Application of Plasma Technology in Cement and Concrete

Kasra Shafiei M.Sc., Prof. Dr.-Ing. Bernd Hillemeier

Address: TIB 1-B4, Room 375, Gustav-Meyer-Allee 25, 13355 Berlin, Germany

E-mail: kasra_shafiei@yahoo.com

Abstract

In spite of decades of research and due to growing application of concrete in different projects, there are still new concepts to produce concrete with more suitable properties. Challenging with extra benefits for the environment is the improvement of impermeability without losing strength. However, despite several advanced concepts for concrete technology, there is a shortage of research on interaction of plasma and its applications in concrete field. Plasma, known as the 4th state of the material, has found many different usages in various scientific and industrial fields recently. A main group of industrial applications are chiefly based on changing the surface properties of materials; particularly enhancing the adhesion and wettability of different surfaces. This enhancement is not only chemical, but also due to physical effects which modifies the features of the surface.

The purpose of this research is to establish and evaluate the possibilities of plasma technology applications in concrete and cement industry. Therefore, in this research work the concentration is based on the primary feature of plasma treatment, which is surface property modification of material such as wettability and adhesion. This concept comes into practice in our experiments within two categories: first the adhesion enhancement of cement matrix and aggregates to improve the interfacial transition zone by treating the aggregate surface; second, affecting the surface interaction of cement lime on 4 different release agent types to improve the final surface quality of the concrete elements.

To reach the goals of research and by means of a corona discharge equipment some samples are prepared. To assess the properties of concrete, various primary tests such as compressive strengths, water absorption and helium pycnometer porosity are done. Results show new achievement in improving the adhesion of quartz aggregates to cement matrices. Parallel to this part, a primary visual evaluation is done to observe the effect of plasma treatment on behavior of cement paste and different release agents. In this section also, adverse behavior of cement lime on different release agents are obviously noticed due to treatment effects.

Keywords: plasma, corona discharge treatment, cement matrix, adhesion, wettability, release agent, concrete final surface, compressive strength, porosity.

1. Introduction

In the last decades, the use of different methods and techniques has been applied to improve the concrete properties, decrease the production costs and minimize the environmental pollutions concerning cement and concrete productions. One of these methods is to modify the surface features of concrete materials in order to improve mostly all of the concrete properties. In other words, modifying surface features of concrete elements would result in improvement of concrete properties in general.

In spite of all the research works until today, our knowledge is so limited about the effect of plasma technology on cement and concrete behavior. Plasma, a popular technique in industry at the moment, is one of the most promising methods to affect the properties of different surfaces diversely.

This research paper is an attempt to introduce and highlight the possible applications of plasma technology in cement and concrete industries.

1.1. Plasma and its appliance

In general, plasma is the fourth state of matter similar to gas in which a certain portion of the particles is ionized [1]. Heating a gas may ionize its molecules or atoms, thus turning it into plasma which contains charged particles: positive ions and negative electrons or ions [2]. Plasma is by far the most common phase of ordinary matter in the universe, both by mass and by volume [3].

However, the artificially produced plasma (Fig. 1), a relatively new scientific and industrial achievement comparing to concrete, is growing in application every day. The plasma is used widely not only in scientific studies, but also in different industries such as food and agriculture, textile, packaging industries and etc. Plasma itself is available in many different types owing to different parameters such as type of generating pole, amount of power, availability and type of gas during the treatment, temperature and etc.

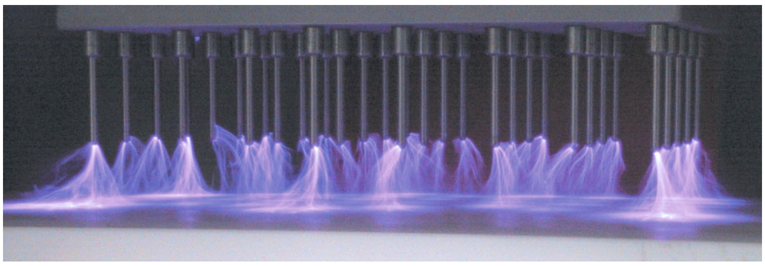


Figure 1: A unit of plasma treatment, especially designed for plate and large area corona discharge treatment

By means of plasma surface modification, desired surface characteristics mainly in polymeric based materials can easily be achieved without changing the bulk properties of substrates [4]. An example for effects of plasma surface treatment in changing the wettability of a glass pane is presented in figure 2.

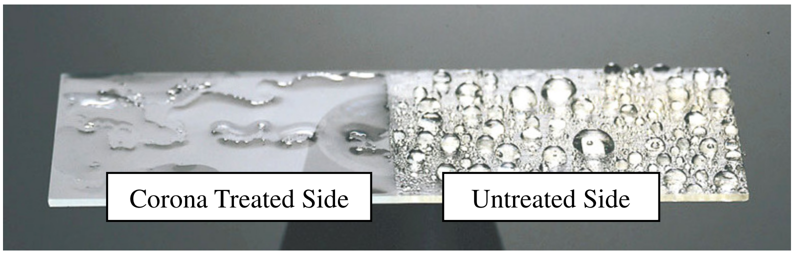


Figure 2: Showing the effect of plasma treatment on the wettability of a glass pane

The mechanism of changing the surface properties with plasma treatment is not always the same. It depends mainly on the material type of the treated element and also on the type of treatment itself. However, there are three mechanisms due to which the surface modification takes place:

1- Cleaning effect [5]: Making the surface clean of dust and oil.
2- Chemical effect [5 and 6]: Combining an element or a compound of elements to the surface, either temporarily (for a couple of hours) or relatively long term (couple of months). This compound could be adapted to the surface by means of applied gas during the treatment. By this way, one can decide what element or material could be set on the substrate during the treatment.
3- Physical effect [5 and 7]: Producing nano scale scratches on the surface which would result in a rougher surface, and consequently a better surface adhesion (Fig. 7).

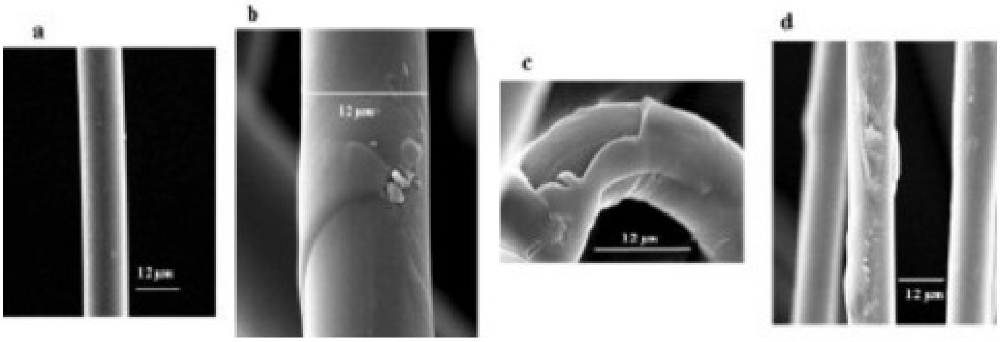


Figure 3 [7]: Illustration of the treatment physical effect. SEM image of Poly Ethylene Terephthalate (PET) Fibers with 12 µm thickness; native (a) and grafted after two cycles of plasma treatment (b, c, and d)

Although plasma is applicable in many industries, its application and benefits are poorly known to the civil sector. The only subject which includes the both topics of plasma and concrete in one research is the application of plasma in order to increase the bond forces between the cement matrix and polymeric fibers. In these groups of researches [4- 8] different plasma techniques are applied to polymeric fibers with various gases during the treatment. The results show enhancement in flexural and tensile strengths and improvement in toughness of the treated samples [4 and 9]. Previous studies [8, 10 and 11] approve that application of different gases during the plasma treatments may be appropriate for different types of polymeric fibers and have unequal modified effects especially on the Polypropylene [12].

Despite effectiveness of plasma treatment for modification of polymeric surfaces, it still could not be widely used by industries. One reason is the economical consideration, which could be vanquished with the development of plasma technology in close future; another reason of limited applications of plasma in industry is the effect of treatment which may be influenced by factors such as temperature and time of application [13].

1.2. Adhesion importance in Concrete

Interfacial Transition Zone: Adhesion plays an important role in concrete quality and properties. The interfacial transition zone, generally the weakest link of the chain, is considered as the strength-limiting phase in concrete. In addition to the large volume of capillary pores and oriented calcium hydroxide crystals, a major factor responsible for the poor strength of the interfacial transition zone in concrete is the presence of microcracks [14]. The existence of microcracks in the interfacial transition zone (ITZ) at the interface with steel and coarse aggregate is the primary reason that concrete is more permeable than the corresponding hydrated cement paste or mortar [14]. In other words, ITZ is partly responsible not only for the permeability, but also for the strength of concrete elements.

However, enhancing the adhesion properties of aggregate, thus influencing the interfacial transition zone could result in a noticeable modification in concrete properties.

Demoulding and Final Surface: The general target of using release agent is to ease the demoulding of various concrete elements mostly with desirable appearance. In order to reach this target, the release agent should basically decrease the wettability and consequently the adhesion of the mould surface and hinder the cement from sticking to the mould. The wettability loss due to release agent makes the lime drops to be more reluctant to be expanded on the surface of the mould, thus the surface would take any air bubble and result in an uneven surface.

However, the idea to cover this weakness of release agents is to increase the wettability while even reducing the adhesion with the help of plasma treatment. In other words, not only the moulds could be removed easier, but also the final surface could be enhanced in quality and smoothness.

2. Experimental

2.1. Materials and equipments

The cement used in all the experiments is CEM I 42.5 according to EN DIN 197-4. Two different kinds of PCE based superplasticizer, one with hardening acceleration effect (PCE-F) and other with retarding effect (PCE-S), are used to observe the interaction of polymeric based materials in the adhesion enhancement due to plasma treatment.

Aggregate in this experiment is sieved in order to ease the observation and interpretation of the results. The aggregate portion passed from sieve #4mm and left on #2mm were washed clean, so that no dust remained on the surface.

In spite of the variety of plasma types and different gases during the treatment, and also owing to the limited available research in this field, standard corona discharge with normal pressure air as the treatment gas is chosen for this series of assessment. This equipment is provided by the Hamburg branch of Tantec business group [15]. The treatment is mainly done in 150 Watt power level for both aggregate and release agent treatment.

The types of release agent used to evaluate their surface properties are of 4 different types:

- Normal mould grease (mineral oil based).
- Ceresit CK 310 (naphthenic mineral oil based); product of Henkel AG & Co.

- Mikon MG 9006 (polymeric based); product of Münch Chemie International GmbH.
- AQUA G (chemical water based); product of Lubritec Enterprise Ltd.

2.2. Testing and Methods

In order to ease the observation on the effect of plasma treatment, it is tried to lower the amount of variables, thus interpretation and result comparison would be easier. Tests were done in two main categories:

1- Evaluation of cement matrix and aggregate adhesion due to plasma treatment:

In this category, the assessment is done with examination of the compressive strength and porosity of the samples. The compressive strength tests are performed for the small cubes of aggregate and lime with the edge dimension of 20 mm. The results are from 1, 3, 7 and 28 days after casting the sample. The porosity is examined only for 28 days old samples.

2- Evaluation of cement lime and release agent interaction due to plasma treatment:

In this category, the interaction of fresh and hardened cement lime is evaluated on 4 different release agents for both normal and treated situation. The main observation in this study is the possibility to change the features of release agents.

The first test has been performed as followed: a drop of cement lime has been put on 4 different surfaces and treatment conditions, each with one type of release agent. The testing plates had an inclined position but all with the same slope. The results are shown in photos and conclusions are made due to the trace of the cement lime drops and the wettability of those surfaces. In the second test, the normal and treated grease release agent is investigated for the hardened cement lime and the evaluation is done due to the appearance of the samples' surface.

3. Results and Discussions

3.1. Aggregate plasma treatment

This investigation is aimed to increase the bond between the cement matrix and aggregate to improve the interfacial transition zone (ITZ). Owing to the high water-cement ratio, calcium hydroxide and ettringite crystalline products in the vicinity of the coarse aggregate consist of relatively large crystals, and therefore form a more porous framework than in the bulk cement paste or mortar matrix [14]. Nevertheless, two opposite theories had been argued before the practical testing:

First, due to better wettability of aggregate surface after the treatment, the internal bleeding around the aggregates could be increased. Thus, more porous ITZ would be formed and this means a weaker transition zone.

Second, the ITZ would be enhanced owing to better adhesion of the paste to the aggregate surface after plasma treatment.

Because of experimental difficulties in evaluating the bond and ITZ, the assessment was not possible immediately and directly. The quality of bond is generally investigated with measuring the properties of concrete such as compressive and flexural strength or porosity.

Another challenge of this experiment is the unexplored wettability for the surface of various aggregates. Consequently it is difficult to estimate how long the treatment would last on aggregate surfaces. Tests in the lab showed that the treatment effects obviously last longer on polymeric surfaces rather than on metallic surfaces. But it was unclear whether the treatment

would affect the aggregate surface and bond to cement matrix or not. On the other hand, in a concrete mixture process the aggregates would be added to the mixer, and the fresh cement lime would be in contact with them during a 5-minute long mixing process. This process could result in the treatment effects to be washed away from the treated aggregates.
To overcome these problems, the decision was made to carry out the experiment with one size aggregate, which is washed thoroughly clean from dust and fine particles and dried in an oven to constant weight. Then the aggregates were treated 5 minutes (Fig. 4) with 150 Watt treatment power and compacted in the prepared cube moulds with edge dimension of 20 mm for each side. Then the cement lime, consisting of cement and water was poured on the aggregates. With vibrating the mould, the cement lime filled all the gaps and space between the aggregates and finally a concrete element with one size aggregate was made. In this way, the cement lime is filling through the aggregate gaps slowly and thus the effects of treatment would not be washed because of mixing process. The cubes were demoulded after 24 hours and put under water in 20±2 °C for curing.

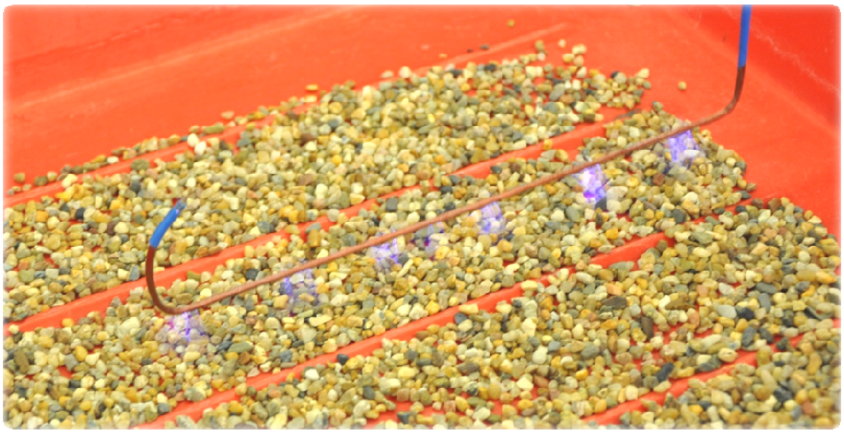


Figure 4: Treatment of prepared aggregate #2-4 mm

The experiment is done in 3 groups of samples, which two of them had PCE based superplasticizer. Each group includes the control and treated samples. Evaluations are done due to compressive strength of the samples, capillary saturation and helium pycnometry porosity. It should be noted that in all the cases, the porosity due to capillary saturation test is greater than the porosity determined on dry samples by means of helium pycnometry which concurs with the result of previous research works [16]. The details of the 3 different mixtures are presented below:

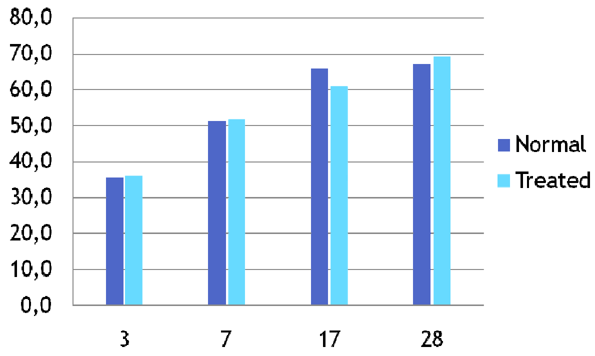
- Nr. 1 Agg. 2-4 mm, CEM I 42.5, W/C=0.45, Cube
- Nr. 2 Agg. 2-4 mm, CEM I 42.5, W/C=0.35, Sp. PCE-F 1%, Cube
- Nr. 3 Agg. 2-4 mm, CEM I 42.5, W/C=0.35, Sp. PCE-S 1%, Cube

In all the results, samples labeled with “N” are normal aggregates and “T” are plasma treated aggregates.

3.1.1. Mix Nr. 1 (Aggregate 2-4 mm, CEM I 42.5, W/C=0.45, Cube)

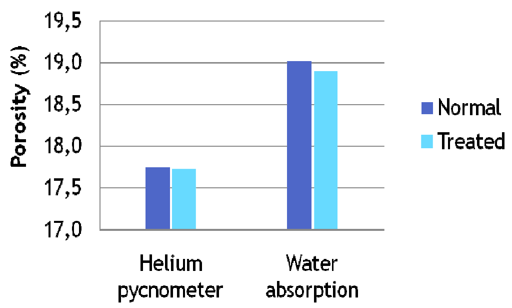
The compressive strength and porosity tables and diagrams are presented respectively in Figures 5 and 6.

Figure 5: Compressive strength diagram and table of Mix Nr. 1 for normal (N) and treated (T) aggregates



	Compressive Strength (MPa)			
Age (days)	3	7	17	28
Nr. 1 N	35,5	51,1	65,8	67,2
Nr. 1 T	35,9	51,6	60,8	69,1

Figure 6: Porosity diagram and table of Mix Nr. 1 for normal (N) and treated (T) aggregates



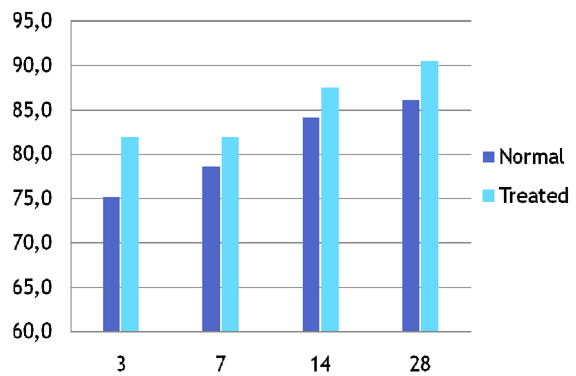
	Helium Pycnometer	Water Saturation
Nr. 1 N	17,7	19,0
Nr. 1 T	17,7	18,9

The results show no considerable difference during and after 28 days at all.

3.1.2. Mix Nr. 2 (Aggregate 2-4 mm, CEM I 42.5, W/C=0.35, SP. PCE-F 1%, Cube)

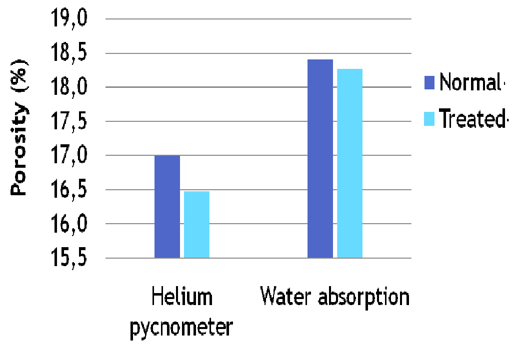
The compressive strength and porosity are presented respectively in Figures 7 and 8.

Figure 7: Compressive strength of Mix Nr. 2 for normal (N) and treated (T) aggregates



	Compressive Strength (MPa)			
Age (days)	3	7	14	28
Nr. 2 N	75,2	78,5	84,1	86,1
Nr. 2 T	81,5	81,8	87,4	90,4

Figure 8: Porosity diagram and table of Mix Nr. 2 for normal (N) and treated (T) aggregates



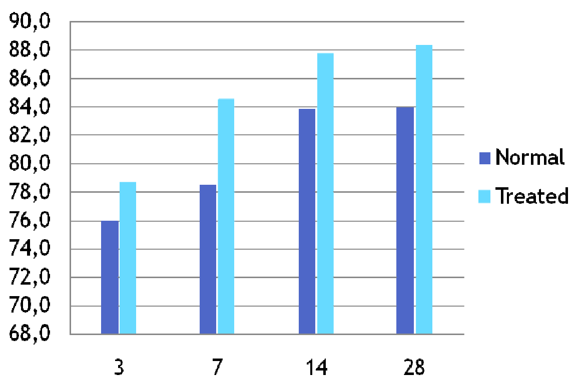
	Helium pycnometer	Water Saturation
Nr. 2 N	17,0	18,4
Nr. 2 T	16,5	18,3

In these samples the porosity is not considerably different but the strength is nearly up to 5 percent increased.

3.1.3. Mix Nr. 3 (Aggregate 2-4 mm, CEM I 42.5, W/C=0.35, Sp. PCE-S 1%, Cube)

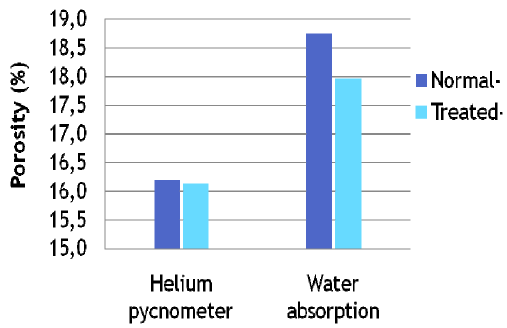
The compressive strength and porosity tables and diagrams are presented in Figures 9 and 10.

Figure 9: Compressive strength of Mix 3 for normal (N) and treated (T) aggregates



	Compressive Strength (MPa)			
Age (days)	3	7	14	28
Nr. 3 N	76,0	78,5	83,8	84,0
Nr. 3 T	78,7	84,6	87,8	88,3

Figure 10: Porosity diagram and table of Mix 3 for normal (N) and treated (T) aggregates



	Helium Pycnometer	Water Saturation
Nr. 3 N	16,2	18,8
Nr. 3 T	16,1	17,9

In this sample also the porosity is not considerably affected but the strength is improved again up to 5 percent.

3.2. Surface treatment on release agents

The aim of this study was to observe the effect of plasma treatment on the interaction of cement lime and the release agent on the surface of the mould. In this experiment, different types of release agent are tested with fresh and hardened cement lime.
After applying the release agent on the surface, each surface was treated in two cycles; each cycle means one time surface scan with the plasma beam. The power of the generator in this treatment was 150 Watt.
The first observation during the treatment is the smoother and thinner surface of the release agent after the plasma treatment. A pile of release agent is collected on the side of the treatment zone (Fig. 11) and only a very thin layer of release agent remains on the surface.

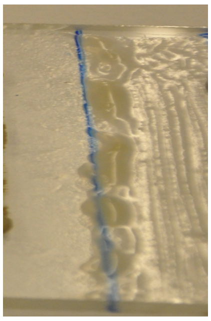


Figure 11: Left side: treated grease; right side: the visible trace of brush with which the grease is applied on the surface; some grease is collected in the middle of the plate due to treatment of the left side

3.2.1. Fresh cement lime on treated release agent

As mentioned, four different types of release agent are tested in this part: Grease (mineral oil based), Ceresit CK 310 (naphthenic mineral oil based), Mikon MG 9006 (polymeric based) and AQUA G (chemical water based). These were applied on the surface of 2 substrate plates, each divided to 4 different zones, whereas, half of them are treated with plasma. Then the plates were set in the same angle of 40 degrees the ground surface. Then the fresh lime paste is poured on the surface to flow. The comparison and evaluation is made due to the behaviour and trace of the cement paste on the surfaces. The following photos show the different behaviour of fresh cement lime on normal (untreated) and treated release agent.
Figure 12 shows the results on grease (mineral oil based) release agent before and after the treatment. It is clear that the cement lime spreads better on the treated grease surface although the adhesion is not changed. This means the finishing surface could be finer as will be illustrated in the next part.

Non-Treated grease | Treated grease

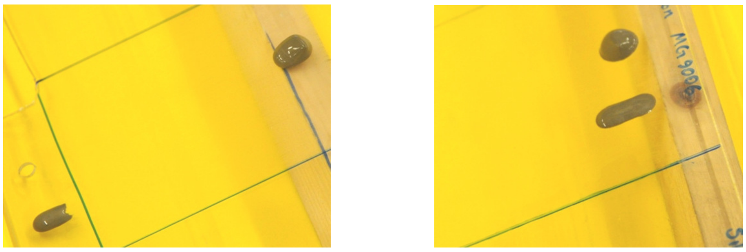
Figure 12: Fresh cement lime on grease (mineral oil based) release agent

Figure 13 shows results of testing on Ceresit CK 310 (mineral oil) release agent. Unlike the grease release agent, the cement lime spreads better on the non-treated surface. In other words, the non-treated surface has better wettability.

Non-Treated mineral oil Treated mineral oil

Figure 13: Fresh cement lime on Ceresit CK 310 (naphthenic mineral oil based) release agent

On the Mikon MG 9006 (polymeric based), the cement lime spreads and holds itself on the treated surface (wettability increased), while on the normal surface it slips without any trace. As could be seen in Figure 14, the cement lime drop is in the bottom of the non-treated release agent substrate and nothing is left behind.



Non-Treated polymer Treated polymer

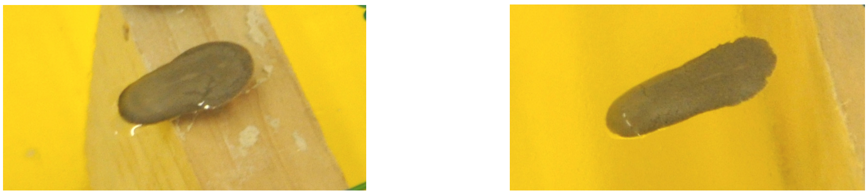
Figure 14: Fresh cement lime on Mikon MG 9006 (polymeric based) release agent

On AQUA G (chemical water based) release agent no difference is observed at the first glance. Both are expanded relatively well on the surface of the release agent (Figure 15).

Non-Treated water based Treated water based

Figure 15: Fresh cement lime on AQUA G (chemical water based) release agent

However with a closer look, some differences could be observed in the wetting attribute of lime water content (Figure 16). On the non-treated one, a dark layer of separated lime water positioned between the lime and the surface and spread on the surface very well. But on the treated surface, there is no separation, while the wetting property is not as well as non-treated one.



Non-Treated water based Treated water based

Figure 16: Closer look to fresh cement lime on AQUA G release agent

3.2.2. Hardened cement lime on treated release agent

In this part, grease (mineral oil based) release agent is applied on the same substrate in two categories of treated and non-treated. Treatment was done with 150 Watt power in two cycles, each cycle with one time surface scanning (Fig. 17). Then a cylinder PVC mould with 13mm thickness is placed on the surface and filled with lime (Fig. 18). After 1 week the samples were taken and the surface of the cylinder, which was in contact with release agent, were taken into examination.

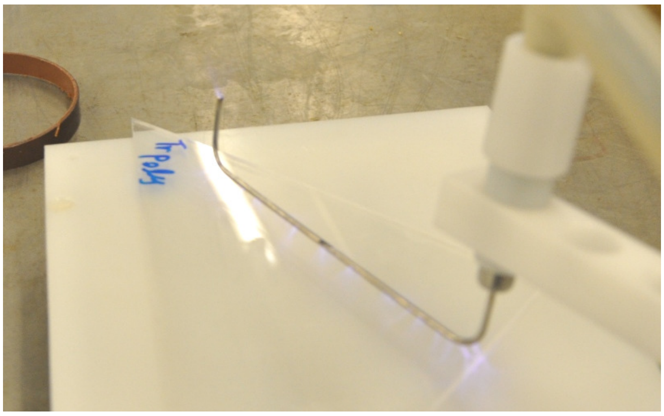


Figure 17: Treatment of a substrate with standard corona discharge

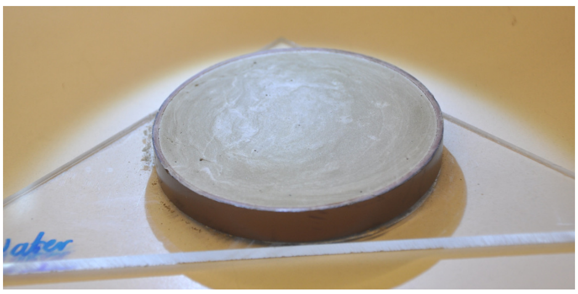
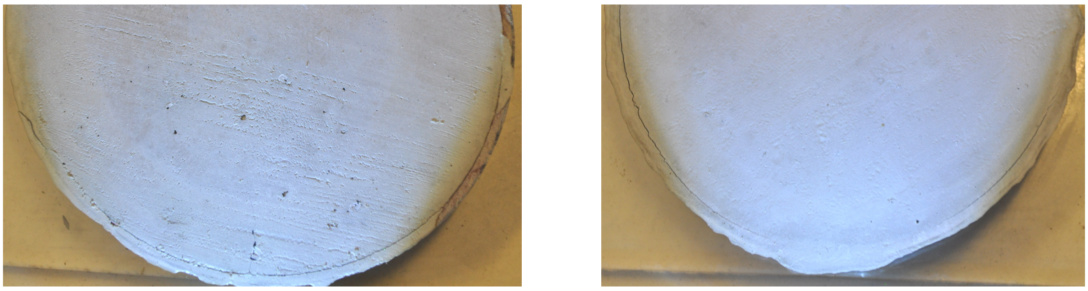


Figure 18: Cylindrical mould on the substrate, filled with lime

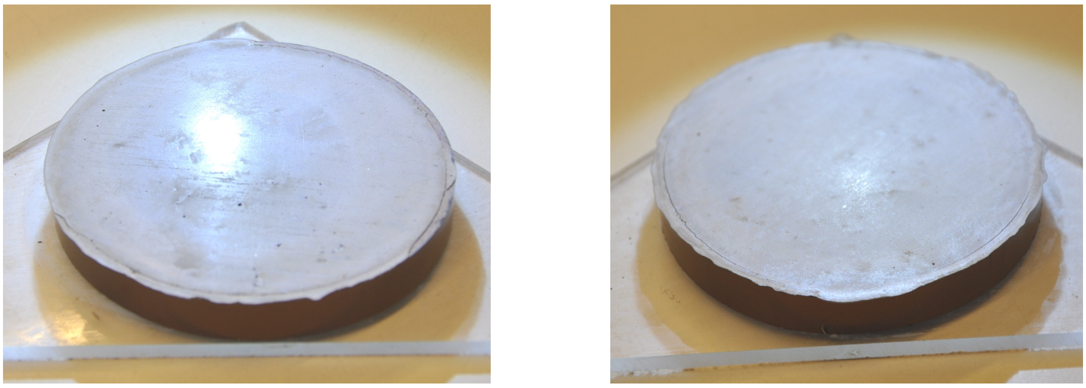
The first difference, illustrated in figure 19, is the surface roughness of the two samples. The roughness in non-treated sample is higher due to the trace of brush, with which grease was applied on the mould surface. However, repeat of the experiment with spray application of release agent on the mould, which is done in Berding Beton facilities in Linthe, showed the roughness of the concrete surface was also higher for non-treated samples. This evaluation is done and reported by Dr. R. Herr.



Non-treated grease surface Treated grease surface

Figure 19: Black points in the non-treated surface (left) shows the roughness of the surface comparing to the treated surface (right)

Testing the light reflection of the samples (Fig. 20) showed that the non-treated grease surface is shiny like glass, while the surface of treated grease is totally mat.



Non-treated grease surface is shiny Treated grease surface is mat

Fig 20: Reflection properties of normal (left) and treated (right) grease with the same light condition

4. Conclusions

To sum up, it is clearly observed that the plasma treatment has effects on compressive strength and porosity, for evaluation of interfacial transition zone; and also on interaction of cement lime with different release agents. It was observed that not only the physical distribution of release agents on the surface were more uniform, but also the behaviour of fresh and hardened cement lime is affected due to standard corona treatment. Different methods and gas application for plasma treatment could bring more benefits, but require more experimental works. The noticeable point in this method is the ability to choose the treatment gas during the treatment process, which could have different influence on the surface properties of materials.

5. Acknowledgement

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