

Research Paper

Mercury Free UV Lamp for Disinfection and Purification of Drinking, Process, and Waste Water – An Approach to assessing its Innovation Potential and Possible Market Entry Strategies

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Ultraviolet radiation sources found many application areas in science and technology. They play an important role within several markets worldwide today. One of these markets is disinfection and photochemical purification of water which has been a growing market for many decades. At the moment low pressure mercury discharge lamps are the state of the art technology. Although they have been developed towards an impressive maturity level, they still show many drawbacks as e.g. strong temperature dependence. Therefore, this paper is dedicated to a mercury free alternative radiation source for this market, namely so called phosphor converted excimer discharge lamps. They are in the centre of present R&D activities, since they offer several advantages compared to the mercury discharge lamps such as very little temperature sensitivity, a high customisability of the emission spectrum, a large form factor, and instant full radiation power after they have been switched on. A brief description of the technology of phosphor converted excimer lamps will be sketched and furthermore their potential as a possible game changer for water disinfection and photochemical water purification market areas will be highlighted.

1 Introduction

The development of ultraviolet (UV) emitting radiation sources may be traced back until 1910 when the first realization of a discharge vessel comprising gaseous Mercury was mentioned in literature (Perkin, 1910). Ever since did the technology of generating electromagnetic irradiation by gas discharges involving the impact excitation of gaseous Mercury mature to a well-developed and reliable concept used worldwide in compact and linear fluorescent lamps.

By today, although already outperformed by light emitting diodes (LEDs) technology w.r.t. efficiency and lifetime, there are still a lot of Mercury based discharge lamps in use for general lighting

(US Department of Energy, 2012). However, the business field of UV emitting lamps offers a broad variety of lamp types from low-, over mid-, to high pressure Mercury discharge lamps. These lamps have been well established and are easily commercially available (Oppenländer, 2003). In 2011 the market size for UV disinfection equipment was estimated to be 885 million USD (Hanft, 2011). By 2015 the overall market volume for UV disinfection equipment increased to even 1.4 Billion USD (Ramamurthy, 2015). This tremendous incline of the market volume clearly indicates the rapid growth of the market for UV disinfection equipment, which is expected to grow even further in the next decades.

The growing interest in UV sources for disinfection and especially water treatment appears to be

in line with the prevailing challenges in that fields, such as an effective disinfection of surfaces or fluid media from hazardous microorganisms or an effective water cleaning from organic pollutants, such as hormones, antibiotics, and other drugs (Li et al., 2009; Oppenländer, 2003; Morimoto et al., 2004). For disinfection purposes, the application of photons emitted from a UV radiation source, with wavelengths from 250 nm (UV-C) to about 300 nm (UV-B), appear to be most suitable, as organisms exhibit strong absorption with maxima in the respective region caused by the molecule of life, the DNA (Zimmer and Slawson, 2002; Sastry, 2000; Hijnen et al., 2006). Whereas the direct photolytic cleavage of pollutants (e.g. hormones, drugs, hydrocarbons or by-products) requires higher energetic UV-C radiation, which is most effective at a wavelength shorter than 250 nm (Kowalski, 2009)

This work will summarize insight into the technology of state of the art UV radiation sources (chapter 2), viz. mercury discharge lamps and light emitting diodes (LEDs) as well as Xe comprising discharge lamps with and without wavelength converting phosphors. The advantages and innovativeness of excimer lamps is shortly explored in chapter 3 while in chapter 4 the advantages of the phosphor converted excimer lamps as an advanced alternative to mercury discharge based UV radiation sources is discussed. In chapter 5, this paper offers an evaluation on the status and impact of phosphor converter excimer discharge lamps in application, highlighting disinfection and purification of water, based on the parameters for product program evaluation set by Cooper in 1990.

2. Technology of UV Emitting Lamps

2.1. State of the art

The market for UV radiation sources is currently governed by two different technologies, namely mercury containing discharge lamps and UV emitting (Al,Ga,In)N (Aluminium Gallium Indium Nitride) based LEDs (Oppenländer, 2003).

Mercury containing gas discharge lamps are the most commonly applied UV source as far as applications relying on high energetic UV radiation between the UV-C (200 – 280 nm) and UV-B (280 – 315 nm) range is concerned. In addition to that, phosphor converted mercury discharge lamps still find application in UV lamps for cosmetic and medical purposes as well as a diminishing application in general lighting in shape of so called “neon tubes” or fluorescent lamps (US Department of Energy, 2012; Ronda, 1995). The general device setup consists of a tubular glass discharge vessel which is equipped with two internal metal electrodes at the

ends. The discharge vessel usually contains a gaseous filling consisting of evaporated mercury and a noble gas e.g. argon or neon to ease the ignition process and to buffer electrons. The thermally emitted electrons from the heated cathode follow the pathway of the electric field towards the anode side. Being accelerated by the applied electric potential, the moving electrons will collide with the buffer gas or evaporated Mercury giving rise to its electronic excitation via a transfer of kinetic energy performed by inelastic collisions. The excitation energy is thus governed by the kinetic energy of the free electrons, which depends on the applied field strength as well as so-called average free length of path, i.e. the mean distance that an electron travels in between of two consecutive impacts (Lister et al., 2004) In particular, the free length of path strongly depends on the gas pressure. Therefore, the applied filling pressure has a pronounced impact on the efficiency and emitted spectrum. With regard to the filling pressure, mercury discharge lamps are subdivided into low-pressure, i.e. the pressure is below 1 -10 mbar, into medium-pressure, i.e. the filling pressure ranged from 1 to 5 bar, and into high-pressure discharge lamps, wherein the filling pressure is larger than 5 bar (Oppenländer, 2003; Van Der Meer et al., 2015).

For the generation of UV radiation solely low- and medium-pressure lamps are of relevance, since high-pressure lamps mainly emit in the visible range and are thus used for general lighting and projection purposes (Morimoto et al., 2004). In other words the enhancement of the pressure results into a red shift of the spectral power distribution due to re-absorption, which also means that the efficiency of the emission of UV radiation declines with increasing pressure.

For further clarification of the different emission spectra due to the gas filling pressure, figure 2 depicts the emission spectra of a typical low and medium pressure Mercury discharge lamp.

For disinfection and especially water treatment purposes low pressure Hg discharge lamps emitting predominantly at 185 nm and 254 nm are widely in use (see figure 1). In the meantime, this lamp type is well established and thus applied at the point of use of water, e.g. in households as well as in very large-scale industrial or community applications. Even though the underlying technology of mercury containing discharge lamps and their corresponding applications are developed to an impressive maturity level, there are some shortcomings which allow the entry of competing technologies into these markets. The most obvious drawback, which is shared by all types of mercury discharge lamps, is the presence of the heavy metal mercury, which implies an environmental risk, e.g. in case

Figure 1 Emission spectrum of a Hg low pressure lamp (source: own representation).

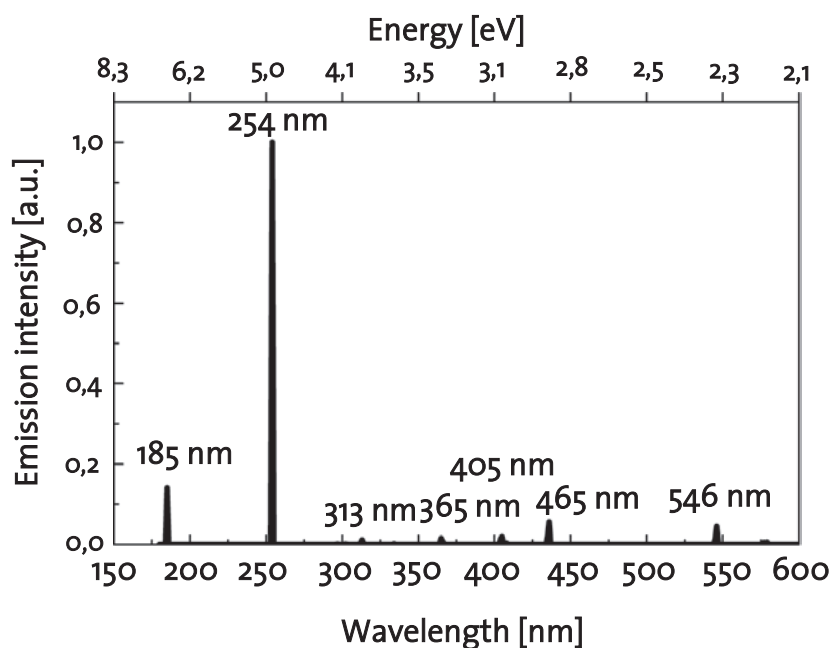
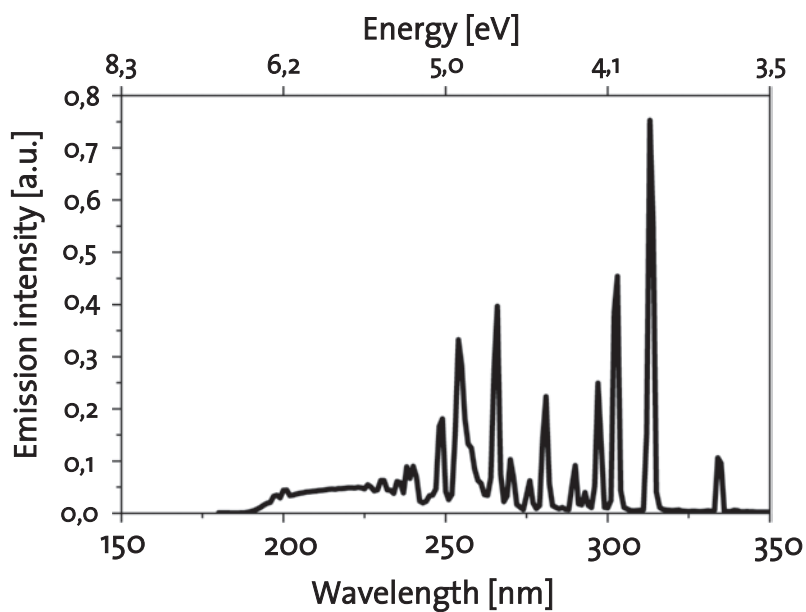


Figure 2 Emission spectrum of a typical Hg medium pressure lamp (source: own representation).



of lamp fracture or due to improper device disposal. In particular, low pressure lamps have additional operational drawbacks or limitations which have to be faced, such as the fragile quartz glass body, a strong dependence of the UV output on ambient temperature, the demand for continuous water flow in terms of cooling, the limitation to continuous rather than pulsed operation, and finally the observed run-up phase until full UV output is reached (Oppenländer, 2003; Chatterley and Linden, 2010).

Another presently applied technology are solid state light sources, viz. UV emitting LEDs based on a nitride type semiconductor chip. These were first mentioned in scientific and patent literature for general lighting purposes in 1994. Since then LEDs have disrupted the conventional technologies used in the lighting industry (Nakamura et al., 1994; Baretz and Tischler, 1996). Solid state light sources rely on electroluminescence, which is the recombination of oppositely polarized charge carriers, in the case of inorganic LEDs within a pn-semiconductor crystal. The energy of the emitted electromagnetic radiation is thus equal to the semiconductor band gap. Due to the continuous development of the fundamental semiconductor technology the market for UV radiation sources experienced a strong encroachment by (Al,Ga,In) LEDs during the last decade. This is particularly true for UV sources that cover the UV-A (315 - 380 nm) range. They have strongly changed the market for UV-A sources as they offer a broad variety of products solely dependent on the semiconductor composition. A glance into recent literature reveals the ongoing development of UV-B and even UV-C emitting LEDs, which are to some extent already available in commercialized products (Chen et al., 2017). J. Chen, S. Loeb and J.-H. Kim (2017) give in their article a valuable overview of the development of UV emitting LEDs for disinfections from the early 2000s until today. Others emphasize the potential of LED radiation sources for water disinfection in comparison to the well-established Mercury low pressure lamps (Chatterley and Linden, 2010). Those paper do not forget to mention that, unless a huge potential in general, an extensive use of UV-C and UV-B emitting LEDs for disinfection is currently limited due to poor optical output power, low lifetime, and high device cost. This particularly holds for LEDs with an emission spectrum in the UV-C range, which is required for disinfection purposes. For direct photolysis of organic pollutants short UV-C radiation (< 250 nm) is required, which is even more challenging w.r.t the above mentioned shortcomings (Chen et al., 2017). An additional problem with regard to the application of LEDs in already established devices, as e.g. flow-through reactors for water

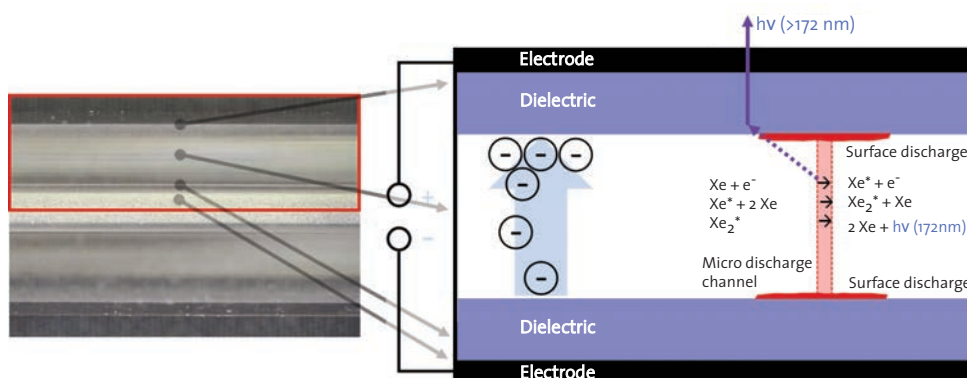
treatment, is the demand for an imperishable and long-term stable package, which effectively shields the LEDs from contact to ambient air, moist or water whilst it enables an efficient out-coupling of the generated UV-C radiation. To our best understanding, established package materials, like epoxy resin, poly methyl methacrylate (PMMA, plexiglass), or even flexible silicones suffer from degradation upon exposure to a high flux of high energy UV photons (Chen et al., 2017; Barton et al., 1998; Fischer et al., 2013; Arques-Orobon et al., 2015).

In summary: Recent literature nicely illustrates steady improvement of deep UV emitting LEDs and as well points out the large potential in water treatment and disinfection. However, it appears that there are certain years of further development to pass, before efficient UV-C emitting LEDs will emerge as a competitive technology on the market for disinfection and water treatment. In contrast to that mercury discharge lamps have reached a mature technology status, which means that the given technological potential is nearly exploited. Neither can their inherent disadvantages be technically overcome nor appears this technology to be adaptive for upcoming challenges.

2.2 Alternative Technology: Mercury free excimer discharge UV Radiation Sources

Since Hg discharge lamps and LEDs suffer from several drawbacks, as explained before, scientists have found an alternative technology. These are the so-called excimer lamps. Since excimer lamps are basically discharge lamps, the portfolio of gas discharge lamps experienced a serious diversification once excimer lamps were first described in 1857 (Kogelschatz, 2003). So-called excimer lamps, or excilamps rely on the generation of excimer species via a dielectric barrier discharge which takes place in a gas-filled discharge vessel. The word “excimer” is made up from the two words “excited” and “dimer” and may thus be understood in accordance to excited dimer (Oppenländer, 2003). The excimer emits its excitation energy in form of electromagnetic radiation upon radiative relaxation into its dissociative ground state (Kogelschatz, 2003). In contrast to a discharge which forms between two conductive metal electrodes, only separated by a certain gas, does the excimer discharge experience a hindrance by at least one dielectric layer, usually glass or quartz, which separates the electrodes. Depending on the gas filling, different excimer species evolve. Literature lists certain excimer species which show characteristic emission of UV or vacuum UV radiation, such as Ar_2^* (126 nm), Kr_2^* (146 nm), Xe_2^* (172 nm), KrCl^* (222 nm) or XeCl^* (308 nm) (Oppenländer, 2003;

Figure 3 Photograph of a tubular excimer lamp (left) and a schematic sketch of its construction and operation mode (right) (source: own representation).



Kogelschatz, 2003; Ledru et al., 2006; Kogelschatz, 1992). From the variety of excimer species that are reported in literature, xenon excimers, generated from the noble gas xenon, arose as the most efficient and stable for the realization of a dielectric barrier discharge lamps. Those lamps comprise a quartz glass discharge vessel which is filled with a certain pressure of Xenon gas and two suitable electrodes, which are shielded from each other by at least one dielectric. This dielectric is in most cases given by the discharge vessel itself but other materials are feasible (Kogelschatz, 2003; Kogelschatz, 2000). Figure 3 gives a schematic illustration, as well as an accompanying photograph of one, simple set-up and operation mode for a Xe dielectric barrier discharge lamp.

These lamps are typically driven by short 1 - 10 ns pulses of high voltage, usually 1 - 10 kV, and a peak current of about 0.1 A in order to generate dielectrically hindered discharges, which are also called glow discharge in literature (Kogelschatz, 2000; Boyd and Zhang, 1997). Actually, the generation of excimers is observed if electrons flowing through a micro-scaled discharge channel, collide with Xenon atoms and thus transfer kinetic energy to Xenon atoms resulting in electronic excitation (Eliasson et al., 1988). Subsequently, the excited Xenon atom can react with another Xenon atom upon forming an excimer. The following losses of excessive binding energy and vibronic relaxation into certain energetic states are governed by a complex interplay between the excimer species and atomic Xenon in a three body interaction. Regarding Xe excimer emission, there are four energy levels of interest: Two higher vibronic excimer energy states give rise to the emission of high energetic photons with wavelength at 148 nm (8.38 eV) and 152 nm (8.16 eV)

upon relaxation into the ground state. Two lower vibronic excimer states which give rise to the emission of lower energetic photons with a mean wavelength of 172 nm (7.21 eV) or 186 nm (6.67 eV) Boyd and Zhang, 1997). The two high energetic emission bands are usually called first continuum whereas the lower energetic emission bands are referred to as second emission continuum. The electronic ground state is non-binding and dissociates within the timescale of nanoseconds after relaxation, thus providing optimum conditions to avoid output loss due to reabsorption. As the non-radiating relaxation pathways are governed by three body interactions, does the overall emission spectrum of a certain Xe dielectric barrier discharge (DBD) lamp strongly depend on the Xe filling pressure. Furthermore, does a higher working pressure aid excimer formation to a certain extent, as three body collisions are promoted by a higher density of Xe atoms. In applications the xenon pressure usually exceeds 250 mbar, resulting in a strong quenching of the first continuum in favour of the second emission continuum (Ledru et al., 2006). In addition to the implementation of a relatively narrow band 172 nm emitter, the diminishment of the first emission continuum results in a prolonged lifetime of the quartz discharge vessel, which could otherwise take serious damage due to solarisation by high energetic photons over time (Schreiber et al., 2005).

3. Mercury Free Excimer Lamp - An Innovative VUV Radiation Source

The Xenon excimer DBD lamp embodied a true and rather radical innovation at its time of development. This innovation already entered the market in form of several applications, such as photo-

lithography, photo-polymerization, photo-etching, photo-enhanced MOCVD (metal organic vapour deposition), ozone generation, and last but not least plasma display panels (Oppenländer, 2003; Morimoto et al., 2004; Kogelschatz, 2000; Hauschildt and Salomo, 2011). In certain areas, Xe excimer lamps already compete with the established low pressure mercury discharge lamps. This is caused by the fact that low pressure mercury discharge lamps also partly emit a fraction of about 12% of the overall output in the VUV region, viz. at 185.0 nm (6.70 eV) (Kowalski, 2009). In comparison to the low pressure Hg lamp, the narrow band 172 nm emitting Xe excimer DBD lamps offers some advantages. For example the high average power density of VUV radiation, an emission spectrum solely located in the VUV range, the relatively low lamp surface temperature, and the absence of mercury as well as instant-on and short pulse operation. The latter three advantages are possible game changers in some application areas.

4. Phosphor Converted Xe Excimer Lamps – An Innovative and Tuneable UV Radiation Source?

The concept of phosphor converted Xe excimer lamps was already addressed in 2002, e.g. by Philips and Ushio. This technology appears to be a consequent and incremental further development of the VUV emitting excimer DBD lamp technology (Feldmann et al., 2003). The application of a radiation converter in order to transform the high energetic 172 nm VUV photons towards less energetic UV photons (190 - 380 nm) opens up a sort of platform concept, wherein the Xe excimer platform is modified by a UV phosphor. The principle of wavelength converting phosphors itself, is well known from its

application in mercury discharge lamps for general lighting. In these lamps for general lighting, UV radiation originating from the Mercury discharge is converted into visible light by a suitable phosphor layer coated onto the inner side of the discharge vessel (Ronda, 1995; Feldmann et al., 2003; Ronda, 1997). Furthermore, this approach also found application in present solid state light sources, i.e. white LEDs, wherein the spectrum of a blue emitting (In,Ga)N chip is converted into a white spectrum in line with the application aimed at (Krames et al., 2007; Cho et al., 2017; Bando et al., 1998).

What appears to be most interesting is the full conversion of the 172 nm emission originating from the Xe excimer discharge into either a slightly less energetic VUV emission or an emission within the UV-C range (200 - 280 nm). Both approaches aim for the treatment of water in terms of photolytic cleaning from organic pollutants or disinfection. The latter approach has also potential for the treatment of surfaces and gaseous media. Furthermore, the conversion into the UV-B/A region could be useful for energy selective driven photochemical reactions. Suitable phosphors, their most intense emission peak, and their possible applications are given in Table 1.

Another quite uncomplicated approach for the realization of a phosphor converted Xe excimer lamp is the direct application of a suitable phosphor as coating onto the inner wall of the discharge vessel. From a technological point of view, this is relatively easy to achieve via a so-called up-flush coating procedures. The lamp body, as printed in figure 3, is filled with a phosphor suspension by applying a small vacuum, sufficient for a laminar vertical rise of the phosphor paint. The phosphor material adheres on the surface of the vessel. The slow enhancement of the pressure towards ambi-

Table 1 List of phosphors, wavelength conversion and possible application areas (source: own representation).

Composition	Emission upon 172 nm Excitation (λ_{max})	Application area
$\text{YPO}_4:\text{Nd}^{3+}$	192 nm	AOP, NO_3/NO_2 cleavage, AOP by $\text{OH}\cdot$ generation
$\text{YPO}_4:\text{Pr}^{3+}$	235 nm	AOP, Disinfection
$\text{YPO}_4:\text{Bi}^{3+}$	241 nm	AOP, Disinfection
$\text{YPO}_3:\text{Pr}^{3+}$	265 nm	Disinfection
$\text{BaZrSi}_3\text{O}_9$	285 nm	Disinfection

ent pressure allows remaining an excessive layer of phosphor on the lamp body. Subsequently, the lamp body is heated in order to evaporate all organic materials. The inorganic phosphor remains as a thin layer on the inner wall of the discharge vessel. The lamp is then filled with an appropriate amount of dry Xenon gas. In a last step the discharge vessel is closed by sealing, which also ensures that the phosphor is shielded from ambient gases, such as oxygen, water (moisture), or wear corrosion by friction. However, the phosphor is in intimate contact to the Xenon discharge channels, which occurs in lamp operation.

The innovative potential of phosphor converted Xe excimer lamps lies in its inherent advantages as discussed in chapter 3 and the wavelength conversion, which may promote this technology to a serious competitor for mercury based devices and open up new areas of application. Especially the property of wavelength conversion reveals an outstanding opportunity to spectrally shift the device's emission from the VUV range (< 200 nm) up to the near visible edge of the UV-A range (380 nm) by the choice of phosphor or the composition of a phosphor blend. This approach can be regarded as a spectral toolbox, allowing the implementation of tailored lamps for specific applications like the disinfection of particular germs, for the cleavage of specific micro pollutants like hormones or drugs or even the promotion of precise photochemical reactions.

The feasibility to construct tailored lamps may end up in more efficient radiation sources in comparison to the established mercury discharge lamps because the device emission spectrum may be tailored according to the spectral absorption maximum of a photochemical system involved in a targeted process. Moreover, they bear the advantageous features of excimer discharge lamps, like the lack of mercury, instant-on and fast switching cycles.

Presently, there are only few fully commercialized products operating with phosphor converted Xe excimer lamps which are regularly available on the market. This product is named "Instant Trust Marina" and is supplied by Philips for the treatment of drinking water on boats and ships. The reason for this lack of products is mainly due to technical problems and material lifetime issues, which arise from the much more challenging conditions caused by the hazardous discharge (accelerated electrons and cationic species) being in close contact to the phosphor.

Besides the demand for more elaborately constructed electronic drivers, giving rise to a high efficiency in excimer generation and respective emission, a commercially successful implementation of phosphor converted excimer lamps requires a

detailed study of involved components and materials. This e.g. covers the choice and long-term stability of the dielectric, which depends on the discharge vessel or the applied electrode material. With respect to this, a lot of knowledge has already been gained throughout the development of phosphor free 172 nm emitting Xe excimer lamps. However, a serious issue that has not been covered yet is the behaviour and stability of the applied phosphor materials. The research project Fluoro UV (funding no. 01LY1303B) as funded by the BMBF (German Federal Ministry of Education and Research) and carried out under the involvement of the Munster University of Applied Sciences, GVB GmbH, Tailorlux GmbH and the DLR (German Centre for Air and Space Travel) exactly addresses this important topic. Therefore, this research project covers the whole product chain, from phosphor synthesis, characterization and improvement, to the lamp manufacturing and lamp maintenance evaluation, the analysis of phosphor aging and the exploration of suitable protective countermeasures as well as the actual evaluation of manufactured lamps in water treatment. Recent results demonstrate the high efficiency of materials like $\text{YPO}_4:\text{Bi}$ and $\text{YPO}_4:\text{Pr}$ in Xe excimer lamps for the direct photolysis of sulfamethoxazole in aqueous solution. This especially holds for the efficient reduction of the measurable amount of total organic carbon (TOC) in which the excimer lamps outperform a reference Hg low pressure amalgam UV luminaire (Nietsch and Jung, 2017; Nietsch, 2017). A significant reduction of TOC content clearly indicates that sulfamethoxazole is not solely cleaved into shorter organic species, but that it is nearly completely cleaved photolytically including any intermediate generated species. Beyond revealing the huge potential of phosphor converted Xe excimer lamps, the Fluoro UV project also points out ways to an understanding of the most profound challenge, namely the rather poor device lifetime. Contributions to this field are especially achieved by conducting detailed analysis of the aging behaviour of the applied phosphor type and the implementation of protective particle coatings as well as further countermeasures to ensure a prolonged device lifetime. However, as trend-setting findings have been made, it appears that there still remain some challenges to enable phosphor converted excimer lamps becoming a real game changer regarding the UV business.

5. Evaluation of the Market Potential of Phosphor Converted Xe Excimer Lamps

The following subchapters aim to evaluate whether or not the phosphor converted excimer

lamp is a true innovation. For this purpose it appears feasible to apply a diverse set of evaluation criteria deduced from recent literature. The basis for this set of criteria is an article from R. G. Cooper (1985) dealing with the evaluation of strategies for new product programs (Cooper, 1985). Since, this article does not aim at discussing strategies for new products, the list was slightly modified to focus on criteria supporting the assessment of phosphor converted excimer lamps as an innovation at a rather early technical state.

5.1. Nature of New Product Developments

5.1.1. Degree of product innovativeness

To this point it is not valid to discuss the degree of innovativeness based on a certain product. The technology of phosphor converted Xe excimer lamps can actually be applied to a broader sector, which could potentially be used in a broad set of products. Therefore, it is noteworthy that there is already one established product on the current market for disinfection of drinking water, which is designed for the treatment of water with germicidal UV radiation given by a phosphor converted Xe excimer lamp. This product is named "Instant Trust" (Philips) and includes a combination of a Hg free (Excimer) lamp driven UV disinfection vessel and different water filters. The Instant Trust Marine aims for the germicidal treatment of drinking water on boats in small scale of 1000 L/h (Philips Corporation, 2017). The local limitation as well as the technical limitations given by a short product life cycle in combination with a small, rather household scaled application do not exploit the full potential of this technology. Especially when recent and upcoming scientific progresses are taken into account. Depending on the exact realisation of the energy conversion via phosphors combined with Xe excimer lamps, e.g. the use of phosphors or phosphor blends, different lamp geometries, scales and lamp powers, a variety of possible applications is addressable. Amongst those, the most prominent ones, which have already been mentioned and discussed in this paper, are given by the treatment of fluid media (mostly water), gases and surfaces for disinfection and clarification from organic pollutants. Beyond that it appears to be likely that upcoming products relying on phosphor converted Xe excimer lamps may e.g. target applications in the treatment of process exhaust gases (e.g. NO_x reduction), photochemistry, photobiology, optical spectroscopy, and material science. Chapter 4 gives a more detailed view into essential technical features and resulting possibilities for application. Concluding it appears to be reasonable to point out the tremen-

dous innovative potential as given by phosphor converted Xe excimer lamps, which could lead to a variety of commercialized products.

5.1.2. Product Quality Level

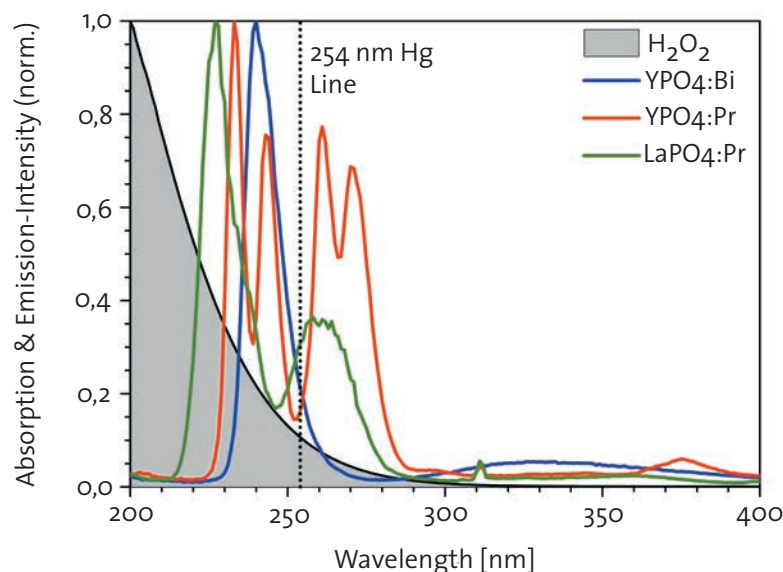
As mentioned in chapter 5.1.1. the article's scope does not address a certain yet commercialized product solution including a phosphor converted Xe excimer lamp. A detailed evaluation of the quality of a certain product can thus neither be objective here. What appears reasonable is to address a set of quality criteria or definitions, which are applicable to describe a variety of products build on the basic technology of Xe excimer lamps utilizing wavelength conversion by phosphors. In this context, the authors decided to choose the quality of implementation, performance and stability as suitable metrics for the evaluation of the product quality level.

Focusing on the possible quality of the implementation and performance of phosphor converted Xe excimer lamp for the treatment of water in order to perform a cleaning from persistent organic pollutants (POP) or germicidal treatments, those lamps may comprise a higher extent of quality in terms of functionality.

Current products that are related on excimer lamps already prove that Xe excimer lamps can be manufactured as electrically efficient emitters of 172 nm radiation. A suitable example is given by Osram, which has several VUV emitting Xe excimer lamps in stock. Referring to publicly available data, lamps of the type Osram XERADEX (L40/120/SB-S46/85) exhibit a wall plug efficacy of around 30% as 20 W of electrical power are converted into 0.04 W/cm^2 irradiance at 172 nm (Osram, 2017). A further on going development may push that efficacy even further. A second setscrew in terms of the device wall-plug efficacy of phosphor converted excimer lamps is given by the external quantum yield of the applied phosphor material itself. The external quantum yield is thereby defined as the number of emitted photons divided by the number of initially absorbed photons at specific excitation energy. Unfortunately, this value is rather difficult to measure for VUV excited and UV-C emitting phosphors and is therefore an often untouched issue. Nevertheless, researchers try to solve this by a performance measurement of a completely assembled lamp. A rough assumption, which is supported by high temperatures for thermal quenching of certain LnPO_4 based phosphors leads to a quantum yield of approx. 80% for a phosphor like $\text{YPO}_4:\text{Bi}$ (under 160 nm excitation) (Jüstel et al., 2004).

A very promising feature that promotes prod-

Figure 4 H₂O₂ absorption and YPO₄:Pr, LaPO₄:Pr, YPO₄:Bi emission spectra (source: own representation).



uct quality in terms of performance is the fact that the radiation output may be tailored spectrally according to the respective process demands. Exemplary, the efficacy of a POP cleavage process using H₂O₂ as auxiliary chemical could be completed faster and more energy efficient using for example YPO₄:Bi³⁺ or YPO₄:Pr³⁺ converted Xe excimer lamp compared to a Hg low pressure lamp (Nietsch and Jung, 2017; Nietsch, 2017; Broxtermann et al., 2017). This is due to a higher spectral overlap of the excimer lamp emission and the H₂O₂ absorption curve. Figure 4 shows the respective absorption and a couple of idealized emission spectra exhibited by different phosphor converted Xe excimer lamps as well as a Hg low pressure lamp.

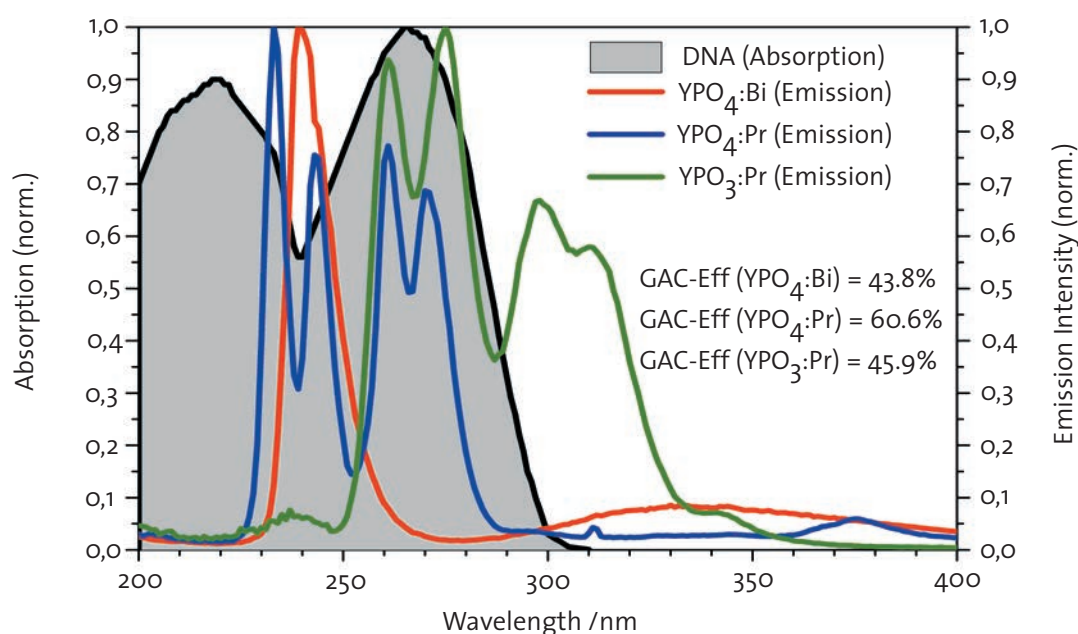
Beyond that the high energetic radiation < 250 nm leads to a further enhancement in POP cleavage, as recent findings demonstrate that even without H₂O₂ addition, a solutions' TOC (total organic carbon) content may be significantly decreased (Nietsch and Jung, 2017; Nietsch, 2017; Broxtermann et al., 2017). It was thereby proven that both phosphor converted Xe excimer lamps are more energy efficient in the photo oxidative depletion (H₂O₂ addition) as well as the bear photolysis (no addition of reactant) of an POP (Sulfamethoxazole) than an analogously tested Hg low pressure lamp (Hg amalgam). The DLR (Deutsches Zentrum für Luft- und Raumfahrt) used respective measurements to calculate a reduction of CO₂ emission due to the consumption of electrical power of up to 95% for

the direct photolysis and a reduction for 85% for the photooxidative treatments, when suitable tested YPO₄:Bi or YPO₄:Pr comprising lamps were compared to the Hg antagonist (Nietsch and Jung, 2017; Nietsch, 2017). This simple example indicates the tremendous prospect that task-specifically tailored phosphor converted excimer lamps may comprise treatment time, energy efficacy and a reduction of CO₂ emission in terms of AOP clarification treatments.

The above mentioned spectral adaptability of the phosphor converted excimer lamps is as well interesting, since the performance of germicidal treatments can be influenced by the lamps' output e.g. by an adjustment the absorption spectrum of the targeted bacterium. A commonly used tool to evaluate the germicidal efficacy of a certain phosphor converted lamp is to weight the emission spectrum of the applied phosphor for the function of the spectral inactivation efficacy exhibited by a certain germ. Figure 5 gives an example involving the absorption spectrum of DNA over the UV region as well as the emission spectra of a selection of UV-C emitting phosphors.

A suitable metric, the so called GAC (germicidal action curve) overlap or germicidal efficacy may then be calculated as given by equation 1, where $I_{\lambda, \text{Sample}}$ stands for the emission spectrum of the phosphor sample (counts vs. wavelength) and $\text{Abs}_{\text{Rel, DNA}}$ for the relative absorption exhibited by isolated DNA. We thereby assume a direct cell core

Figure 5 DNA (UV absorption) and photoluminescence emission spectra of the UV-C emitting phosphors $\text{YPO}_4\text{:Bi}$ and $\text{YPO}_4\text{:Pr}$ (160 nm excitation) (source: own representation).



damage due to the absorption of UV-C irradiation by DNA.

In spite of the huge implementation and performance related benefits of phosphor converted excimer lamps, they currently bear an unneglectable disadvantage. This disadvantage is related to stability as metric for quality and is typified by a short device lifetime due to aging effects. Current research projects, as currently worked on by the Muenster University of Applied Sciences (BMBF Project "Fluoro UV, funding no. 01LY1303B) follow this issue by trying to understand and prevent the pronounced aging effects. Recent research has proven that the aging effects, exhibited by phosphor converted Xe excimer lamps originate from a pronounced aging or degradation of the applied phosphor itself upon contact to the Xe plasma discharge (Broxtermann and Jüstel, 2017). Aging prevention will be a key to a significant improvement of product quality in terms of stability as well as a key factor for a realization and success of any com-

mercial product. Furthermore, it will include direct protection methods like particle coating, as well as certain arrangements regarding product geometry and design to effectively reduce phosphor aging to a minimum extent (Broxtermann and Jüstel, 2016).

Summed up we are facing rather low product quality in terms of long-term stability which contradicts a high level of task specific efficiency and adaptability.

5.1.3. Degree of Product Concentration vs. Diversification

The technology of phosphor converted excimer lamps exhibits a certain potential for diversification by itself. A basic carrier technology, namely Xe comprising excimer DBD discharge lamps, emitting 172 nm VUV radiation, is combined with the wavelength conversion potential given by VUV excitable photoluminescent phosphors. A first lever

Equation 1 (source: own representation).

$$\frac{\int_{200}^{320} (I_{\lambda, \text{Sample}} * \text{Eff}_{\lambda, \text{GAC}})}{\int_{200}^{320} (I_{\lambda, \text{Sample}})}$$

enabling diversification is given by the used lamp geometry. This also includes the implementation of an electrode exterior to the discharge vessel (Kogelschatz, 2000). For the application in conductive media, like water, there is no need for any exterior electrode as the conductive media can be contacted directly. Besides if a lamp is used for the treatment of gases or the treatment of solid surfaces, there must be a conductive material attached to the outer wall of the discharge vessel dielectric, acting as electrode. However, the general technology of Xe DBD lamps offers the opportunity to address liquid and gaseous media as well as the surface of solid media (Oppenländer, 2003).

As sketched earlier, the choice of the phosphor or phosphor blends offers additional and distinct potential for diversification, because this determines the kind of targeted application, e.g. germicidal treatments or clarification from POP. If there is once an established well working concept yielding a long term stable phosphor converted excimer lamp, it appears feasible to target different applications. These may range from small scaled point-of-use consumer applications, over medium sized commercial up to large scale industrial solutions. A well-established portfolio of phosphor converted lamps is thus suitable to address more than just one market in a diverse approach.

5.1.4. Product type, e.g. customnes

Excimer lamps offer a wide variation in terms of the construction shape scalability. With respect to a tubular design, as sketched in Figure 3, those lamps may be constructed with sizes from a few centimetres in length and a diameter of barely a centimetre up to lamps with a length larger than one meter and exhibiting a diameter of several centimetres. This variability as well holds for the desired electrical lamp power, which is technically in direct correlation to the power output of UV radiation. The consumption of electrical power can be adjusted from just a few mW_{El} per cm length up to values up to several W_{El} per cm lamp length. This degree of freedom thus enables application in small point-of-use devices with just a few mJ/m^2 (alike the mentioned Philips product Instant Trust). Also, large scale industrial solutions which require short treatments times for huge volumes and therefore high UV doses in the range of several hundred J/m^2 , as the German Association of Manufacturers of Equipment for Water Treatment (FIGAWA) has published within one of their recommendations in 1987, are possible to realize.

5.2. Nature of Technology (Production & Development) used

5.2.1. Technology fit or synergy with the firm

As phosphor converted excimer lamps embody an on-going development originating from its phosphor free predecessor, it appears very reasonable to assume that the development of commercial products would strongly benefit from a detailed know-how as well as a strong and reliable infrastructure regarding classical discharge lamp technology and excimer discharge technology in particular. Therefore it seems very likely that through sophisticated research and development can be best accomplished by already established players on the market. Know-how, originating from the assembly of classical Hg discharge lamps may be very useful for the implementation of phosphor converted Xe excimer DBD lamps. Furthermore, could existing distributions channels ease a possible market entrance for those products. As those phosphor converted Xe lamps could be used to aim for a substitution of Hg containing products in the future, it appears even more comprehensible that a current supplier of Hg related products could prefer to push the development of such mercury free alternatives themselves rather than leaving this field open to competitors on the market. If a company is able to provide additional knowledge, abilities and potential market share for UV products used in disinfection or other clarification applications, the resulting synergistic effect could be a significant advantage.

5.2.2. Maturity of technology. e.g. state-of-the-art vs. "old" technology

Phosphor converted Xe excimer lamps do not represent a matured well-established technology with respective to hold a share on the market of UV products. The technology is in a rather early state and a successful broad commercialization of related products is yet hindered by a significant lack of quality on terms of stability, namely long-term stability (see 5.1.2.). For the many different applications that have been addressed in more detail within the prior chapters, phosphor converted Xe excimer lamps do not embody a state-of-the-art technology. In most cases it appears suitable to describe them as a possible challenger of the current state-of-the-art technology represented by Hg containing discharge lamps or in case of a new application sought as a development technology. The earlier chapters dealing with the technical background of Hg and Xe excimer lamps, with and without conversion by phosphors, are supposed to give

a broad background regarding the certain features and possible drawbacks of each technology. At this point it is adequate to point out that Xe DBD discharge lamps involving energy conversion via inorganic phosphors pose a challenger technology on a rather early, still pre-commercial status with only one available small scale product on the market called Philips instant trust.

5.3. Type of New Product Markets Sought

5.3.1. Market size growth and potential

According to a McKinsey study from 2012 the general lighting market is a very dynamic one, which steadily increased over the last years. Although a decrease of the GDP was predicted by McKinsey, between 2011 and 2012, the lighting business was prognosticated to grow even further. An analogous trend was observed for the UV radiation business as well. From 2011 to 2015 the market for UV disinfection equipment has risen from 885 million USD up to 1.4 Billion USD (Hanft, 2011). This is an increase of 58% within 4 years and moreover a compound annual growth rate of 14.6% is expected from 2015 to 2020 (Ramamurthy, 2015). Since the technical development in this sector is only of incremental nature and based on old-fashioned discharge lamps, this increase is mainly due to an increased market pull. Since the current innovations within this sector have only been incremental innovations, the development and commercialization of phosphor converted excimer lamps might be a game changer on this rapidly growing market offering several technical advantages as mentioned in 5.1.2. Moreover a development of new sub markets within the market of water disinfection is expected. Due to the spectral tenability of phosphor converted excimer lamps this market will certainly experience a significant diversification, wherein each specialized on a certain emission range especially aiming for certain bacteria, microorganism or virus.

5.3.2. Competitive situation

The market for UV emitting luminaires appears to be a very competitive market, which is in Europe mainly dominated by big companies like Heraeus, Osram, Narva and Xylem (Van Der Meer et al., 2015). In this market, success is strongly governed by product prizes and cost efficacy, especially in a situation in which a new uprising technology like phosphor converted Xe excimer lamps aim to challenge well-established state-of-the-art technology like Hg discharge lamps. This is very perceptible if we draw parallels to the market developments for general lighting over the recent years. This market,

which in 2011 amounted to 140 Billion USD €/a experienced serious changes over the last decades (McKinsey&Company, 2012). These changes went along with the development and commercialization of LED related luminaires and products. The ascent of LED in general lighting stood in strong correlation to serious scientific progress in semiconductor production, especially at a large scale, which made LED related products affordable and available in large numbers, providing sufficient product lifetime, and high performance (Cho et al., 2017).

For those applications and related markets where converted Xe excimer lamps enter as competitors challenging well-developed, quite cost-efficient and qualitatively sophisticated products like Hg low pressure lamps, they will have to prove a clear benefit to the customer in order to outplay the established technology. Along with the most striking benefit presented by the needlessness of Hg, the further advantages arise by the spectral output adaptability throughout wavelength conversion via certain phosphor species as well as the instant-on operation mode. The unique features may offer significant economic and ecological benefits. Concluding one could state that although the UV lighting market is strongly cost driven and mature the phosphor converted excimer lamp offers several benefits which makes it a superior technology regarding its applications.

5.3.3. Stage of the product life cycle

To this point in time it is actually not possible to describe phosphor comprising Xe excimer lamps and related products in terms of a product life cycle. The fundamental technology dealing with the excimer discharge is broadly researched, as numerous scientific articles and reviews to some extent as well used as literature for this article indicate. Furthermore, Xe DBD related products have already found application e.g. in surface treatment, ozone generation and televisions (see chapter 2). However, as already scratched earlier, phosphor converted Xe DBD lamps are still a piece of research as they have not found a broader application beyond laboratory scale, except for Instant Trust by Philips. Basically, this technology has currently no commercial relevance due to the fact that possible product realizations like Instant Trust by Philips more or less represent niche products with a market volume that probably vanishes upon comparison to the overall market for UV products for clarification treatments. At the moment this product has probably not the potential for a wider introduction of phosphor converted excimer related products as the current limitation to poor lifetimes and the current lack for a feasible solutions would clearly hin-

der success on the market.

5.4. Orientation and Commitment to the new Product Program

5.4.1. Whether the program is defensive or offensive in nature

In subchapter 5.2.1. possible synergistic effects that might take effect upon the realization of a product portfolio based on phosphor converted excimer lamps by a company or organization that is already experienced in the assembly and distribution of discharge lamps were discussed. Furthermore, subchapter 5.1.3. describes the benefits of a rather diversified product strategy. Thus it appears as a logical deduction to present a potential product program as rather balanced. A focussed, straight forward product program comprising a sharply focused marketing strategy appears very useful for those excimer products comprising phosphor conversion that tackle novel application areas in which phosphor converted excimer lamps succeed due to their unique selling points. Respective application areas could be e.g. nitrate/nitrite depletion from strongly contaminated ground water or regarding the solution point-of-devices for disinfection and AOP cleavage. Wherever phosphor converted excimer lamps are sought to be a competitor for existing technology, it appears as either feasible to excel established products distributed by a competitor on the market or to foster the own product portfolio through a step-by-step substitution by the new superior product development. The latter case would clearly demand for a defensive strategy whereas the first case strongly demands for an offensive product program.

5.4.2. Whether the R&D effort is pure research vs. applied

The research and development (R&D) effort which is necessary for the realization of sophisticated commercially distributable solutions comprising phosphor converted Xe excimer lamps for any targeted application (water treatment, AOP, germicidal treatments, photochemistry, and so on) will be of truly applied nature. The target of this R&D will clearly aim at a maximum for the so called wall-plug efficacy and lifetime. For an UV-C emitting lamp, the wall-plug efficacy is yielded by calculating the emitted UV-C energy as fraction of the total electric energy consumption. The main goals for applied research aiming for an optimization of the phosphor converted Xe excimer lamp are the optimization of Xe excimer generation, phosphor quantum yield as well as an effective coupling of

the emitted radiation into a respective reaction vessel or medium to be addressed in a treatment. The issue of pronounced lamp aging poses a very, if not the most important challenge to pass. In our opinion, it is probably the key problem that needs to be solved in order to enable broad success.

5.4.3. Political and social drivers

There are two central points which highlight the development of phosphor converted Xe excimer lamps in terms of the so-called trend of "Neo-Ecology" combining economy, ecology, and social responsibility. These points are embodied by the abstinence of mercury or other heavy metal components due to the Xenon based discharge technology and the possibility to perform energy efficient clarifying treatments, in which a task specifically manufactured luminaire reduces energy consumption, thus shrinking the correlated emission of CO₂.

The complete absence of the toxic heavy metal mercury poses a striking ecologically advantage, especially where mercury containing discharge lamps are substituted by excimer driven alternatives. While people are increasingly aware of man-made mercury pollution of nature due to mining, energy generation and mainly from fossil fuels (Hylander and Goodsite, 2006). Industrial sectors like chemical industry increasingly refrained from the use of mercury for in synthesis, purification or analysis over the recent decades (Hylander and Meili., 2005). In that given context, it appears quite interesting, that Hg driven discharge lamps embody the last large scale application for Hg. The large scale is truly not given by a certain lamp, which's mercury content was constantly decreased alongside the technological development, but by the huge number of lamp bodies, still sold and used. By today, even politics address that topic more drastically as legislative programs like MINAMATA (Minamata Convention on Mercury), aiming for a prohibition of the use of Hg in lighting and UV luminaire construction, recently demonstrate (United Nations, 2013). A simple model calculation, assuming a fictional annual sales volume of 1 mill. Hg low pressure lamps, each comprising an estimated amount of 1.5 mg Hg leads to an overall application of 1.5 kg Hg entering the free market for industrial, laboratory and household application (Freie Universität Berlin). If we then assume a rate of 1 in 100 lamps to experience breakage and thereby causing uncontrolled Hg emission into the environment, we would end up at a total annual amount of Hg released into nature of 15 kg. This dramatic impression would even intensify the use of mercury medium pressure lamps, exhibiting a significantly higher amount of Hg would be taken into account. In industrial

application Hg containing lamps are a risk factor which is handled by professionals. In contrast to that, applications involving individual private customers, namely application in household and in portable point of use systems, are influenced by individual emotions and concerns when it comes to the handling of toxic material and the private agenda regarding ecologically friendly technology. Taking this into account makes the phosphor converted excimer lamp, in terms of chemical risk or danger, to an absolutely harmless alternative, which is especially beneficial for the implementation of products in the private sector.

Last to be mentioned here, the special innate benefit of instant-on operation renders UV luminaires based on Xe excimer emission perfectly suitable for the discontinuous operation in small scaled point of use applications, e.g. in household. Since Hg lamps need up to 10 minutes to reach their full light output, a lot of energy is wasted. In that case, the absence of mercury results also in a synergistic benefiting, simplifying shipping, storage, handling and disposal for private users. Summarizing, the phosphor converted Xe excimer benefits from a significant CO₂ reduction, because of its increased efficacy and the political desire to ban Hg in public applications. Moreover, the socialized fear from Hg containing products will additionally support its popularity.

5.4.4. Risk level of projects

Although the technology for phosphor converted Xe excimer lamps is known for decades by now, there is currently no broad product portfolio on the market. This fact already implies that the risk level which comes along with a respective development and implementation of this technology cannot be neglected and has to be ranked as rather high. The success of product based on Xe excimer technology and involving phosphor coating stands and falls with the long-term stability, or product life-time as critical quality criterion (also see 5.1.2.). The short device lifetime, which is according to recent results (see chapter 4) caused by a rapid aging of the applied phosphors upon contact to the Xe plasma discharge, is an ongoing issue of intensive research. This poses a strong boundary towards commercialization that has to be taken in order to enable commercial success, especially when cost intensive applications like industrial scale water treatment are targeted. Due to the high potential of phosphor converted Xe DBD lamps, it appears as strongly justified to spend R&D effort on the implementation of life-time prolonging protective measures, which are thought to be realizable through a thoughtful choice of stable phosphor materials as well as protective

particle coatings and a lamp's construction layout itself.

6 Conclusions

Phosphor converted Xe excimer lamps pose themselves to be an emergent technology for applications in which task specifically tailored UV spectra are demanded. Such applications involve e.g. germicidal treatments of water, gaseous media and surfaces, cleavage of POPs from wastewater through AOPs, NO_x reduction, and surface treatments of polymers and the promotion of photochemical or photobiological processes. They combine the inherent advantages of Xe excimer lamps such as instant on and -off operation, pulsed operation as well as a high efficacy with the various possibilities of spectral tuning given by the use of suitable inorganic phosphors. An intensified use of such lamps instead of established lamps usually based on mercury discharge lead to an improved energy balance for certain processes due to the application of a task specific spectral output as well as to a reduction of mercury involved in UV radiation related products and thus a reduction of mercury exposure to the environment. However, Xe excimer lamps are on the market for a set of applications for quite a time, there is not more than one product relying on a phosphor converted Xe excimer lamp available on the market by now. That is due to the fact that application of phosphor conversion in combination with Xe excimer discharge implies a set of distinct challenges that have to be overcome through sophisticated R&D efforts. The largest problem that has to be solved is given by the fast aging of the involved phosphor materials due to direct contact to the Xe excimer discharge. The phosphor converted Xe excimer lamp is thus evaluated as a promising developing technology bearing a lot of potential for implementation in a variety of future application areas.

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