Optimisation of flue gas cleaning processes by utilisation of the performance profile of PTFE and modified PTFE in heat exchanger and lining applications

Michael Schlipf and Katja Widmann

Introduction

Increasing focus on environmental aspects of coal fired power plants gives the flue gas cleaning processes more importance from year to year. Different kind of equipment installed downstream of the boiler ensure the fulfillment of new environmental regulations. The precipitation of the particles within the electrostatic precipitator (ESP) and the reduction of SO₂ in the flue gas desulphurisation unit (FOD) can be considered as standards. Chemical processes such as selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) reduce the NOₓ emissions significantly in many power plants. New carbon capture systems to minimise the CO₂ content in the exhaust gases, the main product of the combustion process, are presently under development. While coal-fired power plants in general are designed for continuous energy production under full capacity utilisation, due to the fluctuating feed of energy from wind and sun into the energy distribution systems, the coal-fired power plants have to compensate by changing the utilisation coefficient permanently. This generates additional requirements especially for corrosion protection, as the conditions are changing from wet to dry depending on the plant utilisation. Finally, during short- or long-term shut down periods, additional precautions for preservation have to be undertaken.

The present article, describes, how the fully fluorinated polymers Polytetrafluoroethylene (PTFE) and modified PTFE can be used as well for heat displacement systems as for different kind of linings for corrosion protection. However, successful system solutions only can be provided in close co-

Fig. 1. In Polytetrafluoroethylene (PTFE) and modified PTFE the carbon chain is effectively protected against chemical attack. The high bonding energy of the C-F bond combined with the excellent steric shielding of the C-C chain by fluorine atoms makes PTFE and modified PTFE a resin of excellent chemical resistance.

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connection between material properties, design of components or systems and operation conditions.

Main part

The property profile of PTFE and modified PTFE

Polytetrafluoroethylene (PTFE) and modified PTFE are fully fluorinated resins, where fluorine atoms are protecting the carbon chain efficiently from attacking chemicals, see Figure 1. With a bonding energy of 460 kJ/mol the carbon-fluorine bond is the strongest chemical bond known in organic chemistry. Therefore this bond cannot be replaced by any other chemical bond with winning energy by this substitution. Furthermore, simply by the size of the fluorine atom in helical ordering does not leave unprotected spots along the C-C polymer backbone. Both effects are the origin of the excellent chemical resistance of PTFE and modified PTFE which makes them practically resistant to all chemicals being present in typical flue gas mixtures as well under try as wet conditions.

With its molecular weight of up to $10^8$ g/mol for PTFE and $0.2 \cdot 10^8$ g/mol for modified PTFE both polymers are characterised by the highest molecular weight of all thermoplastic materials. They belong to the category of semi-crystalline thermoplastics and after sintering they are composed of about one third of amorphous region and two thirds of crystallites. The high crystalline part enables a continuous service temperature close to the crystalline melting temperature, which is in the range of 325°C up to 330°C. Permanent service up to 260°C will not damage the polymers, even not in the presence of aggressive chemicals. During short-term exposure temperatures up to 300°C are acceptable.

The amorphous content provides the excellent anchoring of the polymer chains within the polymer matrix. Combined with the high molecular weight, this is the base for the good abrasion resistance required for the many cleaning cycles needed to keep e.g. ducts and heat exchangers of flue gas systems under good operating conditions. Applied as HetrarogTM – combs in Ljungstrom® heat exchangers for example this becomes visible in the excellent resistance against polymer erosion during many years in service when cleaning procedures are used frequently under standard operation conditions. In permanent service of a Ljungstrom®-GGH over 12 years in a representative application, the erosion of the comb length measured was less than 5 millimeters and thus extremely small.

The complete covering of the polymer chains by fluorine atoms is the origin of the non-polar, anti-adhesive surface. The sticking of deposit formed from fly ash and aqueous acid mixtures to the surface will be reduced by this non-polarity and additionally it makes cleaning easy at the same time. The contact angle between water and the PTFE surface is about 126 degrees. As a consequence the wetting of the PTFE-surface by water is significantly reduced and, compared to metal or enamel, adhesion forces to aqueous media are minimised. In direct consequence the fouling tendency of PTFE heat transfer elements in Ljungstrom® rotors compared to enamel coated steel surfaces is reduced and additionally, the cleaning behavior is improved. For plant owners this means enhanced availability of gas-heat exchangers.

The “Limiting Oxygen Index” (LOI) of PTFE is about 95; that means, it is not flammable under atmospheric conditions (Atmosphere = Oxygen Index (OI) = 20). Glowing fly ash particles therefore are not critical for the non-flammable resins PTFE and modified PTFE.

How about ageing behavior of PTFE under typical service conditions in power plants at high temperatures and repeating altering stress, combined with permanent presence of aggressive chemicals? The ageing mechanism of polymers is based on two different chemical reactions: in one respect the breaking of a polymer chain followed by its recombination leads to a progressing cross-linking of the polymer, thus enhancing brittleness. On the other hand the polymer is chemically degraded by oxidative attack with substitution of the side chains, becoming visible through enhanced crack sensitivity. Both reactions are not possible at PTFE due to energetic reasons. Therefore, even in permanent service under extreme conditions, PTFE will not show ageing effects and the original property profile remains constant over many years. Only abrasion effects, as mentioned earlier are possible.

The question may arise when it will be beneficial to use PTFE and in which cases the application of modified PTFE is advantageous. The answer can be given in the following way: If chemical resistance and stability under high temperatures are required, standard PTFE does the job.

In applications where additionally high resistance to permeation is needed and weldability is required for the assembly of parts and systems, modified PTFE should be the preferred choice: The lower molecular weight of modified PTFE makes particle fusion during the sintering of the polymer material more efficient and, by closing the gaps perfectly between the material particles, gives it an enhanced barrier property to aggressive chemicals and gases. Another benefit of the lower molecular weight of modified PTFE is its weldability. Either by butt welding or hot gas seam welding, films and parts from modified PTFE can be connected to allow a broad variety of fluoropolymer based system solutions. Finally the reduced cold flow, which gives the material more stability especially under high service temperatures, is the third benefit of modified PTFE. The enhanced material stability required around fixation points of loose lining systems for flue gas ducts is a typical example where the better performing modified PTFE is selected preferably.

Applications for PTFE and modified PTFE to optimise flue gas cleaning

In order to optimise the flue gas cleaning systems and operating conditions in coal fired power plants, nowadays fluoropolymers such as PTFE and modified PTFE are used in many places. Figure 2 gives an overview on the different opportunities for applications: Downstream the electrostatic precipitator (ESP), fluoropolymer linings are typically used to protect the duct system from corrosion. As a new trend in the power plant industry fluoropolymer film lining includes the stack itself. Different reasons are driving the development for-

Fig. 2. Downstream the electrostatic precipitator in a power plant the applications for fluoropolymers begin: Lining of flue gas ducts including stack and heat displacement systems to run modules like the flue gas desulphurisation unit under optimised conditions.
ward in this direction: the trend for more efficient power plants generates lower off-gas temperatures requiring better protection of the stack construction due to wet environment and, as a consequence of different plant utilisation, deposit sticking to the inside surface of the stack may be blown out in phases of full power operation. Both requirements, protection from wet aggressive environment and avoiding deposit formation can be fulfilled by fluoropolymer lining systems.

Inside the heat displacement systems, which provide the optimal temperature conditions for e.g. the flue gas desulphurisation unit, PTFE or modified PTFE can be used as heat transfer elements in Ljungström® heat exchangers, as tube material in tube bundle heat exchangers and for the lining of the modules including their inlet- and outlet-sections.

PTFE and modified PTFE in heat displacement systems:
The Ljungström® GGH

Cooling down the flue gas before entering the FGD and reheating it after cleaning can be realised by various techniques, e.g. either by Ljungström® Gas-Gas-Heat Exchanger (GGH) or by Fluoropolymer tube bundle heat exchangers.

The principle of the Ljungström® air preheater works as follows:

The heat transfer surface consists of thin profiled steel plates, packed in frame baskets and installed inside the rotor. Typical diameter of a rotor is in the range of 15 to 21 meters. During each revolution of the rotor, heat is absorbed by the heating surface passing through the hot gas stream and transferred to the side where the cold gas is passing the rotor segments. Thus, the cold gas is heated up while the rotor inserts are re-cooled again.

In flow direction of the hot gas through the rotor elements, temperature may fall below the dew point level $T_D$ and the chemicals mix starts condensing. Thus a highly-corrosive environment is generated at the “cold end” of the heater elements and steel quickly starts corroding. PTFE is the material of choice for the heat transfer elements which will withstand these aggressive conditions with no damage over years.

In order to explain, why polymers such as PTFE or modified PTFE are capable for a similar heat transportation capacity when installed inside Ljungström® rotors, we can use the following experiment:

One kilogram of a Hetragon® PTFE-comb and a steel plate package of similar weight are heated by hot air up to 90°C. After immersing the heated components into a water basin containing five liters of water, the temperature is rising by 3.2°C when heated with the PTFE comb, but only 1.5°C in case of the steel plate package.

Transferring these results to Ljungström® rotors equipped with either steel plates or PTFE combs, this means, that only approximately half of the weight of PTFE combs compared to steel plates is required in order to transfer the same amount of heat during one turn of the rotor. In terms of weight loading inside the rotor this comes pretty close to the real situation: While the typical specific weight of PTFE combs is about to be 360 kg/m³, steel plate packages are much more heavier with a typical load of around 850 kg per cubic meter.

The consequence for the packings of Ljungström® rotors therefore is as follows: If equipped with PTFE combs, half of the package weight is sufficient to transfer a similar amount of heat per revolution compared to the 'full steel version'.

The equivalence of heat transfer capacity of both system solutions leaves it up to the designer or operator of such GGH to decide, whether to use steel plate packages or Hetragon® PTFE combs. From the economical point of view, it can be advantageous, to start with the replacement of steel plate packages by PTFE combs from the cold end side of the rotor, where the corrosive attack is highest. As both materials, steel plates as well as PTFE combs can be placed in one basket, the ratio of steel to PTFE can be decided totally free. The details of a representative assembly in so-called ‘combi-packages’ can be seen in Figure 5.

Due to the significant differences in weight of steel plates compared to PTFE, the options for weight savings are enormous.

Fig. 3. The heat transfer elements inside Ljungström® rotors can be made out of different materials. With special focus on the cold end side where corrosion attack is harshest, the use of PTFE combs may be the right measure to avoid corrosion totally. Surprisingly, the heat transportation capacity is on a similar level (400 ± 8 % kW/m² · K) no matter whether the heat transfer elements are made from steel, from enamel coated steel or from fluoropolymer ‘plastic’.

Fig. 4. The amount of specific heat to be carried by Hetragon® PTFE-combs is twice as high compared to steel plate package. If PTFE is used as a heat transfer medium, only half of the weight compared to steel is sufficient for the same amount of heat transfer.
Taking a Ljungström® rotor as an example with twenty meters in diameter and one meter in height, the total weight of steel plate packages is about 213 mtons. If only 20% of the height is replaced by PTFE combs, the weight savings are already 24 mtons. Full replacement of steel plate packings by Ljungström® PTFE combs would end in a total weight reduction of 123 mtons. By this amount, the weight of the ‘moving parts’ of the GGH can be reduced.

Further benefits are:
- Significant load reduction for the bearing system
- Minimise vibration
- Reduce sagging at the outer circumference
- Additional reduction of the weight of the static rotor components

All these advantages can be generated without the need for any compensation in heat transfer capacity of the GGH.

The molecular background of specific heat $c_p$ and thermal conductivity $k$ and its impact on material selection

Depending on the design of heat exchangers, different properties of the materials are addressed to be essential for the function of the ‘thermodynamic machine’. In Ljungström® GGH, the specific heat $c_p$ of the rotor packings makes the decision on the efficiency of the thermodynamic machine, as it defines the amount of thermal energy which can be picked up by the material and, by rotation, carried to the other side. As long as the walls of the packing materials are thin enough, only a low degree of thermal conductivity $k$ is required in order to enable a quick pick-up and release of the thermal energy.

In tube bundle heat exchangers or in pipe heat exchange constructions, the thermal conductivity $k$ of the tube or pipe material is the key to success. When exchanging heat, the energy has to go through the walls of the tubes or pipes to enable the energy flow from the high-temperature side to the medium with the lower temperature.

A typical design for tube bundle heat exchangers in FGD displacements systems works in the following way: After leaving ESP and before entering the scrubber high-temperature, non-cleaned flue gas flows along the outside of tubes, heating up the heat transfer medium inside the tube, which is typically water. The heated water then flows through the tube bundles of the ‘heater-side’ of the displacement system, while the cool, cleaned, flue gas after leaving the scrubber flows along the outside of the tubes picking up the energy from the water through the tube walls.

How are the mechanism of specific heat $c_p$ and thermal conductivity $k$ in steel and polymer materials and what does this mean for the usage of both materials in the different types of heat exchangers?

The explanation is being given in the following Figure 6a and 6b.

The mechanism of specific heat $c_p$ (Figure 6a)

While in metals the atoms only can perform vibrations around the state of equilibrium, in polymers, the molecules can carry high amounts of energy in the activated degrees of freedom in translation and rotation. The free volume between the molecules in the amorphous regions allows this high degree of molecular mobility. As a result, the specific heat $c_p$ of metals is low while that of polymers is high.

Therefore, in Ljungström® heat exchangers where $c_p$ plays the key role, polymers such as PTFE can outperform metals in terms of heat transfer capacity by far.

The mechanism of thermal conductivity $k$ (Figure 6b)

While in metals the atoms are in close contact to each other, motions of the atoms are transferred easily with no delay to the neighbor atoms, thus conducting a heat impulse quickly through the material. This is known as the excellent thermal conductivity $k$ typical for metals.

The free volume between the molecular chains in polymers makes the kinetic impulse transfer to the neighbors difficult and heat impulses cannot move forward easily. This is the origin of the low thermal conductivity, which polymers are known for.

As a result, the thermal conductivity $k$ of metals is high while that of polymers is low. This has to be taken into consideration when polymers such as PTFE or mod. PTFE are applied as tube material in bundle heat exchangers: the exchange area required is significantly higher when polymers are used instead of metals. Manufacturing the tube walls as thin as possible does not only help to reduce the material demand, but also enhances the efficiency of heat transportation through the tube walls.
Conductive filler to the fluoropolymer is not recommended in this case, as the full polymer material performance is required in this application to withstand the pressure under elevated temperatures over many years in service. Therefore, reducing the physical strength of the tube material by filler addition is not acceptable. The expected lifetime of these systems can be very high, as no corrosion will occur even after many years in application.

Replacing steel by Hetraron™ PTFE combs – The calorimetric details

When utilising the specific properties \( \gamma_p \) and \( k \) of PTFE for the optimisation of Ljungström™ heat exchangers, the benefits can be significant when replacing steel plates by PTFE combs. Table 1 shows the calorimetric details.

The different material options for Ljungström™ heat exchanger packages can be seen in the listing, together with its values for specific heat \( \gamma_p \) and thermal conductivity \( k \). Positioned inside Ljungström™ rotors, \( \gamma_p \) describes the capability of the packaging for heat transportation and \( k \) stands for the speed, how quickly the energy can be picked up from the surrounding fluid gas stream and how quick it will be unloaded again to the cooled, cleaned air coming from the outlet of the FGD scrubber after a revolution of the rotor of 180 degree. The specific weight for steel packages with about 850 kg/m\(^3\) is significantly higher than those for PTFE comb packages made from either unfilled PTFE or thermally conductive PTFE with its 360 resp. 300 kg/m\(^3\).

However, as the specific heat for PTFE with its 1.01 J/g · K is more than twice as high as that of steel, 0.46 J/g · K, the 360 kg of unfilled PTFE combs can carry nearly the same amount of thermal energy, as this is true for a one cubic meter steel package with its 850 kg (see also Figure 3).

The question may arise whether the very low thermal conductivity \( k \) of PTFE (0.35 W/m·K) may negatively influence the heat transfer capacity of the packed rotors due to nonsufficient heat transfer in the energy pick up and unloading sectors of the rotor. The development engineers took this into consideration and developed the Hetraron™ PTFE combs with 1.2 mm wall thickness only. As a result, the contact time with the streaming fluid gas touching the comb walls on both sides is long enough, to fully heat up and cool down the heat transfer elements during each revolution.

The following assumptions had been made for the calculations summarised in Table 1:

- The specific weight of profiled steel plate packages inside the rotor is more than twice as high as the specific weight of Hetraron™ PTFE combs. Enamel coating contributes positively to specific heat \( \gamma_p \) and negatively to thermal conductivity \( k \).

Table 1. Different materials can be used as heat transfer packages in Ljungström™ heat exchangers. The specific heat \( \gamma_p \) is the key criteria for the efficiency of this type of heat exchanger. Thanks to its high specific heat polymer materials such as PTFE can carry a similar quantity of energy per revolution as the much heavier steel packages.

<table>
<thead>
<tr>
<th>Comb material</th>
<th>Colour</th>
<th>Specific heat capacity ( \gamma_p ) J/g · K</th>
<th>Thermal conductivity ( k ) W/m · K</th>
<th>Specific gravity g/cm(^3)</th>
<th>Specific weight of combs kg/m(^3)</th>
<th>Heat transportation per revolution ( kJ/m^3 · K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE unfilled</td>
<td>white</td>
<td>1.01</td>
<td>0.35</td>
<td>2.16</td>
<td>360</td>
<td>364</td>
</tr>
<tr>
<td>PTFE thermally conductive</td>
<td>black</td>
<td>1.24</td>
<td>0.43</td>
<td>2.13</td>
<td>300</td>
<td>372</td>
</tr>
<tr>
<td>Steel</td>
<td>black</td>
<td>0.46</td>
<td>40</td>
<td>850</td>
<td>391</td>
<td></td>
</tr>
<tr>
<td>Nickel alloy</td>
<td>black</td>
<td>0.46</td>
<td>15</td>
<td>850</td>
<td>391</td>
<td></td>
</tr>
<tr>
<td>Enamel</td>
<td>glossy</td>
<td>0.71</td>
<td>1</td>
<td>880</td>
<td>420</td>
<td></td>
</tr>
<tr>
<td>Enamel-coated steel</td>
<td>glossy</td>
<td>0.5</td>
<td>8</td>
<td>850</td>
<td>420</td>
<td></td>
</tr>
</tbody>
</table>

The two main reasons why differentiation is made in this way is due to the different coefficient of thermal expansion of fluoropolymers and metals and the limited availability of high-temperature glues with chemical resistance. With an average coefficient of thermal expansion for the temperature range of 0 to 200°C of 12·10^-6 1/K for PTFE and modified PTFE, these fluoropolymers are expanding or contracting ten times more than steel under temperature variations. Therefore, if temperature is changing too much, high shear forces will be generated between bonded lining layers and the bonding layer will be destroyed.

The different techniques applied in representative applications in power plants can be seen in Figure 7.

Corrosion protection with fluoropolymers in lining applications

As demonstrated in the Figure 2, it is evident that the potential area for fluoropolymer lining applications in the flue gas duct system begins immediately downstream ESP. Depending on the conditions in service, differentiation is made between the following two lining systems:

- Bonded lining systems for service temperatures up to appr. 120 °C for storage & transportation tanks
- Loose lining systems in applications with temporary or permanent service temperature higher than 120 °C or in areas, where direct bonding is not possible (e.g. stack lining)

The selection of an adequate material, especially the use of modified PTFE laminate with its reduced tendency of permeation, combined with the required thickness of the lining system, provides excellent corrosion protection. Low permeability and enhanced thickness of the barrier layer does not enable the chemicals to get in direct contact with the steel components over the full lifetime of the system. Therefore, protective layers of modified PTFE up to 6 mm, sometimes even more, are typically used in this kind of corrosion protection system. As can be seen in Figure 8, the fluoropolymer laminates using fluoropolymer laminates and loose lining systems in its typical applications in power plants. Left: Bonded lining system in containers and tanks for storage of chemicals and aggressive end products such as condensate. Right: Loose lining systems with mechanically fixed films from modified PTFE in the hot segments of the duct system.
Loose lining systems: Duct lining in power plants with film based on modified PTFE

In order to avoid damaging by shear forces, generated by different coefficient of thermal expansion for mod. PTFE and steel, in the broader service temperatures range from ambient up to 200°C or more, loose lining systems are preferred. While bonded lining systems are designed on the principle “thick sheet generate lifetime barrier properties”, loose lining systems can work with much thinner lining films, as these systems can perfectly work even with accepting a small amount of permeation of chemicals through the lining film. Figure 9 shows the principle in detail: The mechanical bonding of the fluoropolymer film by “fix-points” with no direct adhesion to the steel construction leaves an interpace free between the steel substrate and the protective film. Chemical corrosion only can start if two assumptions are given: the presence of a chemical potential, the so-called “Nernst-potential” and an electrolyte, e.g. condensate or liquid water, which allows the electrons to flow from the oxidised component, the steel substrate, to the reactive partner which undergoes chemical reduction. As long as back ventilation assures the removal of the permeated gases and keeps the interpace between the film lining and steel construction dry, no corrosion can start due to lack of electrolyte.

While bonded lining systems in general are vacuum proof, loose lining systems can accept only limited pressure differences. If the under-pressure at the side of the film lining gets too low, bowing of the film will happen and bending movements will start around the “fix-points”. By using the ventilation openings as vacuum ports, this intrinsic limitation of loose bonding system can be overcome.

Summary & Outlook

Fully fluorinated polymers such as PTFE and modified PTFE with its universal chemical resistance to all chemicals in flue gases enable various applications along the flue gas stream in power plants. Heat displacement systems for optimal temperature conditions within the individual cleaning modules and lining systems for corrosion protection is given the main focus in this article. Hetragon™ PTFE combs as heat transfer elements in Ljungström heat exchangers enable to re equip and to upgrade existing plants with no major investments required and provide significant lifetime expansion. No reduction of heat transfer capability in GGH occurs when steel elements are replaced by PTFE; significant weight savings for the rotors allow even bigger constructions in the future.

Two different systems for corrosion protection with fluoropolymer laminates are presented in detail: Bonded lining systems for service temperatures up to appr. 200°C and loose lining systems for the higher temperature ranges up to 200°C or more. While the first one is designed based on the high barrier principle to avoid direct contact of the aggressive chemicals with the steel substrate, the latter one also provides full corrosion protection even under accepting a permanent flow of a low amount of permeate. As PTFE and modified PTFE are resistant to all chemicals present, no matter whether the system is dry or wet, no preservation is required for temporary or long-term shut-down of the plant in all areas, where fluoropolymers are used for corrosion protection. Furthermore, fluctuating plant utilisation, as it becomes more and more state of art in these days as the varying availability of the renewable energies have to be compensated by coal fired power plants, will not generate additional corrosion problems.

As the main conclusion it can be stated, that the long lifetime of fluoropolymer system solutions improve the Cost-of-Ownership for the owner of power plants.