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Prevention of M-A-P-fouling using DLC in a sewage treatment plant

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Abstract
This research deals with applications for coatings with amorphous carbon films, also called Diamond-Like Carbon (DLC) in the wastewater sector for the prevention of fouling with magnesium ammonium phosphate (M-A-P, $MgNH_4PO_4$, struvite). In a major sewage treatment plant a 300 mm long DN100 pipe was installed, which was coated inside with a-C:H:Si (hydrogenated amorphous carbon coating doped with silicon) coating of 5-10 µm thickness using a PACVD reactor at the Wels Campus of the University of Applied Science Upper Austria. The test trials (1 month, 5 months) showed heavy M-A-P fouling with uncoated test-tubes made of stainless steel of 1,5 mm and 15 mm. In contrast DLC-coated tubes had no contamination at all. Furthermore, there is an economic estimate about using DLC-type coatings inside pipe-stocks presented which showed the need for further scale-up and for the development of a suitable welding technology for DLC-coated pipe-stocks.

Introduction
Sludge treatment in wastewater facilities has become a major topic of interest, as the sludge is used for energy generation and other applications. Therefore it has to be processed within a narrow range of parameters. In these operations fouling with magnesium ammonium phosphate (M-A-P, $MgNH_4PO_4$, also called struvite) often inhibits proper function. Not only pipes are affected, rather pumps, centrifuges and aerators are also subject to the accumulation of struvite [1, 2].

For this purpose in [3] the influence of the surface on M-A-P formation was tested using a Phipps and Bird jar tester with the following conclusions:

- Stainless steel is significantly faster affected with fouling than Teflon and acrylic.
- With increasing surface roughness, there is an increase in the rate at which materials are affected by M-A-P fouling.
- With increasing surface roughness, there is a reduction of resistance that specific materials may have had to M-A-P fouling.
- Suitable materials need to be smooth and resilient, as centrate liquors are often coarse and abrasive.

Said experiments did not include DLC coatings. These coatings are not used very much in the process industry but have promising potential. Therefore University of Applied Science Upper Austria (FH OOE) Wels Campus in cooperation with Rübig GmbH & Co KG Wels, Austria, developed a DLC-coating device. Using plasma-assisted chemical vapor deposition (PACVD) technology, it is possible to depose layers with thicknesses up to 60 µm in a process known as „Thick DLC". Other technologies can only coat much thinner layers, typically about 15 µm, so these layers have a lower mechanical load capacity.

An additional advantage of producing DLC layers in a PACVD operation is that cavities can be properly coated. This is especially relevant with workpieces used in the processing industry. It is also possible to coat heavy pieces, often the case in the processing industry. One of the characteristics of DLC is its low friction coefficient, which is of use in machines such as high pressure piston pumps [4]. However, in the processing industry it is known that a low friction coefficient is also relevant to minimizing the build-up of fouling in fluid flows, as it has some correlation with surface energy [5]. The use of plastic pipes is therefore recommended for fouling prevention, but plastic has the clear disadvantage that it can only be used at moderate temperatures and pressures. Also the roughness increases over time, so the anti-fouling effect deteriorates [6]. Research into the possibility of prove the anti-fouling effect of steel tubes coated with a-C:H:Si was conducted at the FH OOE Wels Campus. C:H:Si-coated tubes were used in a sewage plant which was capable of cleaning about 250,000 population equivalents, as there were major problems with M-A-P fouling there. A population equivalent in wastewater treatment is the number expressing the ratio of the sum of the pollution load produced during 24 hours by industrial facilities and services to the individual pollution load in household sewage produced by one person in the same time.

DLC coating
In general, DLC films combine a series of interesting properties, such as high hardness, excellent wear resistance and low friction coefficient. Moreover, these films are chemically inert in the most aggressive environments and exhibit remarkable anti-corrosion behavior.

There is a systematic classification of carbon films divided into the following groups [7]:

1. Plasma polymer films
2. Amorphous carbon films
3. Crystalline carbon films

The variety of plasma polymer films and of amorphous carbon films is illustrated in Fig. 1 where carbon films are plotted as a function of the hydrogen content and the ratio of sp^2-sp^3 hybridizations in the C-C bonds.

In order to modify its properties such as thermal stability, electrical resistivity, surface energy, friction coefficient, elements such as F, Si, N (X) or even metals (Me) can be added (see Fig. 1).

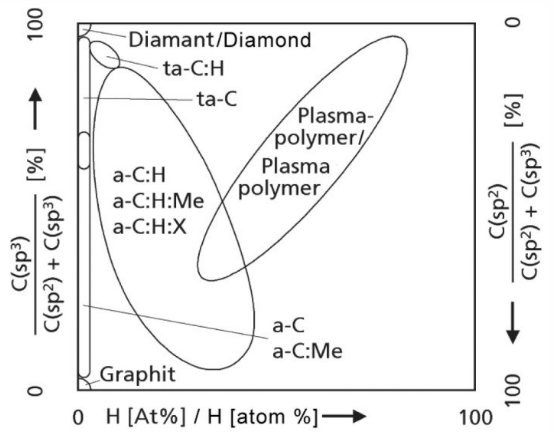

Fig. 1, Overview of carbon films [7]

PACVD plant

The a-C:H:Si coatings in question were deposited using PACVD. The apparatus used for the experiments is a commercially available hot wall reactor as depicted in Fig. 2.

The system consists of a chamber with an auxiliary heating system, a gas supply and distribution system and a pumping system with pressure control. The discharge is maintained by a pulsed DC power supply. The reactor is made up of a stainless steel vessel, which acts as an anode, and a substrate holder that serves as the cathode. The substrate holder allows the positioning of parts up to a diameter of 400 mm and 600 mm in height. A viewport is available for the observation of the discharge. The PACVD system was modified to enable the deposition of Si-doped carbon layers by the installation of a separate Si precursor line.

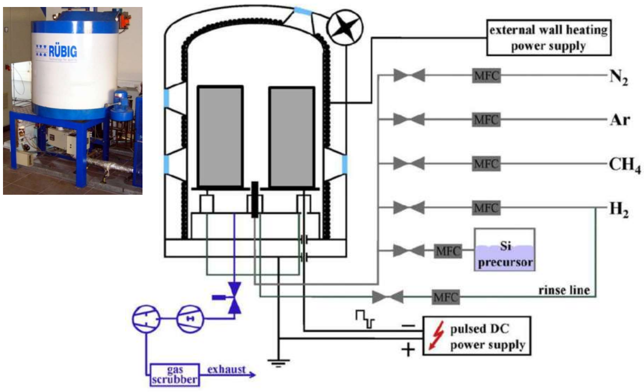

Fig. 2, Schematic view of a PACVD plant [8]

This Si precursor line consists of a storage tank, a mass flow controller and a piping system, which is heated to avoid condensation of the Si precursor. The process gas consisted of a mixture of C_2H_2, H_2, Ar and the silicon precursor HMDSO (hexamethyldisiloxane) regulated by mass flow controllers. The process pressure was achieved by a screw pump and a roots blower and controlled by a throttle valve at pressures from 0.7 up to 3.5 mbar.

DLC coatings for pipes

The main objective in this project was to prove the usability of DLC as an economic and effective means to coat inner walls of pipes. The procedure was divided into the following steps:

- Finding adequate coating set-ups and test them.
- Improving the capability to coat into cavities.
- Finding promising use-cases in the processing industry and test the effectivity under real conditions.

As mentioned above, a number of experiments on new DLC coating layers had been conducted at the FH OOE, so a solid basis of know-how had already been accumulated.

The possible use-cases in the process industry are mainly corrosion protection, wear protection and anti-fouling or anti-adhesion surfaces. The strongest benefit was found in the latter application, as this is still an area with room for significant improvement. There was the idea to test the effect under real conditions and establish so a numeric classification of the improvement. Further there are several sources for fouling, but the crystalline type is of major importance and has the benefit, that it can be easier reproduced than others.

Magnesium ammonium phosphate

Magnesium ammonium phosphate (M-A-P), also known as “struvite”, has the chemical composition $MgNH_4PO_4$. It can be found as a deposit in crystalline form in various parts of a wastewater treatment plant and causes serious operational problems.

When magnesium is still present - a hardness agent in almost all tap water – M-A-P can form and precipitate at certain pH values. M-A-P forms preferentially in turbulent and heavily-circulated areas, such as pumps, pipes and sliders. Here, carbon dioxide (CO_2) can evaporate, thus increasing the pH value. In said wastewater treatment plant, the pH of the centrate is already in the critical range of 7,9 to 8,1. Increasing the total pressure could lead to a prevention of the emergence of M-A-P but this option is not possible [9].

Investigated sludge pumping system

In the examined wastewater plant there is a 200 m long steel pipeline (DN 100) from the digester to the building with the dewatering units. This pipeline is affected by the growth of M-A-P crystals at regular intervals. Chemicals are periodically used to remove these crystals, but all of the deposits can never be fully removed. This increases the risk of pipe clogging, thereby endangering the stable, continuous operation of the sewage treatment plant. Especially with pipe narrowings and bows in the pipe system, M-A-P deposits were detected in less than seven days.

The entire line is usually blown out with compressed air at intervals of 1-2 months and then filled with citric acid. This is able to dissolve all deposits in the line over a period of about 24 hours. However, this process requires additional personnel and operating costs. Fig. 3 shows the theoretical procedure at said plant: a fluid flows through the clean pipe for a certain time (blue arrow), then deposits of M-A-P clog the cross section (pink). After rinsing with citric acid (yellow arrow) the pipe is clean again.

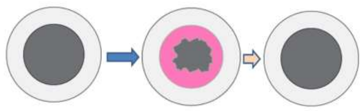

Fig. 3, M-A-P fouling and cleaning with citric acid, theoretical model

Over a longer period of about 12-24 months, critical parts of the piping system are opened to check the system components and to do maintenance if necessary. However, this is still preferable to a possible total failure of the line, the rectification of which would entail digging and high costs.

The coefficient of friction between pipe and fluid plays a major role in crystal fouling. Stainless steel has a higher coefficient of friction than, for example, plastic. As a result, M-A-P easily adheres to these pipes. Other types of soiling, such as hair, sand and fabric fibre, negatively affect the coefficient of friction as well.

However, the stainless-steel pipes used are a common building material in sewage treatment plants. The use of plastic pipes with a lower coefficient of friction is not common for these dimensions and with these durability periods. In addition, over time plastic pipes also acquire a "rough" inner surface.

DLC on a pipe section

A DN100 pipe section of 300 mm in length was installed in the existing pipe system. A corresponding test tube was coated with DLC in the laboratories of the FH OOE, Campus Wels (Fig. 4).

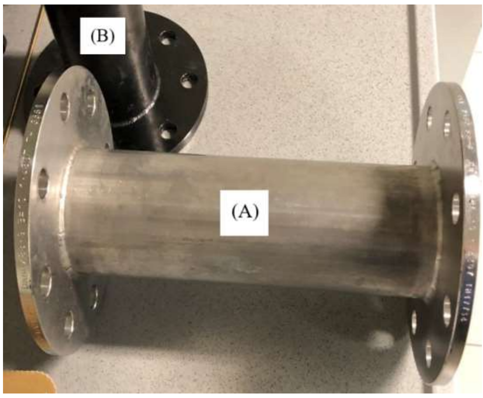

Fig. 4, Pipe section without DLC (A) and with DLC (B)

The uncoated tube was then used for validation for about the same duration of time. The pipe section was manufactured with a front and rear flange (Fig. 5).

Table 1: Schedule of pipe installations

No	type of pipe	mount	use [d]
01	Uncoated	14.01.2019	31
02	DLC-coated	14.02.2019	53
03	Uncoated	08.04.2019	144
04	DLC-coated	30.08.2019	161

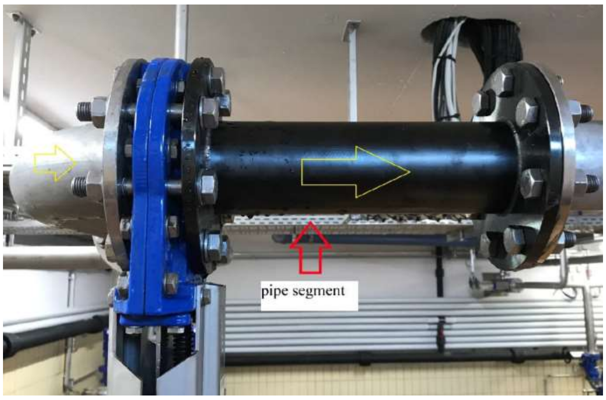

Fig. 5, Line section with DLC pipe section No 02

The coating was applied in the PACVD reactor in a temperature range between 400 and 550 °C with a process time of about 7 hours, resulting in a layer thickness of about 5-10 µm. The thickness and other parameters were chosen based on past results of this set-up. The layer characteristics are of a-C:H:Si type (see Fig. 1).

Test trials 01 and 02 – one month each
As Tab. 1 shows, the tests trials 01 and 02 each lasted one month. The test was finished before the regular flushing of the system was done. Fig. 6 shows that the uncoated section acquires a 1.5 to 2 mm M-A-P layer whereas the DLC coated one has no adhering contaminations.

Test trials 03 and 04 – five months each
According to Tab. 1 the test trials 03 and 04 were of about five months each. The tests were finished before another flushing of the system was carried out, but in between there was regular rinsing cycle using citric acid.

Findings indicate that the rinsing cycle cannot clean the standard type tube fully. As shown in the upper part of Fig. 7 there is a build-up of a M-A-P layer in the first treatment period (blue arrow), but then there is no full cleaning (red arrow), so some residuals still remain, resulting in even greater subsequent build-up. After five months the cross-section area had narrowed by up to 50%, resulting from a 15 mm thick M-A-P layer. It has to be noted that this layer (Fig. 8) also consists of other deposits, making it very firm and more persistent.


Fig. 6, Contaminations after campaign 01 and 02 (DLC)

In clear contrast, campaign 04 ended without any sticking contaminations again. The surface prevented any sticking under the given conditions. The result came as no surprise after campaign 02, but as the plant requires regular flushing for most of its installations, it was not fully possible to examine the long term build-up with DLC.

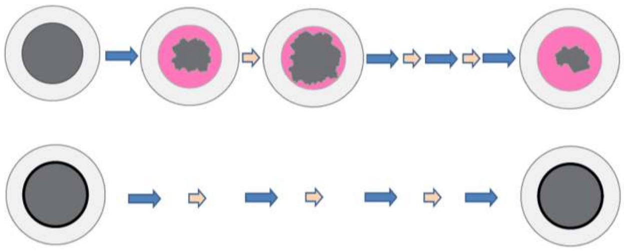
Fig. 7, Comparison on campaign 03 and 04


Fig. 8, Contaminations after campaign 03 and 04 (DLC)

Concept for implementation
In a first approach, a cost estimation was carried out on the basis of 1 m D100 pieces with flanges as in Fig. 4, which is referred to as “DLC-Pipe-Stock-01”. A large commercial standard PACVD reactor [10] was assumed to be used, which has a volume of 1500 mm in diameter and 2400 mm in height. Batches of 33 tubes were evaluated. For a pipeline of 200 m seven passes would be required. There were no special means foreseen so the tubes would be coated on the outside as well (see Fig 4B), which can be viewed as additional corrosion protection. Compared to a standard line the total installation cost of such a “fully flanged” DLC-pipe stock would be in the range of about four times the standard equipment.

Potential of flanged DLC pipe stocks
One obvious way to reduce costs of producing “DLC-Pipe-Stock-01” would be to use longer sections. Typically 6 m

sections would be required to meet market standards. There is the future possibility to test 2 m sections of standard D100 pipes of stainless steel in commercial DLC reactors at a service coating shop. In such a test, first the proper quality of the coating over the whole length has to be shown. The resulting ratio of length to diameter would be 20, while in the test trials it was 3.

After that step, there come tests of how to effectively load the reactor with 2 m sections of flanged D100 pipes. It is not yet clear what spacing is required and if the theoretical maximum, which was found in the range of 33 in this example, is valid or can be exceeded.

The results of this report show that suitable flanged fittings such as bows for such a pipe-stock can be coated in a standard DLC-reactor without any major restrictions.

Another step would then be to gradually increase pipe lengths up to the above-mentioned 6 m sections. There are theoretical concepts for building such a facility, as the PACVD process has basically no height limit, but there are major investment costs for such a plant. First, the filling procedure would require a building height of at least about 15 m. The operation of such huge reactors has also never been fully tested, and additional means of managing the plasma in the reactor might be required. The biggest disadvantage of such a tall reactor would be that it would only be economical if operated primarily with tall pieces, which cannot be processed in standard DLC reactors of typically 2.4 m height.

Potential of welded DLC pipe stocks

At FH OOE (Dept. of Engineering and Environmental Technologies, Dept. of Technologies of Materials) research into how DLC-coated pipes can be welded together without leaving areas lacking DLC-coating protection is ongoing. The given situation of M-A-P fouling is likely to be improved even with moderately good welding and it could be tested at the aforementioned sewage plant using the test section (Fig. 5) by cutting the DLC-coated section in the middle and instead welding the connection.

Pipes without flanges could bring an increased output of the described tall DLC reactor. That would require that flanges are welded after DLC coating. This is another area for investigation.

One final step would be the validation of the pipe-stock in terms of European standards as well as ASME standards. If this validation fails or remains incomplete, such a solution would then not find great use. An important potential of welded DLC pipe stock is also found in areas of high temperatures (up to 450 °C) and high pressures, in which only the welding technology and the method of validation by the standards are a limitation, but not the coating itself.

Conclusions

It was shown that a flanged stainless steel tube DN100 of a length to diameter ratio of 3 could be properly coated with DLC inside using PACVD technology. Furthermore, there were tests in the sludge treatment area of a sewage plant in campaigns of 1 and 5 months. DLC coated tubes showed no residuals after said periods whereas the standard tubes suffered a build-up of 1,5 mm and 15 mm of a fouling layer consisting of M-A-P (struvite) and other deposits. The DLC layer was also to withstand the monthly flushing of the system with citric acid. The significant antifouling property of DLC was therefore confirmed under real conditions.

The economic situation of DLC coated tubes was investigated on the basis of 1 m pipes of same type and a total line length of 200 m pipe-stock assuming coating costs at a standard PACVD reactor. The total cost would be about four times higher than the standard type pipe stock. There is potential to further increase the length of PACVD reactors up to 6 m height and to introduce welding of DLC-coated pipes. Both together would reduce the cost dramatically and then DLC coated steel tubes would be an antifouling option in the process industry even with coarse particles in the fluid, high pressure and temperatures up to 450 °C.

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