The influence of carbon nanotubes on the properties of water solutions and fresh cement pastes

D Leonavičius¹, I Pundienė¹, G Girskas¹, J Pranckevičienė¹, M Kligys¹ and M Sinica¹
¹Vilnius Gediminas Technical University, Scientific Institute of Thermal Insulation, Linkmenu str. 28, LT-08217, Vilnius, Lithuania
E-mail: dainius.leonavicius@vgtu.lt

Abstract. It is known, that the properties of cement-based materials can be significantly improved by addition of carbon nanotubes (CNTs). The dispersion of CNTs is an important process due to an extremely high specific surface area. This aspect is very relevant and is one of the main factors for the successful use of CNTs in cement-based materials. The influence of CNTs in different amounts (from 0 to 0.5 percent) on the pH values of water solutions and fresh cement pastes, and also on rheological properties, flow characteristics, setting time and EXO reaction of the fresh cement pastes was analyzed in this work. It was found that the increment of the amount of CNTs leads to decreased pH values of water solutions and fresh cement pastes, and also increases viscosity, setting times and EXO peak times of fresh cement pastes.

1. Introduction
Cement-based materials are typically characterized as quasi-brittle materials with low tensile strength and low toughness, which lead to the development of cracks in different structures [1]. Reinforcement using fibres (such as polypropylene and nylon), natural cellulose (such as hardwood and softwood pulps), and inorganic fibres (such as steel, glass and carbon) is the typical and effective method to control cracking in cement-based materials [2]. Recently, because of the extremely high mechanical, thermal and electrical properties, which may also help to prevent development of cracks and improve the strength properties of cement-based materials, CNTs have gained the interest of the researchers [3-9]. Cwirzen et al. [7, 8] reported the increase (approx. 50%) in compressive strength of cement paste samples when 0.045 – 0.15% of CNTs (from cement mass) were used in the forming mixture.

Yakovlev et al. [9] obtained the increase in compressive strength of cement-based foamed concrete samples approx. 70% (from 0.18 MPa to 0.306 MPa.), when 0.05% of CNTs (from cement mass) were used in the forming mixture. The use of CNTs also caused a significant reduction of the average pore diameter in the cement-based foamed concrete samples. Makar et al. [10] found, that CNTs could accelerate the hydration reaction of C₃S in the forming mixtures of ordinary Portland cement. The results obtained by Abu Al-Rub et al. [11] showed, that the flexural strength of cement paste samples, containing short (0.2 % from cement mass) and long (0.1 % from cement mass) CNTs, after hardening for 28 days increased approx. 26.9% and 65% respectively, compared with a plain cement paste samples. Wang et al. [12] presented that the index of flexural toughness increased up to 57.5%, when CNTs (0.08 % from cement mass) was used. The changes in the morphology of new formations lead
to a significant increase of the mechanical strength of the cement-based materials, modified with ultra-
small amount (within 0.02 – 0.0025% from cement mass) of CNTs [19-21].

The major challenge, associated with the incorporation of CNTs in cement-based materials is poor
dispersion. CNTs have an extremely high specific surface area (greater than 200 m² g⁻¹) and are able to
aggregate and form bundle structures because of their high surface energy. Proper dispersion and
mixing methods are known to be key factors affecting the performance of nanocomposites, as poor
dispersion of CNTs leads to several defects in the nanocomposites and decreases the reinforcing effect
of the CNTs [14, 15]. Currently, there are two methods that are commonly used for CNTs dispersion.
The first is chemical modification, which introduces functional groups on the surface of CNTs using
chemical reagents, high energy discharge, ultraviolet radiation or other processes [16, 17]. The second
is physical modification, which employs mechanical stress through processes such as crushing and
ultrasonic treatment to activate the surface of the CNTs [18]. Li et al. [5, 6] employed the
carboxylation procedure to improve the bonding behavior between CNTs and a cement paste, and
obtained increase in flexural (25%) and in compressive (19%) strengths. Scanning electron
microscopy (SEM) showed, that the hydration products of cement paste were found to be connected
by CNTs and bundles and crack bridging were observed, when CNTs (2% from cement mass) were
dispersed in isopropanol using ultrasonic treatment [13].

However, the production way of CNTs (in form of pellets, solutions or powders) can affect the
rheological properties of cement-based materials. It is important to consider the fact, that ultrasonic
treatment activates water, destroys hydrogen bonds and increases the pH value of water. The influence
of CNTs (in form of pellets), dispersed in water in different amounts (using ultrasonic treatment) on
viscosity and pH value of water solutions and fresh cement paste almost has not been studied. This
aspect is very relevant and is one of the main factors for the successful use of CNTs in cement-based
materials. The main purpose of this work was to estimate the influence of CNTs, used in different
amounts (0 to 0.5% from cement mass) on the pH and electric conduction values of water solutions
and fresh cement pastes, and also on rheological properties, flow characteristics, setting time and EXO
reaction of the fresh cement pastes.

2. Materials and research methods

Portland cement CEM I 42.5 R from JSC AKMENĖS CEMENTAS (Lithuania), with a specific
surface of 3190 cm²/g. Mineral composition of clinker (in %): C₃S – 63.98; C₂S – 7.74; C₃A – 6.38;
C₄AF – 12.68.

Distilled water characterized by pH – 5.8 and electric conduction – 8 µS, was used.

The pellets, named as GRAPHISTRENGTH CW2-45, containing multi-walled CNTs with purity
>90% at concentration of 45% (by weight of mixture), dispersed in carboxymethylcellulose at content
of 55% (by weight of mixture), provided by a company ARKEMA (France) were used. For the
preparation of water solutions, the pellets, containing the necessary amount of CNTs – 0, 0.002, 0.02,
0.2, 2 and 20 g (this corresponds to the percentage content of the composition in Table 1), were
immersed in 100 ml of hot (95 – 100°C) distilled water for 10 minutes without mixing. After that,
CNTs were dispersed using ultrasonic treatment for 5 minutes with an ultrasonic disperser UZDN-2T
(frequency 22 kHz, power 480 W) in 200 ml capacity cylinder. Prepared CNTs solutions were diluted
with 1100 g of distilled water (this quantity was counted according to the cement paste composition),
and mixed with a mixer. Prepared water solutions with CNTs were cooled to room temperature
(20°C), and then pH, electric conduction and dynamic viscosity were measured. The same water
solutions with CNTs were used for the preparation of fresh cement pastes (Table 1). Water to cement
ratio (W/C) in all samples was the same – 0.3. The amount of CNTs in the forming mixture varied
from 0.00005% to 0.5% (from cement mass) and concluded from 0.002 to 20.0 g. Such amounts of
CNTs were selected according to the experience of the other authors [7, 8, 13, 19-21].

The effect of different amount of CNTs on the dynamic viscosity of water solutions and fresh
cement pastes was tested using vibro-viscosimeter SV-10 (capacity – up to 12.000 mPa·s, accuracy –
0.01 mPa·s). The dynamic viscosity of water solutions were measured immediately after the
preparation, and of fresh cement pastes – immediately after the mixing and continued for 30 minutes. Electric conduction and pH tests for CNTs water solutions and for fresh cement pastes modified with CNTs were performed with the instrument MPC 227 (pH electrode – INLAB 410 with a measuring accuracy of 0.01, electric conduction electrode – INLAB 730 with a measuring range from 0 mS/cm to 1000 mS/cm).

Table 1. Compositions of forming mixtures of fresh cement pastes by weight.

| Sample series | Portland cement, g | CNTs, g | W/C | Water, g |
|---------------|-------------------|---------|-----|---------|
| CNTs-0        | 4000              | 0       | 0.3 | 1200    |
| CNTs-0.00005  | 4000              | 0.002   | 0.3 | 1200    |
| CNTs-0.0005   | 4000              | 0.02    | 0.3 | 1200    |
| CNTs-0.005    | 4000              | 0.2     | 0.3 | 1200    |
| CNTs-0.05     | 4000              | 2.0     | 0.3 | 1200    |
| CNTs-0.5      | 4000              | 20.0    | 0.3 | 1200    |

The hydration characteristics of fresh cement paste were followed by an exothermic (EXO) profile, according to the ALCOA methodology [22]. Heat development in the fresh cement paste, which comes out on the exothermic reaction of the hydration of cement minerals, was determined at 20°C using 1.5 kg samples, which were placed in an insulated 10×10×10 cm textolite chamber. A thermocouple (type T), embedded in the sample, was linked to a data capture system and temperature was recorded as a function of time.

Table 2. Dynamic viscosity, pH and electric conduction in water solutions with different amount of CNTs.

| Amount of CNTs in water solution, g | Viscosity, mPa·s | pH     | Electric conduction, µS |
|-----------------------------------|------------------|--------|-------------------------|
| 0                                 | 0.74             | 6.89   | 15                      |
| 0.002                             | 0.68             | 6.75   | 83                      |
| 0.02                              | 0.65             | 6.6    | 98                      |
| 0.2                               | 0.63             | 6.42   | 125                     |
| 2.0                               | 0.96             | 6.07   | 159                     |
| 20.0                              | 3.5              | 5.78   | 245                     |

3. Test results
The dynamic viscosity measurements of water solutions show (Table 2), that small amounts (0.002 – 0.2 g) of CNTs reduces viscosity down to the 15%, higher amount (2.0 g) – increases viscosity up to the 30% and maximal amount (20 g) – increases viscosity 4.7 times, compared with the dynamic viscosity of pure distilled water. This may be due to carboxymethylcellulose, which is used in the production technology of the pellets, containing CNTs (in water solutions it works as a thickener). However, in water solutions with small amounts of CNTs opposite processes are taking place and dynamic viscosity of water solution decreases. In order to better clarify the impact of CNTs on properties of water solutions, electric conduction and pH measurements were carried out. It is known, that electric conduction depends on the amount of ions in water solution. Research results show that increasing amount of CNTs in water solutions, increases the electric conduction from 15 to 245 µS (16.3 times), pH decreased from 6.89 to 5.7 respectively, with an increase in amount of CNTs in water solutions. It is interesting to note that pure distilled water, not treated by ultrasond, has pH of 5.8.

It can be stated that CNTs are not completely inert material. It is possible that CNTs binder (carboxymethylcellulose), existing in the pellets, after ultrasonic treatment in hot water, moves into water solution and impacts its electric conduction and pH. It is known that carboxymethylcellulose is a weak acid, which may reduce pH and electric conduction of water solution.
The effect of different amount of CNTs in fresh cement paste (Fig.1) showed, that the highest dynamic viscosity (2100 mPa·s, after 30 minutes) has a control sample (CNTs-0). Initial dynamic viscosity of fresh cement pastes decreased approx. 20% and reached 400 mPa·s when minimal amounts of CNTs (0.00005 and 0.0005%) were used. Practically there is no difference in dynamic viscosity between these both fresh cement pastes within 20 minutes. Dynamic viscosity of sample CNTs-0.0005 reaches 1.870 mPa·s, and of sample CNTs-0.00005 – 1.610 mPa·s during the last 10 minutes of the experiment. The lowest dynamic viscosity was observed in the sample CNTs-0.005. The variation in dynamic viscosity during 30 minutes was from 390 to 600 mPa·s. The dynamic viscosity slightly increased and after 30 minutes reached 730 mPa·s, when the amount of CNTs was 0.05%. Dynamic viscosity of sample with maximal amount of CNTs (0.5%), increased immediately and reached 675 mPa·s (after mixing) and 920 mPa·s (after 30 minutes). It can be concluded that lower amounts of CNTs (0.00005-0.005%) reduced dynamic viscosity of the fresh cement paste much more noticeably, comparing with the larger amounts of CNTs (0.05-0.5%).

Figure 1. Dynamic viscosity of the fresh cement pastes, depending on the amount of CNTs.

In case of the fresh cement pastes, electric conduction and pH help to describe the course of the hydration process during the dissolution of cement, in the presence of CNTs. Electric conduction and pH tests of fresh cement pastes, were performed within 30 minutes. The fast increase of electric conduction within the first 30 minutes showed the dissolution process of cement minerals and penetration of ions into the solution. Additives have the greatest impact exactly at this stage, because in further stages stabilization of electric conduction takes place, as germs of crystals appear. When stable electric conduction values are reached, the generation of hydrates and reduction of electric conduction starts.

Electric conduction of sample CNTs-0 grows from 15.5 to 18.4 mS within 30 minutes (Fig.2). Increase in amount of CNTs from 0.00005 to 0.5% slightly reduces the primary electric conduction (from 15.3 to 14.6 mS). Lower amounts of CNTs (0.00005 and 0.0005%) in the fresh cement paste have less influence on the primary electric conduction (15.3 and 15.25 mS respectively). Higher amounts of CNTs can decrease electric conduction approx. 5 % – till 14.6 mS. Electric conduction of the fresh cement pastes with CNTs is greater after 30 minutes, as smaller amounts of CNTs were used. The difference in electric conduction between control sample and sample with maximal amount of CNTs is 3.2 mS (approx. 17 %). It means that CNTs have an influence on the hydration retardation of cement minerals and on the lower electric conduction of the fresh cement pastes.
Figure 2. Electric conduction and pH of the fresh cement pastes, depending on the amount of CNTs.

As well as in water solutions, CNTs act in the fresh cement pastes (Fig.2). pH grows from 12.9 to 13.3 in sample CNTs-0 within 30 minutes. Increasing amount of CNTs (from 0.00005 to 0.5%), reduces the primary pH from 12.6 to 12.26. Typically as in the electric conduction research, lower amounts of CNTs (0.00005 and 0.0005%) in the fresh cement paste have less influence on the primary pH. Noticeable changes could be observed when larger amounts of CNTs were used. Similarly to the electric conduction tests, the lower amount of CNTs was used in the fresh cement pastes, the higher pH values were obtained after 30 minutes. The difference of pH between control sample and sample with maximal amount of CNTs is 0.9 (increasing amount of CNTs can reduce pH of the fresh cement paste to the 6.8%).

Lower electric conduction and pH of the fresh cement pastes showed, that CNTs have an influence on the hydration retardment of cement minerals. The difference of pH of the fresh cement pastes was approx. 0.5, when samples with minimal and maximal amounts of CNTs were compared. Measurements of dynamic viscosity, pH and electric conduction of the fresh cement pastes generally correlated. The increased amount of CNTs reduced electric conduction, pH and dynamic viscosity of the fresh cement pastes. However, decrease of dynamic viscosity takes place only up to a certain limits (the same tendency was observed in water solutions with CNTs). As mentioned earlier, carboxymethylcellulose, characterized by acidic pH value, can have influence for it.

Higher amounts of CNTs (from 0.05% to 0.5%) continue to retard hydration of cement minerals, because of their physical properties (as increased dynamic viscosity was found in water solutions (Table 2)) and increases dynamic viscosity of fresh cement paste. This must be kept in mind when counting new compositions of forming mixtures with CNTs.

Research results of initial and final setting times of the fresh cement pastes showed, that increased amount of CNTs in the fresh cement pastes from 0.00005% to 0.0005%, practically don't have an influence on the initial setting time (Fig.3). Increased amount of CNTs in the fresh cement paste to 0.005% increases its initial setting time from 150 to 190 minutes. When amount of CNTs in the fresh cement pastes varied from 0.05% to 0.5%, initial setting times were fixed in the range of 260-360 minutes.

Research results of final setting times showed, that increased amount of CNTs in the fresh cement pastes gradually increases the final setting time (prolongs it from 200 to 290 min.), until amount of CNTs doesn't exceed 0.05%. The final setting time increased from 290 to 420 minutes, when the amount of CNTs was 0.5%. Research results showed that amount of CNTs, higher than 0.05%, may significantly retard hydration of cement minerals.
Figure 3. Initial and final setting times of the fresh cement pastes depending on the amount of CNTs.

The change of exothermic reaction (EXO) temperature in time reflects the detailed research about thermal profiles of hydration process in the fresh cement pastes with CNTs. The fresh cement pastes with different amounts of CNTs were tested, to estimate whether the released heat impacts the temperature of samples during hydration of cement. Changes of hydration temperature in sample CNTs-0 (Fig.4) showed that maximal EXO temperature reached 87.5°C. Minimal and maximal amounts of CNTs (0.00005% and 0.5%) decreased EXO temperature approx. 5°C and 15°C (20%), respectively. Generally it can be stated, that increased amount of CNTs in the fresh cement paste, decreases the maximal EXO temperature from 82.5 to 71.6°C. The highest temperature changes observed when the amount of CNTs was from 0.05% to 0.5%. These results confirmed electric conduction and pH measurements (Fig.2). They showed that CNTs in the fresh cement paste reduced its electric conduction, impeded penetration of ions to the solution and decreased pH. Lower pH leads to a slower dissolution of cement minerals, and this reflects into EXO temperature of the reaction.

Figure 4. Variation of EXO temperatures versus time of the fresh cement pastes depending on the amount of CNTs.

Also, it was found that increased amount of CNTs in the fresh cement paste, increases the reaching time of maximal EXO temperature from 363 to 862 minutes. The maximal EXO temperature of CNTs-0 sample was reached after 349 minutes from the beginning of the test. We can see that increased amount of CNTs from 0.00005 to 0.05% increases the reaching time of maximal EXO temperature from 363 to 474 minutes. The maximal amount of CNTs (0.5%) increased the reaching time of maximal EXO temperature for more than 500 minutes (almost twice).
Research results showed, that CNTs in the fresh cement pastes significantly reduced its electric conduction (down to 17%), pH (down to 6.8%), dynamic viscosity (down to 3 times), extended setting time (down to 2.2 times) and this resulted in increased the reaching time of maximal EXO temperature (up to 2.2 times) and reduced hydration temperature.

4. Conclusions
- Research results showed that pellets (which consist of CNTs, bonded with carboxymethylcellulose) were not completely an inert material. It was established, that increased amount of CNTs (from 0 to 20 g) in water solutions increases its electric conduction from 15 to 245 μS, and decreased pH from 6.89 to 5.78. Lower amounts of CNTs (from 0.002 to 0.2 g) decreased (approx. 15%) its dynamic viscosity, while higher amounts (from 2.0 g to 20 g) – increased it (1.3 to 4.7 times). It can be stated that the binder (carboxymethylcellulose) of the CNTs, existing in the pellets, which is known as a weak acid, has an influence on electric conduction, pH and dynamic viscosity of water solutions.
- Lower amounts of CNTs (0.00005 – 0.005%) in the fresh cement paste within 30 minutes significantly reduced their dynamic viscosity (to 67.5%) as well as higher amounts of CNTs (0.05 – 0.5%) decreased dynamic viscosity (to 56.5%), compared with a dynamic viscosity of the control sample. It was found that increased amount of CNTs (0 – 0.5 %) in the fresh cement paste reduced its initial electric conduction to 5.9%, compared with the control sample.
- The smaller amount of CNTs was in the fresh cement paste, the higher was its electric conduction after 30 minutes. The difference in electric conduction between the control sample and sample with a maximal amount of CNTs was 3.2 mS (approx. 17%). This showed that CNTs significantly retarded hydration of cement minerals, impeded penetration of ions to the solution and this led to a lower electric conduction of the fresh cement paste.
- The smaller amount of CNTs was in the fresh cement paste, the higher was its pH after 30 minutes. The difference in pH between the control sample and sample with a maximal amount of CNTs was approx. 6.8% lower.
- The minimal amount of CNTs (0.0005%) in the fresh cement paste, did not affect its initial setting time. Increased amount of CNTs to 0.005% extended initial setting time approx. 21%. Increased amounts of CNTs from 0.05% to 0.5% extended the initial setting time approx. 1.7 and 2.4 times, respectively. The final setting time of the fresh cement pastes gradually extended by 45% when amount of CNTs did not exceed 0.05%. The final setting time extended 2.2 times when amount of CNTs in the fresh cement paste reached 0.5%.
- It was found that increased amount of CNTs in the fresh cement paste decreased a maximal EXO temperature (approx. 20%) – from 87.5°C (in the control sample) to 71.6°C (in the sample with a maximal amount of CNTs. The reaching time of a maximal EXO temperature increased by 2.5 times. Amounts of CNTs (0.05 and 0.5%) mostly reduced maximal EXO temperature (13°C and 16°C respectively) and increases the reaching time of maximal EXO temperature over 125 and 513 minutes, comparing with the control sample.
- It can be concluded that different amounts of CNTs in the fresh cement pastes, reduced its electric conduction and pH, decreased dynamic viscosity, prolonged setting time and reaching time of a maximal EXO temperature, reduced maximal EXO temperature and significantly retarded hydration of cement minerals. Larger amounts of CNTs (from 0.05 to 0.5%) increased the dynamic viscosity of the fresh cement pastes approx. 10%, because of their physical properties (results of dynamic viscosity in water solutions), and this must be kept in mind, when preparing forming mixtures with CNTs.

References
[1] Bajare D, Bumanis G, Shakhmenko G and Justs J 2012 High performance and conventional concrete properties affected by ashes obtained from different type of grasses 12th Int. Conf.
on Recent Advances in Concrete Technology and Sustainability Issues (Michigan) vol 289
(American Concrete Institute) ed T C Holland, P R Gupta et al p 317

[2] Musso S, Tulliani J M, Ferro G and Tagliaferro A 2009 Influence of carbon nanotubes structure on the mechanical behavior of cement composites Compos. Sci. Technol. 69 1985–90
[3] Makar J M and Beaudoin J J 2004 Carbon nanotubes and their application in the construction industry 1st Int. Symp. on nanotechnology in construction (Paisley) p 331
[4] Campillo I, Dolado J S and Porro A 2004 High-performance nanostructured materials for construction Proc. of 1st Int. Symp. on nanotechnology in construction (Cambridge)
[5] Li G Y, Wang P M and Zhao X 2005 Mechanical behavior and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes Carbon 43 1239–45
[6] Li G Y, Wang P M and Zhao X. Pressure-sensitive properties and microstructure of carbon nanotube reinforced cement composites 2007 Cem. Concr. Compos. 29 377–82
[7] Cwirzen A, Habermehl-Cwirzen K, Nasibulin A, Kaupinen E, Mudimela P and Penttala V 2009 SEM/AFM studies of cementitious binder modified by MWCNT and nano-sized Fe needles Mater. Charact. 60 735–40
[8] Cwirzen A and Habermehl-Cwirzen K 2008 Surface decoration of carbon nanotubes and mechanical properties of cement/carbon nanotube composites Adv. Cem. Res. 20 65–73
[9] Yakovlev G, Keriene’ J, Gailius A and Girniene’ I 2006 Cement based foam concrete reinforced by carbon nanotubes Mater. Sci-medzg. 12 147–51
[10] Makar J M and Chan G W. 2009 Growth of cement hydration products on single-walled carbon nanotubes J. Am. Ceram. Soc. 92 1303–10
[11] Abu Al-Rub R K, Ashour A I and Tyson B M 2012 On the aspect ratio effect of multi-walled carbon nanotube reinforcements on the mechanical properties of cementitious nanocomposites Constr. Build. Mater. 35 647–55
[12] Wang B, Han Y and Liu S 2013 Effect of highly dispersed carbon nanotubes on the flexural toughness of cement-based composites Constr. Build Mater. 46 8–12
[13] Makar J M, Margeson J C and Luh J 2005 Carbon nanotube/cement composites-early results and potential applications Proc. of the 3rd Int. Conf. on Construction Materials: Performance, Innovations and Structural Implications (CA) p 1
[14] Xie X L, Mai Y W and Zhou X P 2005 Dispersion and alignment of carbon nanotubes in polymer matrix: a review Mater. Sci. Eng. R. Rep. 49 89–112
[15] Colston S L, O’Connor D and Barnes P 2000 Functional micro-concrete: the incorporation of zeolites and inorganic nano-particles into cement micro-structures J. Mater. Sci. Lett. 19 1085–88
[16] Liu J, Casavant M J and Cox M. 1999 Controlled deposition of individual single-walled carbon nanotubes on chemically functionalized templates Chem. Phys. Lett. 303 125–29.
[17] Huang W, Lin Y, Taylor S 2002 Sonication-assisted functionalization and solubilization of carbon nanotubes Nano Lett. 2 231–34
[18] Sandler J, Shaffer M and Prasse T 1999 Development of a dispersion process for carbon nanotubes in an epoxy matrix and the resulting electrical properties Polymer 40 5967–71
[19] Makar, J M and Chan G 2009 Growth of cement hydration products on single-walled carbon nanotubes Journal of the American Ceramic Society 92 1303–10
[20] Yakovlev G I, Pervushin, G N, Buryanov A F, Kodolov V I, Krutikov V A, Fisher H B and Kerene Y 2009 Modifying porous cement metrices with carbon nanotubes Construction Materials 3 99–102
[21] Sanchez F and Sobolev K 2010 Nanotechnology in concrete – a review Construction and Building Materials 24 60–71
[22] 1999 Alcoa calcium aluminate cement test methods brochure (Revision 5, 08/99, available through Alcoa Industrial Chemicals, Frankfurt)