in the volume. Previous attempts to create nano-reinforced composite materials suffered from flocculation and improper dispersion of admixed nanofibers. Now, the hybrid material can be intermixed directly with water creating strong and brittle composite.*

Keywords: ***Carbon, nanotubes, mortar, paste, fracture energy***

1. Introduction

The main objective of this work is to determine the mechanical properties of the cement paste/mortar reinforced with carbon nanofibres/nanotubes (CNF/CNT) directly synthesized on the cement and sand particles. The synthesis of the CNF/CNT directly on the particles surface brings the advantage in elimination of the tedious dispersion process. The cement hybrid material (CHM – cement with carbon nanofibers) can be directly mixed with water and/or sand, creating a strong and quasi-brittle composite material. Fig. 1 shows the SEM image of the CHM, the Portland cement particles are completely covered with the CNF.

CNT/CNF reinforcement on the nanoscale brought fruitful results for a variety of materials (Hammel et al., 2004). Previous experiments have shown the twofold increase of paste compressive strength (Nasibulina et al., 2010). This would imply reduction of cementitious binders in ordinary concrete in a similar manner as replacement by supplementary cementitious materials. Unfortunately, several experiments are carried out by physicists, who are unfamiliar with cement science. The consequence is in improperly-conducted experiments which are hardly reproducible in their labs and worldwide. Experimental evidence still presents the basis of scientific approach and the reproducibility forms the stepping stone in science. This is another goal of presented article.

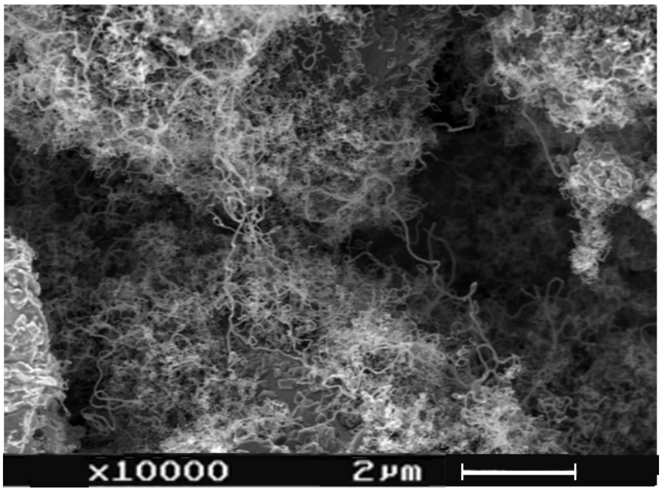

Fig 1. SEM image of the CNF synthesized directly on the cement grains surface. Reprinted from L. Nasibulina et al. (2010).

To elucidate the effect CNF/CNT on surfaces, two batches from CHM and modified sand were prepared. Samples in the first batch were prepared from the CHM and water in the case of paste, or CHM, water and unmodified sand in the case of

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mortar. The second batch was fabricated from ordinary Portland cement, water and sand with surface synthesized carbon nanofibers.

Fracture energies and compressive strengths of these cement-based composites were determined. It was found that for the case of CHM batch, the compressive strength of the cement paste increases with the amount of CHM in the mixture. On the contrary, the compressive strength of mortar decreases with the amount of CHM in the mixture. This phenomenon is partially explained by the ITZ behavior and CHM properties. The measurements on the second batch show almost no change in the fracture energy with the addition of carbon-modified sand. The explanation lies in a small length of the CNF/CNT (about two μm) compared to the length of ITZ (about 20 μm).

2. Materials and methods

2.1. Cement binder, CHM, sand

The cement, CEM I 42.5 R originated from Mokrá, the Czech Republic, was used as the source material for all specimens. Specific Blaine surface had the value of 355 m^2/kg for the coarse cement and 587 m^2/kg for finely-ground cement. The chemical composition is given in the Table 1.

The cement hybrid material (CHM) and the carbon-modified sand were synthesized by L. Nasibulina et al. by the chemical vapor deposition method (Nasibulina et al., 2010). The Portland sulfate-resistant cement (CEM I 42.5N) was used as the base for CNF/CNT growth resulting in CHM, see Table 1 for the chemical composition. In the synthesis, acetylene was utilized as the main carbon source for its low decomposition temperature and affordability; CO and CO_2 presents promoting additives (Nasibulina et al., 2010). The CNF/CNT growth runs at temperature about 600°C in fluidized bed reactor see Fig. 2 for the scheme of the reactor. The CNT typically grown on the cement particles are 30 nm in diameter and 3 μm in length (La Mudimela et al., 2009), the specific surface area of CNT is about 10 – 20 m^2/g. CNT exhibit elastic modulus in the range of 180 - 588 GPa and tensile strength from 2 to 6 GPa (La Mudimela et al., 2009; Li et al., 2005).

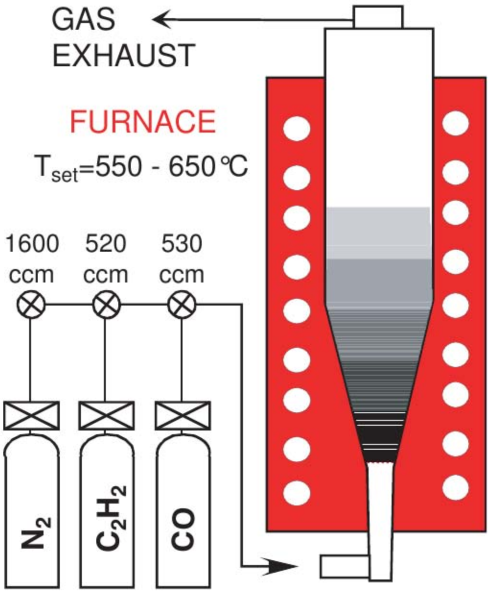

Fig 2. Scheme of the fluidized bed reactor, overtaken from L. Nasibulina et al. (2010).

Table 1: Oxide Component Content of CHM Base Cement and Cement originated from Mokrá

Component	**Content (wt%)**	
	CHM-Base Cement	**Mokrá Cement**
CaO	63.1	65.6
SiO2	20.2	19.0
SO3	3.0	4.0
Fe2O3	4.0	3.5
Al2O3	2.2	5.0
MgO	2.0	1.1
K2O	0.3	1.1
Na2O	0.5	0.1

In the batch with CHM, pure silica sand with the fraction 0 – 2 mm, was utilized in the mortar specimens. Three fractions PG1 (0 – 0.25 mm), PG2 (0.25 – 1 mm) and PG3 (1 – 2 mm) were mixed in the ratio 1:1:1. In the batch with carbon-modified sand, sand fraction 0 – 1 mm was mixed with the carbon modified sand in the mass ratio 0 – 0.3.

2.2. Specimen preparation

Two sets of samples were prepared and cast into steel form:

- Cement grains with synthesized carbon nanotubes – Five cement paste sets and five mortar sets were cast. The water/binder ratio was set to 0.35 and the carbon nanotubes/paste ratio varied from 0.0 to 0.038. The CHM was intermixed with the pure cement and (in case of mortar) with the dry silica sand; the water with superplasticizer was added at the end. Table 2 shows the batch compositions.
- Sand particles with synthesized carbon nanotubes – Five sets with the coarse cement and five sets with the fine cement were cast. The water/binder ratio was set to 0.5 and the carbon-modified sand/mortar ratio varied from 0.0 to 0.2. The Portland cement was intermixed with dry sand and carbon-modified sand; the water with superplasticizer was added at the end. Table 3 shows the batch compositions.

Table 2: Carbon-modified cement paste and mortar composition; weight fractions per one sample.

Sample		Total binder weight	Cement hybrid material	Water/ binder ratio	Total water weight	Super plasticizer (63% water)	Sand fraction 0 - 2 mm
CHM	Paste	234 g	0 - 70 g	0.35	81.9 g	0.47 g	–
	Mortar	75 g	0 - 22.5 g	0.35	26.25 g	0.38 g	225 g

Table 3: Carbon-modified sand mortar composition; weight fractions per one sample GC - ground cement, Blaine surface 587 m^2/kg, RC – raw cement 355 m^2/kg.

Sample		Total binder weight	Fine cement	Water/ binder ratio	Total water weight	Super plasticizer (63% water)	Sand fraction 0 - 1 mm	Carbon – modified cement
Carbon–modified sand	Mortar RC	75 g	–	0.5	37.5 g	0.3 g	157.5 – 225 g	0 – 67.5 g
	Mortar GC	75 g	75 g	0.5	37.5 g	0.3 g	157.5 – 225 g	0 – 67.5 g

Hand stirring of each specimen took four minutes, consecutive vibrating and form filling took extra four minutes. The specimens sized 40x40x80 mm were cured in the water bath at ambient temperature.

After 28 days of curing, the specimens were cut on diamond saw; in the case of the paste specimens were cut to nine parts (approx. 13x13x80 mm), in the case of mortar to four parts (approx. 19x19x80 mm). According to RILEM standards for mechanical testing (RILEM, 1985) notches were sawn in the middle of the beams to the 45% of the height. The production of such small-sized specimens is much more efficient than direct casting into small molds. The casting and vibration of small amount of material is ineffective and the quality of specimens (including surface defects or material inhomogenity) is significantly worse than the quality reached by cutting from larger bodies.

2.3. Assessment of fracture energy

The fracture energy, G_f, was determined according to the RILEM standard (1985). See Fig. 3 for the experiment scheme. Three point displacement-controlled bending test was carried out to obtain the load-displacement curve. The work of external force P could be calculated as

$$W_f = \int_0^{u_i} P du \qquad (1)$$

where P is the external force, u is the load-point displacement and u_i presents the final displacement at which the load is equal to zero. The average (effective) fracture energy in the ligament, according to the RILEM standart, is defined as

$$G_f = \frac{W_f}{bl}, \quad l = d - a_0 \qquad (2)$$

where l represents the length of the ligament, b the thickness of the beam, d the total height of the beam and a_0 is the depth of the nodge. The support span L was in case of mortar set to 65 mm and in case of cement paste set to 50 mm.

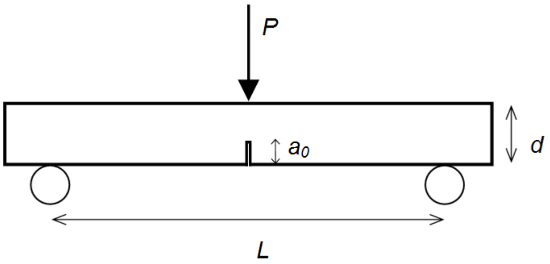

Fig. 3 Scheme of the three point bending test used for the fracture energy determination.

3. Results and discussion

3.1. Compressive strength

The results on the CHM-based paste samples show that replacing 3.5% cement with the CHM could increase the compressive strength by 25%, in our case from the average value of 56 MPa to the average 70 MPa. However, in the case of CHM-based mortar samples, the increase of CHM led to decrease of compressive strength. The mortar samples with 7% replaced cement exhibit a 15% lower

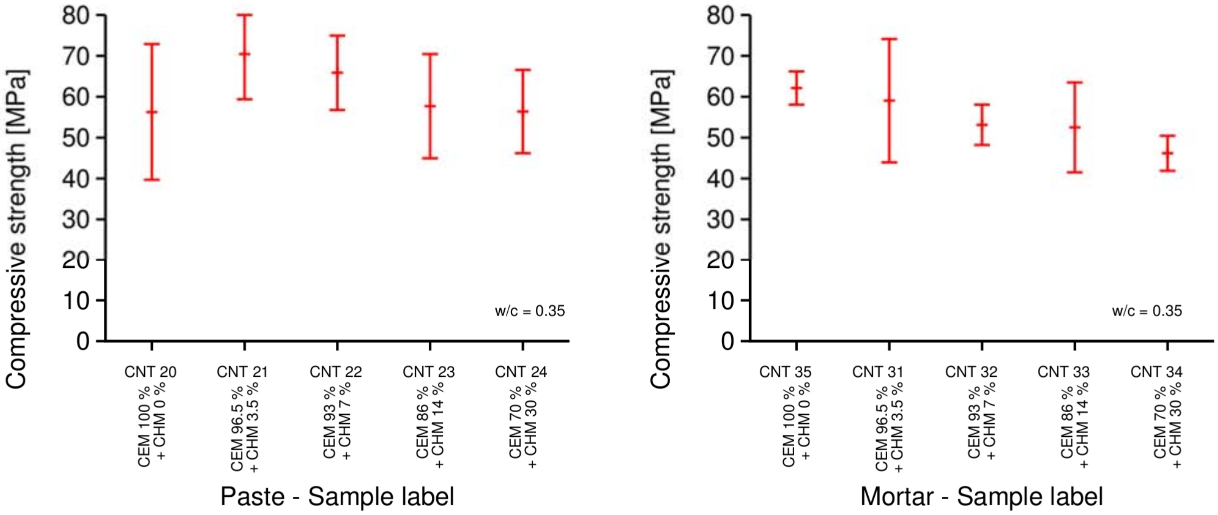

Fig 4. Compressive strength of mortar and paste samples with different cement/CHM ratii.

compressive strength, in our case decrease from the average of 62 MPa to the average of 53 MPa. See Fig. 4 for the compressive strengths of mortar and paste samples with different cement/CHM ratii.

The results on the mortar made from fine cement with the carbon-modified sand show that replacing 30% of sand with the carbon modified sand could increase the compressive strength by 25%, in our case from the average value of 44 MPa to the average 58 MPa. It should be noticed, that the compressive strength of the mortar based on the coarse cement with unmodified sand is 57 MPa. See Fig. 5 for the compressive strengths of mortar samples with different mass ratii of carbon modified sand/raw sand.

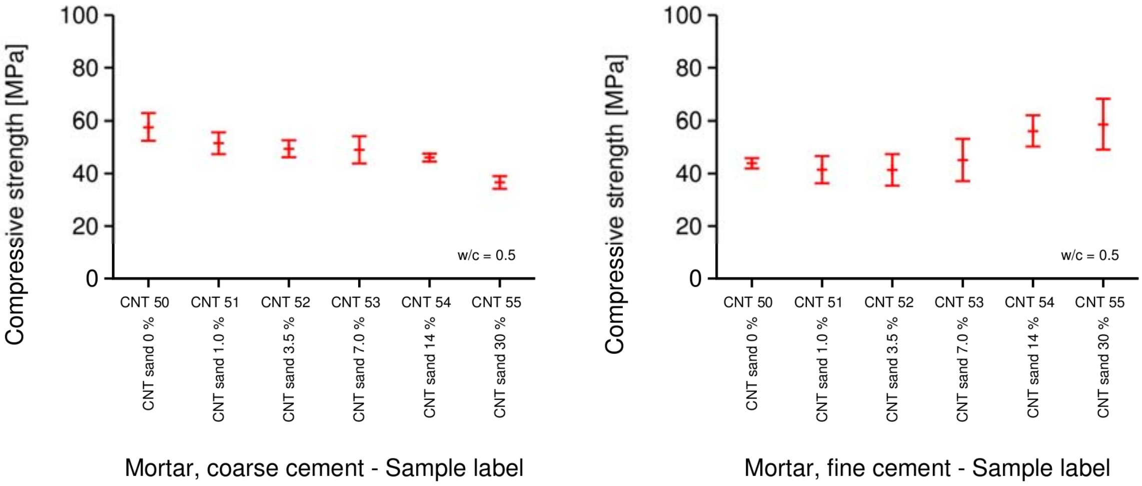

Fig.5 Compressive strength of mortar with different weight ratii of carbon modified sand/raw sand, left coarse cement, right fine cement.

3.2. Fracture energy

The fracture energy results are depicted in the Figs. 6 and 7. The CHM paste samples exhibit a significant increase in the fracture energy even in a small amount of cement replacement by CHM. Replacing 3.5% of cement causes an increase in the fracture energy by 14%. The mortar CHM samples do not exhibit almost any change in the fracture energy. The mortars prepared from carbon-modified sand and from the finely ground cement exhibit slight increase in the fracture energy.

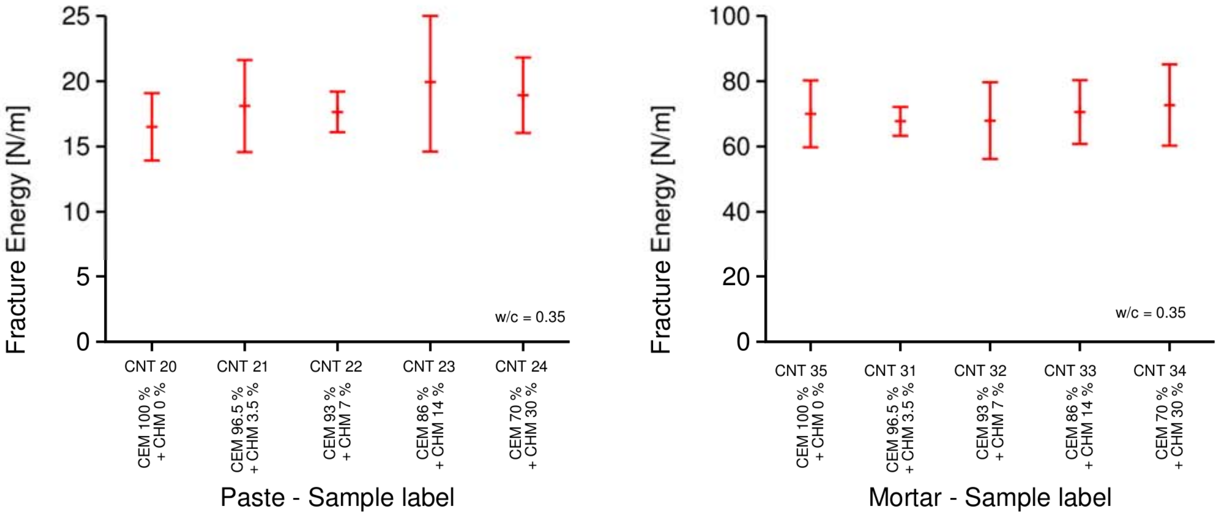

Fig.6 Fracture energy of CHM-based paste and mortar samples with different cement/CHM ratii.

3.3 Discussion and hypotheses

Let us introduce some hypotheses partially explaining the behavior of cement paste/mortar with the CHM. The paste samples reinforced with the CNT/CNF exhibit the expected increase in the compressive strength as well as in the fracture energy. Raki et al. (2010) hypothesized that the CNT act as a nano-reinforcement agent improving the C-S-H gel properties. Makar & Chan (2010) thought that the carbon nanotubes appear as nucleating sites for the cement hydration product.

In the case of the carbon-modified cement, the decrease in compressive strength on CNT-reinforced mortar samples could be caused by the higher amount of water in the ITZ which was pushed out by the extremely hydrophobic carbon nanotubes. Preliminary experiments with high compacted (60 MPa) mortar samples with the w/c ratio 0.35 do not exhibit the compressive strength reduction.

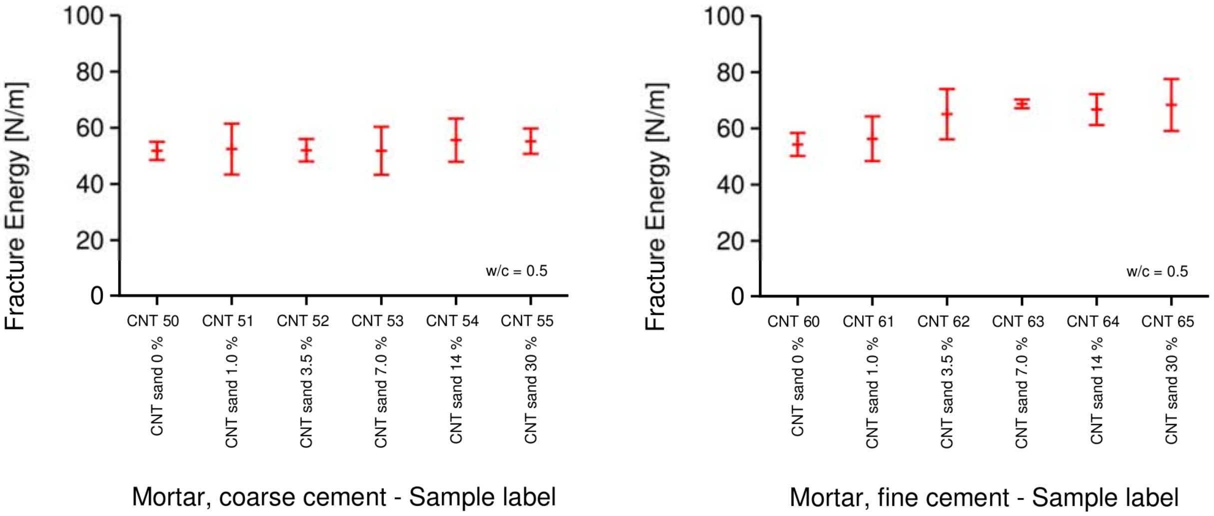

Fig.7 Fracture energy of mortar with different weight ratii of carbon modified sand/raw sand, left coarse cement, right fine cement.

From calorimetric tests carried out at our laboratory is evident, that the CNT/CNF does not affect the long-term (understand days) reaction kinetics, and do not prevent the cement particles from hydration.

The changes in the compressive strengths from the Figure 5 required additional measurements of density to identify the source of strength gain. The plot of compressive strength of all mortar samples versus the density is given in Figure 8. As is obvious from this figure, the mortars prepared from the carbon-modified sand do not exhibit any evident effect of CNT to the compressive strength and all the changes from Figure 5 could be explained by different densities of the samples.

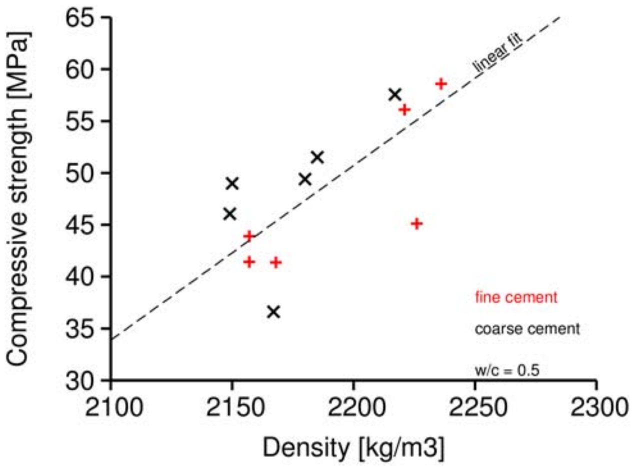

Fig.8 Dependence of compressive strength on density of mortar from carbon-modified sand.

The increase in the fracture energy for the fine-cement mortar with the carbon-modified sand (Figure 7 left) compared with no change in the fracture energy for the coarse-cement mortar (Figure 7 right) indicates a small length of the CNT. Meaning the CNT are unable to bridge the ITZ in the case of coarse-cement mortar. The ITZ closely corresponds to the cement particles mean diameter, which can be recalculated from the Blaine surface. The ITZ corresponds to 20 μm for the coarse cement (Blaine 355 m^2/kg) and, 3-4 μm for the fine cement (Blaine 587 m^2/kg). Since the CNT are only about 2 μm long they have no chance to improve the micromechanical properties of the ITZ in the case of the coarse cement. On the other hand this CNT can help in the case of the finely ground cement.

4. Conclusion

The cement pastes/mortars reinforced with CNT/CNF directly synthesized on the surface of the cement grains exhibit comparable mechanical properties as the cement pastes/mortars reinforced with the separately added carbon nanotubes as introduced in Metaxa et al. (2010). Previous attempts to create nano-reinforced composite materials suffered from the flocculation and improper dispersion of separately added nanofibers/nanotubes. The main advantage of this new method presents the elimination of the demanding CNT/CNF dispersion; now, the hybrid material can be intermixed directly with water and/or sand, creating a strong and quasi-brittle composite similar to ordinary cement paste/mortar.

Since we have not proven any evident effect of CNT/CNF to the compressive strength of mortar, dare we say that our results are in strong contrary to the measurements of Ludvig et al. (2011) and Nasibulina et al. (2010), who published a 2-3x increase in compressive strength of mortar when the CNT/CNF are used. Unfortunately these sources do not provide densities or porosities of the measured samples and thus the results remain questionable.

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