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State of the art of particle emissions in thermal spraying and other high energy processes based on metal powders

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1 **8970 words**

2

3 Abstract

4 Thermal spray is a high energy-based process, like additive manufacturing and powder atomization, leading to fine 5 particle emission. But there is little information about these nanoparticles and their characteristics: workers' 6 exposure, filtration efficiency, dustiness. This paper aims to update the knowledge of the thermal spray community, 7 to focus on thermal spraying and to a lesser degree on powder atomization and additive manufacturing technology, 8 regarding emissions due to the high energy-based process. The three processes are presented before introducing an 9 updated survey of thermal spray activities in France. The main thermal spray equipment is wire arc and plasma 10 spraying. The main metal used is Al and Ni. The paper also highlights the lack of knowledge among workers on 11 thermal spray emissions. Most workers are not made aware of collective protection (emission filtration equipment 12 used) and personal protection (PPE). A complete bibliographical review is presented on the problem of ultrafine 13 particle emissions mainly for the thermal spray process. Ultrafine particles are always characterized inside a working 14 environment. The objective of this article is to list all publications related to ultrafine particle emissions around the 15 working environment of a thermal spray process to raise awareness of the academic and industrial communities 16 about the actual risks associated with this exposure. Finally, the authors are looking at the list of dust filtration 17 equipment by presenting their advantages and disadvantages for particle filtration.

18

19 Key words

20 Thermal spray; emissions; nanoparticles; dust equipment; filtering; safety

21

22 **1. Introduction**

High temperature processes related to metal powders (e.g. atomization, thermal spraying, additive manufacturing)

lead to the production and release of fines and nano-sized metal particles (Trompetter et al., 2016; Stefaniak et al.,

25 2019). There is a lack of knowledge about the properties of these emissions and their management (collection,

26 confinement or remediation), although the consequences of these ultrafine particles on health have been widely

demonstrated, in particular because of their inhalation without respiratory protection or collective aspiration
(Reijnders et al., 2006).

29 The current French legislation requires reducing emissions into the environment in both gaseous and particulate 30 form. This is particularly true for industries using powder metallurgy processes. Among the various existing 31 processes, thermal spraying is probably the one with the most numerous configurations both in terms of energy 32 sources (plasma, flame, electric arc) and materials used (metals, ceramics, polymers, composites, etc.). The principle 33 of this technology is to combine a heat source with gases to melt a precursor material usually in the form of 34 micrometric powder, and to accelerate the resulting molten particles towards a substrate. 35 Another powder metallurgy process which is currently on the rise is additive manufacturing, in particular selective 36 laser melting of metal (so-called SLM technology). The energy source is a laser radiation applied to melt the powder. 37 This process generates metal vapors. The operations are carried out in a closed chamber during the production phase. 38 The common approach of these two powder metallurgy processes is to use of a powder as a raw material. In the case 39 of metals, one method to make these powders from a liquid molten bath is atomization. Different methods can be 40 used: blowing the surface of the molten bath with a jet of cold gas or blowing a stream of molten metal liquid with 41 cold gas from surrounding nozzles, in order to generate droplets atomization that quickly solidify to form the 42 powder.

43 Whichever process is used among the three presented, an exhaust management device allows to treat particles 44 emitted to collect and/or treat them. However, there is relatively little information on the performance of this system, 45 especially since the characteristics of these emissions are not well known. In addition, gas and particulate emissions 46 do not only affect the core of the process, but the challenge is to consider the entire manufacturing chain, particularly 47 the pre- and post-process stages. Environmental management allows good practice of emission control. Different 48 issues are at stake, including organizational structure, practices, procedures and processes. The main objective is to 49 provide companies with more information about environmental issues and emissions, for example decisions on the 50 substitution of raw materials, decisions on the implementation of central or decentralized treatment or control for 51 wastewater/waste gas, etc. (Brinkmann et al., 2016).

The general purpose of this paper is to update our knowledge about emissions due to thermal spraying particularly, and to a lesser degree to additive manufacturing and powder atomization processes. The authors will first detail the different processes. The results of a survey conducted about thermal spraying in France will then be presented

- 55 followed by a review of papers on thermal spray emissions. They will also discuss scientific results and survey data.
- 56 Finally, the authors will present an overview of dust equipment for emission control.
- 57

58 **2. High energy processes based on metallic powders**

59 **2.1 Metallic powder manufacturing**

60 The metallic powder manufacturing currently benefits from the growth of additive manufacturing (Thomas, 2016; 61 Tofail et al., 2018). The market is divided into two broad categories: plasma and gas atomization. For additive 62 manufacturing or plasma spraying, the particle shape and size distribution are very important to optimize the use of 63 the powder in the process and optimize the properties of the coatings or parts obtained. Powders resulting from 64 plasma atomization perform better than other powder manufacturing processes (uniformity, spherical shape, very 65 fluid). Gaseous atomization is the most popular technique used to produce metallic powders. The objective is to transfer kinetic energy from a high velocity gas stream expanded through a nozzle, to a filament of molten metal, 66 resulting in disintegration into metal droplets. During this process, the material in the form of a metal bar is melted 67 by induction in a crucible. Once the metal is completely liquid, the stopper bar used to prevent the liquid from 68 transferring to the lower part of the process is removed to allow the molten metal to flow. The metal melt jet exits 69 70 vertically by gravity from a hole/nozzle. The jet is surrounded by a gas flow from one or several jets which blow the 71 liquid metal to generate a stream of droplets which solidify quickly to produce the powder (see Figure 1). The 72 behavior of the metal liquid jet is important in determining the particle size distribution. Different atomization 73 devices are available to generate metal powders. 74 The main global providers of metal powders using a plasma atomization process are located in Quebec: Tekna, 75 AP&C and PyroGenesis Additive. Regarding gas atomization, a technique which is over 100 years old, 76 manufacturers operate mainly in metallurgical industry: Carpenter and Praxair in the United States, VDM Metals in 77 Europe and Sanyo Special Steel in Japan, for example. On the French territory, the main manufacturers are Toyal, 78 Hermillon, Erasteel/Aubert & Duval, Tekna. Some research laboratories or technology platforms such as ICB-79 LERMPS, ONERA/MATMECA or Metafensch aim to develop specific metal powders or alloys. 80

81 2.2 Additive manufacturing

Additive manufacturing can be described as the transformation of a 3D model into a 3D object, using a raw material 82 and a heat source (Niaki et al., 2000). Additive manufacturing is a family of processes including selected techniques 83 depending on the state (solid, liquid) and nature (plastic, polymer, metal, etc.) of the filler material (Dobrzanski, 84 2017). First a virtual 3D CAD model is designed. This file is then converted to be understood by the additive 85 manufacturing equipment (STL being the most commonly used). The software 'slices' the STL files into thin layers. 86 Once the software has sent the instructions to the additive manufacturing equipment, the pattern is built layer upon 87 88 layer (see Figure 2). The Selective Laser Melting (SLM) additive manufacturing process deposits a few ten 89 micrometers thick bed on a support plate. The powder is melted locally with a laser spot based on the geometric 90 parameters defined by the CAD file of the final part. The melted powder solidifies rapidly forming strings of solid 91 material. At the end of this stage, the support plate goes down a little to allow the deposit of a new powder bed. This 92 is repeated until completion of the finished product. 93 The additive manufacturing market is rapidly growing due to increasingly mature users and diversified uses (Debroy 94 et al., 2019). Sales of equipment have seen an average annual growth of nearly 27% in recent years (Pipame, 2017). 95 The R&D French sector includes 57 centers of excellence (Institut Carnot France, 2017) and 2.116 companies (BPI 96 France, 2018). Aeronautics, space, medicine, luxury, mold/tool manufacturing, automotive are the main business 97 sectors. In France, metallic materials are the most used with 40% of activities (Institut Carnot France, 2017). The 98 metal additive manufacturing market is estimated at €60.6 million in France: 30% for powders, 40% for equipment, 99 and 30% for the manufacture of parts (Observatoire de la métallurgie, 2019). The French market is expected to

100 double between 2018 and 2025, notably through the expansion of part manufacturing, to reach €122M in 2025

101 (Pipame, 2017).

102

103 **2.3 Thermal spraying**

Thermal spraying is a common surface technique used in many industries such as transport, energy, biomedicine, electronics, etc. (Vardelle et al., 2016; Abbas et al., 2019). This technology belongs to the family of dry surface treatments. The principle is to spray a powder on a support to modify its properties, using a thermal and kinetic source (see Figure 3). Materials in the form of powders are usually injected into a heat source where they are heated and accelerated before being deposited on a substrate to form a coating. Thermal spraying shows great flexibility due to the following characteristics (Vuoristo, 2014): wide range of processes and sprayed materials (pure metals, metal 110 alloys, hard metals, ceramics, polymers), attractive production rate, high deposit efficiency, versatility of processes 111 and adaptability to the shape of the components. Selecting the type of gun/torch used involves looking at different 112 thermal/kinetic properties (jet at higher or lower temperature, at higher or lower speed). This selection is decisive as it will determine the conversion of energy available in the jet for the treatment of injected materials. The thermal 113 spray process is selected depending on the material to be used (which also depends on the coating application: anti-114 115 corrosion, anti-wear, reloading, reduction of friction, thermal or electrical insulation, etc.), the substrate nature, etc. 116 (Fauchais et al., 2014). The different systems are Atmospheric Plasma Spraying (APS), High Velocity Oxy Fuel 117 (HVOF), wire arc spraying, cold spray, etc. Among the various processes based on metallic powders and high 118 energy, thermal spraying is undoubtedly characterized by the widest range of configurations of energy sources 119 (plasma, flame, electric arc) and materials used. Thus, emissions are very diverse in terms of produced gases 120 (ionization, recombination, combustion phenomena, etc.) and emitted particles (material, average size, reactivity, 121 etc.) (Pawlowski, 2008). Moreover, the range of reactions complexity can vary. Thermal plasma is also used to 122 manufacture nanoparticles (Samal, 2017). 123 A detailed survey of the INRS (French National Research and Safety Institute for the prevention of Occupational 124 Accidents and Diseases) has mapped thermal spray facilities in France based on the processes and materials used, 125 and the line of business (Savary, 2014). It shows that approximately 780 to 960 companies working in thermal 126 spraying, with 75% of companies owning only one process in contrast with 2% of them working with five types of 127 equipment. The main process was wire arc spray (more than 50% of companies). The APS process was five times 128 fewer and the HVOF ten times fewer. This was consistent with the main material used, ZnAl (14%), followed by Ni

base material (9%) and Al (8.5%). In France, thermal spray was mostly linked to small companies, using only one
 process.

131

132 **3. CaRPE survey**

To update the INRS work (Savary, 2014), a survey of French thermal spray companies was conducted in 2019. The questions were aiming at improving the understanding of their activities (processes, materials) regarding emission hazards (personal protective equipment) and capture systems (cleaning, filtration, measurements). The questions are listed in the Table 1, and the answers are presented in Figures 4 to 9. 138 for 2019. The key is to know the company working environment when it comes to thermal spray activities. 139 Figure 4 shows that more than 80% of the French companies surveyed are equipped with wire arc spraying and APS processes. Then HVOF/HVAF reach 78%. These results are in line with the INRS wide survey (Savary, 2014). For 140 APS and HVOF/HVAF, the base materials are Ni and Cr, as shown by the INRS survey (see Figure 5). For wire arc 141 142 and flame spraying, Al, Cu and Fe base material are mostly used. In the INRS survey, Zn was predominant. These 143 results indicate that small companies contacted for the survey probably did not answer due to lack of time or the 144 primary purpose of the survey: emissions. Most of the time, companies are reluctant to discuss emissions and staff 145 protection issues. 146 The survey shows that the majority of thermal spray booths is inaccessible during operations and the main air capture 147 is usually located at the emission source and on the booth wall (see Figure 6). Furthermore, 67% of companies do not 148 have suction over the powder feeder to evacuate aerosol formation during powder pouring. 149 Regarding the companies' dust exhaust system, the most popular one is filtration using a fibrous media, namely a 150 cartridge (see Figure 7). It is interesting to highlight that 20% of companies do not really know which equipment is 151 installed. Furthermore, the effectiveness of the media is unknown in most cases, and various classes of media are 152 used (EPA, HEPA). This information shows companies' lack of interest in selecting a dust collector, because there is 153 little information (scientific papers, studies) about the efficiency of dust collectors. 154 Figure 8 presents the protective equipment worn by operators during thermal spray operations. In most cases, it 155 includes face masks and FFP3 cartridges. But there are still some companies where operators do not wear respiratory

Among around 100 companies, only 10 answered. As a result, the statistics presented barely give a qualitative trend

156 PPE. Despite information in the literature regarding emissions and exposure, a company policy is paramount.

157 Furthermore, the right equipment must be worn for each step where there is a risk of contact with powder/dust (booth

158 cleaning, powder pouring, etc.). Moreover, the efficiency class of respiratory protective equipment filters is not FFP3

equivalent for all. Booths are usually cleaned once a week. But the selected method to remove dust is still surprising.

160 For example, 33% of operators use a broom and 22% use a compressed air-blower. Finally, Figure 9 confirms that

161 66% of companies set aside the emission problem and do not plan emission measurements, such as sampling on a

162 workstation or on the dust collector exit.

163

137

164 **4. Emissions from processes**

165 Whatever the process (atomization, thermal spraying or additive manufacturing), using powder and a heat source 166 leads to particle emissions. For thermal spraying, the range of materials is very large (almost all metals) with a 167 powder size scaling from micrometers to sub-micrometers and nanometers, depending on the surrounding 168 atmosphere around the process (air, neutral gas, vacuum). Emissions vary greatly based on these conditions. 169 Moreover, the thermal spray deposition efficiency range is largely dependent on the process, 10 to 99.9% (Fauchais 170 et al., 2014). A significant proportion of particles, residues and matter gets lost in the booth. The initial average size 171 of the powder ranges from 5 to 150 micrometers. But after spraying, some matter is vaporized, sprayed out of the 172 substrate, lost after rebounding at the surface. To date, the conversion rate of micrometric particles into ultrafine 173 particles is not known. No study has investigated this question. In most cases, an aerosol is generated. For powder 174 atomization, the process is based on aerosol manufacturing by the blowing of a liquid jet. Selective laser melting 175 generates matter emissions when the laser spot melts the powder. Figure 10 illustrates these emissions around the 176 thermal source. 177 The scientific community has been studying emissions from powder metallurgy processes for several years. 178 Regarding metal powder atomization, the aim is to collect all particles generated by the process. Most of them enter 179 the final container under the atomization tower. But some of them accumulate inside the tower leading to possible 180 emissions during maintenance. As it is a closed-circuit process, emissions are channeled inside during the 181 manufacturing phase. No study was found on the characterization of emissions during metal atomization. 182 Selective laser melting with metals usually occurs inside a specific device in a closed loop. During metal processes, 183 emissions are channeled inside the equipment, whereas for plastic and polymers, some equipment do not use any 184 exhaust and filtration system. As a result, the operator is exposed to emissions of ultra-fine particles. On plastics,

these emissions have been found in very high concentrations (Stephens et al., 2013; Azimi et al.). Regarding metal

186 particles, Keller et al. (2018) and Bau et al. (2019) highlighted the high number of nanoparticles generated during the

additive manufacturing process near the source inside the process: 2.5.10⁶ to 4.5.10⁶ #/cm³. Operators who handle

188 metal powders run the risk to be exposed to particles (Graff et al., 2017; Mellin et al., 2016). Another study confirms

the presence of nanoparticles (around 15 nm) around metal additive manufacturing equipment (Gomes et al., 2019).

190 A review of Chen et al. confirms these results, showing that these emissions are very real and unintentional during

191 the operator's handling (Chen et al., 2020). A methodology must be developed to avoid exposures, especially

regarding the management of this risk (Souza et al., 2019) and the design of the working environment of the process(Ljunggren et al., 2019).

194 For thermal spraying, the available studies essentially focus on describing thermal spray activities in terms of 195 processes, materials and applications. Some scientific papers nevertheless look at characterizing emissions for a few 196 combinations of materials, in most cases around the process. In France, the INRS has carried out studies in thermal 197 spray activities (Mater and Savary, 2014). Their survey reveals that in 12% of French thermal spray companies, 198 employees do not wear respiratory protective equipment (Savary, 2014), as confirmed by our CaRPE survey. 199 Moreover, even if there is a ventilation system in the booth, a significant number of employees enter without 200respiratory equipment (Savary, 2015). A study was carried out on the emissions of arc-wire spray processes that emit 201 metal vapors (Grippari, 2012). The measurements showed numerous particles with an aerodynamic diameter less 202 than 100 nm. The INRS also raises the alarm against the large quantity of ultrafine particles below 100 nm generated 203 by the arc-wire spray process and recommends a number of technical measures to use filtration to treat the nature of 204 effluents (Bémer et al., 2010). This same institute has also published some emission data on NiCr alloy and some 205 elements of information on aluminum and zinc materials in various processes (first level information only). A study 206 conducted by another French health institute measured levels 15 times higher than the occupational exposure limit 207 value for CrVI for sprayed materials containing chromium or chromium oxides (CARSAT, 2013). Similarly, 208 operators who thermally spray Cr using plasma are exposed to CrVI with concentrations above VLEP-8h of $1 \mu g/m^3$ 209 (Jacoby et al. 2017). Levels of urinary excretion of Ni metal for exposed thermal spray operators, all processes 210 combined, are relatively high compared to those unexposed. Viana et al. and Salmatodinis et al. show that high 211 concentrations of ultrafine particle emission are measured during the APS process $(3.7 \times 10^6/\text{cm}^3)$, with a particle 212 size distribution between 28 nm and 45 nm (Viana et al., 2017; Salmatodinis et al., 2018). These emissions of 213 nanoparticles can transfer outside the spray enclosure where workers are not necessarily protected by PPE 214 (Salmatodinis et al., 2020). With the HVOF process, the same trend is found with exposure concentration of dust 215 particles reaching 140 mg/m³ (Huang et al., 2016). A study compared three spray processes for material residues 216 (cobalt, chromium, and nickel) in the urine of operators (Chadwick et al., 1997). The plasma process is the most 217 emissive. In Greece, a thermal spray company completed some measurements to control air quality (Petsas et al., 218 2007). It appears that concentrations of particles and heavy metals were predominant during the cleaning and 219 maintenance phases of the spray booth. The INRS survey indicates that 23% of operators use a broom or a blow gun

to clean work areas (Savary, 2015). The Thermal Spray Society (2013) publishes documents on risks surrounding the
process and recommended protections. However, these documents only give an overview of the issues encountered
and do not provide a clear answer on how to ensure health and safety in the workplace.

223 The scientific literature demonstrates the unintentional manufacturing of nanoparticles during thermal spraying. As the deposition efficiency is mostly around 50-60%, a part of the initial feedstock loss is transformed into ultrafine 224 particles under the heat source. Some of these particles are sucked by the extraction system, but nanoparticles can 225 226 deposit around different parts in the booth (robot, coated piece, booth corners, etc.). So, at the end of spraying, the 227 operator is always exposed to nanoparticles through his actions in the booth (object displacement, walking on the 228 ground, air flow due to his movements, etc.). The release due to the induced air motion can play a role in the 229 exposure. The CaRPE survey demonstrates that wearing protective equipment is not ubiquitous and not all 230 companies are aware of the risks of exposure to ultrafine particles. Operators wear protections without any 231 knowledge regarding the risks and consequences of not wearing any. This is even more damaging because the two 232 most used materials are Cr and Zn. Several analyses show that Cr can be found in urinary samples, and CrVI can be 233 formed during spraying via different processes. Zn material mainly used with wire arc spray process under 234 atmospheric conditions can generate ZnO oxide at the nanometer scale which could induce a health hazard 235 (Subramanian et al., 2018). To make matters worse, according to the INRS and CaRPE surveys, booth cleaning is 236 often carried out with a broom or a compressed-air blower only to induce the resuspension of ultrafine particles in 237 the air. Normally, nanoparticles are quickly sucked by the air extraction systems, limiting the operator's exposure. 238 But as shown by Bemer et al. (2010) (2013b), the most widely used dust collector with a cartridge fibrous media is 239 rapidly clogged up with nanoparticles. The difficulty to clean cartridges, even by gas pulse, can explain the pressure 240 drop inside the exhaust pipe of the booth. As a result, dust particles from the thermal spray remain at high levels in 241 the booth, increasing the operator's exposure after the coating manufacturing.

242

5. Dust equipment for emission control

244 Thermal spraying induces gaseous emissions that contain particles of various average sizes, morphologies,

compositions. Around the process, the waste gas generated can be divided into ducted and diffuse emissions. The

first type can be cleaned whereas the second one can only be prevented. Industrial emissions can usually be classified

as shown in Table 2 (Brinkmann et al., 2016).

Waste gas treatment devices aim at processing different chemical elements such as gas, particles, vapors of volatile liquid substances, gaseous air contaminants. The system is linked to a unique emission source as the treatment unit is exclusively designed for a specific waste gas composition. Most processes show material melting through their heat source at relatively high temperatures. The raw material is a powder in a melting state, upstream (thermal spraying, additive manufacturing) or downstream (powder atomization) of the process. The induced emissions consist of a variety of gases and particles (composition, particle size, concentration, etc.).

An aerosol is defined as a set of solid or liquid particles in suspension (maximum limit speed of fall <0.25 m/s) in a gaseous medium (Kulkarni et al., 2011). This term includes both fumes, dusts and mists, but not vapors. Fumes are defined as dispersions of very fine solid particles resulting sometimes from condensation or incomplete combustion. Dust is defined as any suspended solid particles. A particle is defined as a small part of solid or liquid material suspended in the air or likely to be. Within an emission, particles are mainly distinguished by their size (see

259 Figure 11):

• PM10 particles: aerodynamic diameter less than 10 μm;

261

• PM2.5 aerodynamic diameter less than 2.5 µm;

• PM1 aerodynamic diameter less than 1 μm.

This classification was created based on inhalation hazards level. Particle characteristics are linked to the deposit area in the pulmonary system. The fraction of inhaled particles depends on their aerodynamic diameter (diameter of a sphere with the density of 10³ kg/m³ and a falling rate in calm air environment which is equal to that of the particle in the same conditions) and on the type of breathing (nose, mouth). The pulmonary area will depend on the inhalable fraction of well-defined sub-fractions: thoracic and alveolar. Regarding the three processes based on metallic powders and high energy (thermal spraying, powder atomization, additive manufacturing), the main components of emissions are solid particles. So, the waste gas treatment device will depend on the particle characteristics.

270

A dust collector is designed to collect the dust containing particles and separate these particles from the gas. The
 choice of process starts with an efficient characterization of the fumes to be treated, including:

- solid or liquid particles,
- temperature, because it will alter the density, the viscosity, the humidity, the conductivity of particles and
 affect the selection of the material for filters, for example;

276	• granulometry;
277	• concentration at the capture inlet and at the outlet;
278	• vector fluid;
279	• fluctuating, pulsed or continuous gas flow;
280	• neutral, corrosive or flammable medium;
281	• pressure.
282	Dust collectors can be wet (removal of dust from the air by water filtration) or dry (removal of dust from the air
283	through filter media or electrostatic forces). The collected air is filtered by dust extractors. In order to capture the
284	dust, different attraction methods are available: gravity, molecular (cohesion and adhesion forces) and electrical (or
285	repulsion).
286	Therefore, different types of equipment were designed to filter or sort this dust, among which 5 main techniques
287	(Siret, 2001):
288	• settling chambers;
289	• centrifugal separators or cyclones;
290	• electrostatic precipitators;
291	• filtration by fibrous media;
292	• wet dust collectors.
293	
294	5.1 Dry collectors
295	Settling chambers consist of an empty chamber where the fumes/waste gases circulate with a low speed. This leaves
296	time for gravity to separate particles from gas(>10-50 μ m). To improve the deposition efficiency of particles, it is
297	necessary to:
298	• adjust the chamber design with baffles or lamellae to reduce gas velocity;
299	• increase the active force of particles by centrifugal force (baffled precipitator, centrifugal separator) or
300	electric force (electrostatic precipitators);
301	• capture particles in liquid droplets (hydraulic dust collectors, wet electrostatic precipitators);
302	• agglomerate particles by electrical or sonic agglomeration.
303	Settling chambers are often used as a first device in filter systems to remove large particles.

305	In a centrifugal separator, fumes will be rotated to use inertia to collect particles. Centrifugal force moves the dust		
306	towards the wall to be collected (cyclone effect) thanks to a double vortex. Cyclones are sedimentation chambers		
307	where the effect of gravity is increased by centrifugal force. The largest particles are removed. Performances are set		
308	by the geometry of the system (height, diameter, tangential velocity). Efficiency increases with high airspeeds in a		
309	small diameter and long cylinder. This is the cheapest and most robust equipment with a very wide operating		
310	amplitude (temperature, pressure). However, performance is limited to particle sizes greater than 10 microns. The		
311	efficiency is 95% for particles> 15 μm. The smallest ones should be separated with another device. Wet cyclones aim		
312	to increase efficiency when separating fine particles.		
313	There are two main types of cyclones:		
314	• reverse flow cyclone (lateral inlet);		
315	• straight-through cyclone (axial inlet);		
316	Other less used types are: electro cyclones with an electrode that charges particles to hit the walls, multi-cyclones.		
317			
318	Electrostatic precipitators (ESP) use an electric force applied to the charged particles by ionization of the fumes. A		
319	wire placed in a tube or pulled between two plates is brought up to a highly negative voltage creating a corona		
320	discharge. The gases that make up the smoke are then excited, tearing out electrons that, by collision, create ions and		
321	radicals that will charge particles. They are then subjected to an electric field to be attracted to a counter electrode		
322	where they will pile up and form a deposit. There are different separators: dry wire plate or pipe ESP, wet wire plate		
323	or pipe ESP. However, this equipment has been listed as a possible explosion risk due to its technical configuration		
324	and its electrostatic property which can be a source of ignition (Chhabra, R. et al., 2019). ESPs are not recommended		
325	for materials with explosive properties (Peukert et al., 2001). The authors believe that ESP would be suitable to		
326	remove ultrafine oxidized dust. In the case of metal dust, a pre-combustion step would be required to avoid the		
327	formation of an explosive atmosphere in the ESP. Ultrafine metal dust is likely to react with water to produce		
328	hydrogen (e.g. aluminum dust) and in that case, neither dry ESPs nor humid ESDs can be used exposed to air. If the		
329	risk analysis shows that such a system could be used (e.g. passivated powders, mixture with inert solid particles, low		
330	flow rate associated with a sufficient ventilation rate), it is likely that an explosion mitigation system should be		
331	implemented such as an explosion vent.		

333	The dust collector by fibrous media (fabric filter) consists of a main box (filter elements, high-pressure air pulse
334	cleaning system, hopper collecting dust). Polluted air enters at the bottom of the dust collector to come out above
335	after passing through the filters. Unlike with cyclones where disposal is continuous, with fibrous media collectors,
336	particles accumulate on the outer surface of the filter media and form a deposit that will induce a pressure drop
337	during the operation of the dust collector. These filters are cleaned to limit the pressure drop caused by clogging
338	fibers, fabrics or other felts. There are different cleaning methods:
339	• shaking, where the filter is gently shaken in all directions on a mechanical device;
340	• counterflow gas, where the suction is stopped and air is blown through the filters in the opposite direction to
341	that of the filtration;
342	• gas pulse, where a pulse of medium air pressure is propelled inside the sleeve, generating a wave of pressure
343	and deformation that will allow the dust cake to come off. This type of unclogging is possible without the
344	need to isolate the whole box, and sleeves nearby can continue to operate. The benefits of this method are
345	its high efficiency and the possible use of non-compartmentalized filters. In contrast, the sleeves are more
346	stressed and wear faster.
347	These actions remove the cake made of particles which is collected in a hopper. Unclogging is performed at regular
348	intervals depending on the pressure drop. The first unclogging operations make it possible to find pressure drop
349	values close to those of a new fibrous media, for the first cycles. Once deposited on the fibrous media, particles
350	remain either on the surface or inside the media. This phenomenon increases during the process. After a while, the
351	filter elements become irremediably clogged and must be replaced. The presence of ultra-fine particles accelerates
352	the clogging phenomenon. The media is less efficient due to the strong adhesion of particles. To delay the clogging,
353	it is advisable to reduce the filtration speeds by increasing the filtration area, or to add a coarser filter (prefilter for
354	large particles). There are three filter media technologies:
355	• fibrous media;
356	• consolidated porous media, such as sintered ceramics but generating high-pressure losses;
357	• unconsolidated granular porous media, such as sand columns but showing low efficiency against fine
358	particles.

359	When filtering an aerosol, a particle is screened by a fibrous filter (particle size larger than the pore size). In the		
360	absence of external force fields such as a magnetic field, particles are captured via gravity through a fiber filter in 3		
361	steps:		
362	• inertia: particles cannot follow the current line during fiber crossing and collapse against it (diameter greater		
363	than 1 μm);		
364	• direct interception when particles follow the current line but approach the fiber at a distance shorter than		
365	their radius (greater than 100 nm);		
366	• Brownian scattering for particles smaller than 100 nm, where their trajectory passes close enough to the		
367	fiber to undergo a deflection under the influence of the Brownian motion.		
368	Electrostatic forces can also be added with a metal media before calculating the filter efficiency. Between 100 nm		
369	and 500 nm, a minimal degree of operational efficiency is reached because the three capture mechanisms are not		
370	preponderant. Some particles are too large to be affected by the diffusion phenomenon and too small to be		
371	intercepted or impacted. These are the most penetrating particles (MPPS: Most Penetrating Particle Size). It is in this		
372	area that the efficiency of high efficiency particles (HEPA) and ultra-low penetration (ULPA) air filters is calculated.		
373	The fiber filters consist of natural, metallic, or synthetic fibers. Generally, fibers consist of fiberglass, polyester or		
374	cellulose. They are defined by different factors:		
375	• compactness: volume of the fibers/volume of the filter;		
376	• basis weight: filter mass/filter area;		
377	• thickness;		
378	• size distribution of the fibers;		
379	• nature of the fibrous filters: fibrous woven, felt or nonwoven.		
380	These fibrous filters can be mounted on different filtration systems: bag filters, cartridge filters. They can operate		
381	alternatively or continuously (it is possible to isolate the filter to be unclogged without stopping the ventilation).		
382	Each of these filters exists in various ranges of efficiency depending on the industrial field and the fumes particles		
383	characteristics: very high efficiency (nuclear, clean room), high efficiency (indoor air, air conditioning), average		
384	efficiency (industrial effluents). For a medium and high efficiency, the deposition of particles (cake) on the surface		
385	of the media is eliminated mechanically whereas for very high efficiency, particles are captured inside and therefore		
386	filters must be changed.		

An absolute filter is composed of a high-density pleated media made of fiber glass. Particles from the waste gas are
 collected. The design is often a cylindrical cell, and a pre-filter is necessary to remove the biggest particles. The
 absolute part is set for ultra-fine particles and nanomaterials.

The Carpe survey shows that the most popular filter is the cartridge filter (see Figure 7). But 20% of companies are unaware of their filter characteristics. In the thermal spray community, fibrous media filters are the most adapted to filter emitted particles. However, difficulties related to the regeneration of filters clogged by metallic nanoparticles are still relevant today. The rapid increase of the pressure drop with ineffective unclogging is still being investigated to control this issue (Khirouni et al., 2020a). To date, it means a frequent replacement of filter media.

395

396 5.2 Wet collectors

397 A wet collector, often named wet dust scrubbing, uses a liquid to intercept particles contained in the fumes. This

398 device is widely used for its efficiency in reducing particulate emissions and especially soluble compounds such as

399 acid gases and heavy metals. Wet collectors are often associated with other technologies, especially electrostatic

400 precipitators. There are two mechanisms for dust capture: by impaction on a wet wall (packed column) or by

401 collision with a dispersion of liquid droplets injected into a gas (venturi, spray column). The most common principle

402 is impaction by inertia.

403 There are therefore several types of wet separators (Siret, 2001):

- 404 spray towers: the spray occurs from top to bottom. They are widely used but not for dusting due to their low
 405 efficiency. The stripping mattress is composed of a mesh of fine ordered or disordered fibers, which capture
 406 particles. The efficiency is very good up to 1 μm;
- 407 cross-current: the spraying is perpendicular to the flow of smoke. They are suitable for dust (99% efficiency
 408 for particles> 2 μm) but have a fairly high energy consumption (pump);
- foam: fumes cross a liquid layer supplemented with a surfactant. The phenomenon of diffusion explains an
 efficiency rate of 90% for 500 nm particles. There are a few pressure losses, but the cost is quite high;
- venturi type: this type is especially designed for dust while the previous ones basically focus on the

412 purification of gaseous compounds. Gases are accelerated, which facilitates the interaction between the413 aerosol and the liquid regardless of the significant pressure loss. The efficiency rate is 99% for a dimension

414 of 1 µm but the energy consumption is important;

415

416

bubble columns: the transported dust meets liquid bubbles and mixes with them, establishing a transfer from one phase to another;

• fibrous packing, moving-bed, plate, etc.

418 Tables 3 and 4 show the main characteristics of the different filters (abatement efficiency, benefits and limitations).

419

420 6. Thermal spray and emissions control efficiency

421 Thermal spraying combines micrometric powder and high energy sources (flame, plasma, electric arc). The 422 formation of the coating from the precursor generates nanoparticles that can be found in the spray booth or in the 423 environment close to the cabin. The exposure of operators is then obvious and protective equipment has to be worn 424 (Heriaud-Kraemer et al., 2003). In most cases, the nanoparticles are the result of the process as the initial feedstock is micrometer sized, even if nanoparticles (ceramics) can be used (Toma et al., 2008). Moreover, the solution precursor 425 plasma spray process uses only salt solution feedstocks to manufacture coatings with physical and chemical reactions 426 inside the heat source (Bertolissi et al., 2012). The use of plasma spraying under very low pressure allows vaporizing 427 the initial powder creating nanoparticles and nanostructures (Fan et al., 2019; Darut et al., 2019). So, the resulting 428 429 fine dust generated by the process must be captured by the exhaust system which has to be selected or configured 430 based on the thermal spray dust properties. This way, an efficient ventilation flow inside the booth facilitates the 431 capture of nanoparticles in the filtration system. The air velocity impacts directly on the dust drive to suctions panels. 432 It is linked to power characteristics of the exhaust filtration system and to pressure losses in the pipes and filter 433 media. If the velocity is too low, dust accumulates on the booth floor or walls. That is why cartridge media (major 434 filter system in thermal spray activity (Bemer et al., 2013b) as confirmed by the CaRPE survey) are cleaned by 435 compressed air jet to prevent pressure loss and allow good ventilation. But with some processes, in particular wire 436 arc spraying, filtration cartridges are often clogged. Bemer et al. underline the irreversible character of clogging due 437 to the nature of the dust collected (Bemer et al., 2013a). Even with the use of a counter-current pulse-jet, cleaning 438 seems to be inefficient. Granular beds, based on Brownian diffusion mechanism to capture ultrafine particles, could be a good alternative to conventional cartridge filters but no industrial pilot has yet been tested (Bemer et al, 2015a; 439 Bemer et al., 2015b). A recent work of the INRS shows the possibility to improve cartridge cleaning using a pre-440 deposit (micrometer particles) on the surface of the filter media in order to improve the removal of ultrafine particles 441 442 that would be deposited on the surface (Khirouni et al., 2020b). A different approach was proposed by Cho et al.:

443 spraying compressed air directly on the external surface of the filter rather than injecting pulse-jet air on its internal surface (Cho et al., 2020). This so-called air-washing cleaning method allows successful cleaning and regenerate the 444 fibrous media, but also to reduce particle emissions. Some modeling has been developed to study the concentration 445 of released nanoparticles during a thermal spray process (Ribalta et al., 2016). The measurements confirm the results 446 447 of previous studies. When the thermal spray process occurs in a booth, a negative pressure is applied to confine dust inside. A problem can occur: the filtering system does not collect nanoparticles efficiently. The negative pressure can 448 449 reintroduce the polluted air in the booth, according to the positioning of the exhaust system outlet in relation to the 450 air compensation entry. In any case, nanoparticles will be rejected into the environment if the exhaust system is not 451 appropriate.

452

453 **7. Conclusions**

454 Nanoparticles emission is crucial for processes based on metal powders and high energy such as thermal spraying, 455 powder atomization and additive manufacturing. During processes, particles are in a liquid/vapor state in the thermal source. Generated nanoparticles are incidental. As a result, companies and operators must be aware of the risk and 456 release into the environment. The different surveys on thermal spray activity demonstrate the lack of information and 457 communication between the industry and scientific community. Various published papers state the health risk for 458 459 unprotected operators around the process. A significant number of operators work without a protection adapted to thermal spray activity. It would therefore be necessary to characterize these emissions, and to make operators aware 460 of monitoring and reduction. Different filtration devices can be used to treat thermal spray effluents and therefore 461 462 adapted to the ultrafine particles generated. However, the use of fibrous media (filter cartridge essentially) is the 463 most appropriate to retain this waste. The clogging issue of these media and therefore the suction flow pressure drop 464 in the spray enclosure are still relevant. The risk is an increase of particles in the working booth and their presence at 465 the end of the spraying, in contact with the operator. 466 The main recommendations for the thermal spray activity as well as the risks that may be encountered will be studied

467 in a second part of this project. Various sampling operations and emission analyses of plasma spraying equipment

468 will be carried out. Different areas will be targeted, such as at the level of emissions channeled upstream and

469 downstream of the filtration system, at the workstation level as well as fugitive emissions. Various measurements

- 470 will be carried out: real-time particle size distribution, mass concentration of total suspended dust, heavy metals,
- 471 sampling characterization by EDX/MET, etc.
- 472

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- 477
- 478

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- 647
- 648
- 649 Figure captions
- 650 Figure 1: Powder atomization principle
- 651 Figure 2: Additive manufacturing principle
- 652 Figure 3: Thermal spray principle
- 653 Figure 4: Different processes used by the French companies (CaRPE survey)
- Figure 5: Sprayed metal-based materials used by French thermal spray companies (CaRPE survey)
- 655 Figure 6: Thermal spray environment (CaRPE survey)
- 656 Figure 7: Thermal spray dust exhaust equipment characteristics (CaRPE survey)
- 657 Figure 8: Personal respiratory protective equipment of workers and booth cleaning (CaRPE survey)
- 658 Figure 9: Achievement of emissions measurements (CaRPE survey)

- 659 Figure 10: Pictures of melted metal droplets and jets during a) powder atomization, b) thermal spray and c) selective
- 660 laser melting processes
- 661 Figure 11: PM particles description
- 662

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663 Table captions
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- 664 Table 1: Questions of CaRPE survey for thermal spray companies
- 665 Table 2: Ducted and diffuse emissions
- Table 3: Efficiencies, maximum gas flow and particle content of the main dust collectors (Brinkmann et al, 2016)
- Table 4: Benefits and limitations of the main dust collectors (Brinkmann et al, 2016; Peukert et al., 2001; Hallé et al.,
- 668 2015; and experience from the authors)



























chievement of measurements at the level of operators complex on workstation)





















	•How many employees use thermal spraying processes?	
	•How many different thermal spray processes are you equipped with?	
Company	•How many thermal spray booths are you equipped with?	
Company	•What is the annual order of magnitude regarding raw material for thermal spraying (powder,	
activity	wire, etc.)?	
	•Which processes are you equipped with?	
	•What are the sprayed metal based materials used with each process?	
	•What is the main work environment in the workshop?	
Emissions and	•What type of air capture are you equipped with?	
dust	dust•What types of dust exhaust equipment are you equipped with?ipment•Do you have suction over the powder feeder (suction arm, etc.)?	
equipment		
•How efficient is the filter medium of your cartridge or bag dust collector?		
	•What personal respiratory protection equipment most thermal spray operators wear?	
	•What is the efficiency class of respiratory protective equipment filters?	
Personal	•When must PPE be worn?	
protection	•How often do you clean the thermal spray booths?	
	•How do you clean the thermal spray booths?	
•Are aerosols or particle emissions measured?		
Emission	•Do you take measurements at the level of operators (sampler on workstation)?	
control	•Do you take ambient measurements?	
	•Do you take measurements out at the dust collector exit?	

Table 1: Questions of CaRPE survey for thermal spray companies

Table 2: Ducted and diffuse emissions [1]

Ducted emissions	Diffuse emissions	
• process emissions released through a	• process emissions from the process	
ventilation pipe via the process equipment	equipment inherent in running the plant,	
• gas flow from energy-providing units, such as	released from a large surface or through	
process furnaces, steam boilers, combined heat	openings	
and power units, gas turbines, and gas engines	• non-ducted emissions (e.g. 'working losses'	
• waste gases from emission control equipment,	and 'breathing losses', when not captured and	
such as filters, incinerators/oxidisers or	ducted) from storage equipment and during	
adsorbers, likely to contain unabated pollutants	handling operations (e.g. drum filling, trucks	
or pollutants generated in the abated system	or containers)	
• tail gases from reaction vessels and condensers	• uncommon emissions, resulting from	
• waste gases from catalyst regeneration	operations other than routine processing of	
• waste gases from solvent regeneration	the facility including emissions during start-	
• waste gases from vents from storage and	up or shutdown and during maintenance	
handling (transfers, loading and unloading) of	• secondary emissions resulting from thewaste	
products, raw materials and intermediate	handling or disposal (e.g. volatile material	
• waste gases from purge vents or preheating	from sewers, waste water handling facilities	
equipment, which are used only in start-up or	or cooling water)	
shutdown operations	• fugitive emissions (see Glossary), such as	
• discharges from safety relief devices (e.g.	equipment leaks from pump and compressor	
safety vents, safety valves)	seals, valves, flanges, connectors and others	
• exhaust air from general ventilation systems	piping items, or other equipment items, such	
• exhaust air from vents from captured diffuse	as drain or vent plugs or seals	
sources, e.g. diffuse sources installed within a		
facility		

	Abatement efficiency (%)	Waste gas flow (Nm ³ /h)	PM content (g/Nm ³)
Settling chambers	10-90	100 - 100 000	No restriction
Cyclones	$PM_{>50} - 99$ $PM_{10} - 30-90$ $PM_{2.5} - 0-40$ $PM_1 - 5$	1 – 100 000	1 – 16 000
Electrostatic precipitator	99 PM _{2.5} – 97-99.2 PM ₁ – 97	1 800 – 2 000 000	1 - 110
Fibrous media	99 – 99.9	300 - 1 800 000	0.1 - 230
Absolute filter	99.999 PM _{0.1} – 99.999 PM _{0.01} – 99.99	100 - 300	1 - 30
Wet dust scrubber (spray tower)	PM ₁₀ – 70 -99	2 500 - 170 000	No restriction

Table 3: Efficiencies, maximum gas flow and particle content of the main dust collectors (Brinkmann et al, 2016)

Table 4: Benefits and limitations of the main dust collectors (Brinkmann et al, 2016; Peukert et al., 2001; Hallé

et al., 2015; and experience from the authors)

	Benefits	Limitations
	Simple construction, no moving part hence low	Poor removal efficiency, especially for small
	maintenance and low operating costs	particles (below 50 µm)
	Very low pressure drop	Unsuitable for sticky particles
Sottling	Suitable for higher temperatures	Not suitable when the density difference
chambors	Low investment costs	between gas and particulates is small
chambers	Low energy consumption	Relatively large equipment
	Can be applied to processes with large	Decrease of efficiency for low concentration at
	fluctuations, e.g. with high and low	the inlet
	temperatures	
	Simplicity of the installation	Relatively low PM abatement efficiency,
	Recovery of raw material	particularly below PM ₁₀ . In the current
	No moving parts, hence few maintenance	regulatory framework, it should be used solely
	requirements and low operating costs	as a pre dust-removal system
	Low investment and maintenance costs	The higher the efficiency the higher the
	Dry collection and disposal, except for wet	pressure drop and the energy consumption
	cyclones	Axial entry cyclones cannot be used with
Cyclones	Relatively small space requirements	particles likely to cause excessive erosion or
	Low consumption of energy	clogging of the vanes in the inlet
	Relatively low pressure drop	Unable to handle sticky or tacky materials
	High density of particle flows can be treated	Emissions to waste water with wet cyclones
		Noise
		Regular cleaning necessary to avoid self-
		heating risk with accumulation of combustible
		dusts

	High abatement efficiency (> 97 %) even for	High initial investment costs
	small sized particles (high efficiency until 10 nm) and high concentration of particles	Ozone can be formed by the electrodes, which
	(efficiency can be increased by adding fields or	be a source of environmental pollution
	zones)	Less suited for processes with varying gas
	Capacity of treatment of important inlet gas	streams, temperatures or dust concentrations.
	flows	adjustments. Varving operational conditions is
	Low maintenance costs and possibility to work	easy, if the installation is designed for the worst
	at temperatures higher than 300°C	case situation.
	Low energy consumption	Re-entrainment can be a problem due to high
	Low-pressure drop, hence energy requirement	gas velocities, poor rapping or poor gas flow
	induced or forced draft fan is needed to	Sensitive to maintenance and settings
Electrostatic	overcome system pressure drop)	Relatively large equipment size
precipitator	Possibility to work under vacuum	Highly qualified staff is required
	Suitable for a wide range of temperatures,	Special cautions to protect staff from the high
	pressures and gas flows	voltage (electrical hazards)
	Dust can be removed dry, making reuse possible	Dry ESP must be avoided with combustible
	(for dry ESP)	dust, as it generated dust explosion risks. Pre-
	Partial removal of acid fumes (for wet ESP)	ESP treatment.
	Wet ESPs can abate sticky particles, mists and	The abatement capacity depends on the
	highly resistive or explosive dusts	electrical resistivity of dust particles (with dry
	At a voltage of > 50 kV, abatement efficiency is	ESPs)
	more compact manufacturing (for wet ESP)	Dry ESPs not recommended for the removal of
		sticky or moist particles

	Corrosion near the top of the wires due to air
	leakage and acid condensation, which is also an
	issue with wet ESPs (although acid gases are
	also absorbed by the water)
	Wet ESP is adapted to combustible/ explosible
	dust provided that dust does not react with the
	liquid phase (e.g. some metallic powder that
	tend to produce hydrogen when in contact with
	water). Protection measures must be also
	implemented (explosion vent, earthing of the
	equipment to avoid electrostatic discharges,
	regular cleaning is also necessary to avoid the
	creation oof sparks between the electrodes).
	Also all electrical safety measures must be
	correctly implemented.
	Wet ESPs are relatively expensive and require
	post-treatment of sludge water
In general, fabric filters provide high abatement	Fabric filters are not suitable for wet or sticky
efficiencies for coarse and fine particles	dusts because of the risk of filter clogging
Efficiency and pressure drop of continuously	Heating the waste gas stream prevents
cleaned filters are relatively unaffected by large	condensation of fluid on the ceramic filters
changes in inlet dust loads	Static electricity may hinder the cake from
Dust is sorted dry without using consumables.	being removed from the fabric
The separated dust might be reused in the	Big size of the equipment
preceding process or recycled	Reverse air bag filter system requires
Residual emissions are virtually independent of	numerous mechanical moving pieces which
the intake concentration	can be then source of failures. It then needs
Relatively simple operation	

	Reliability	regular maintenance. On the contrary air-pulse
		filters are much easier to maintain.
		Filters must be antistatic (not claimed as
		antistatic but truly antistatic) and correctly
		earthed to avoid electrostatic discharges that
		could ignite explosible dusts
		High clogging by ultrafine particles
	Abatement of submicron particles of fine dust is	Care has to be taken with explosive hazards
	possible	High maintenance and frequent filter
	Very high abatement efficiency with very low	replacement required
	residual emission	Not suitable for the abatement of wet dust
Absoluto	Outlet air is very clean and can flow within the	Not suitable for high dust loads (except if
filtor	plant	prefiltration is carried out)
inter	Modular structure	Glass fiber medium is not suitable for waste
	Not sensitive to small fluctuations in the waste	gases which contain alkalis
	gas stream	High clogging by ultrafine particles
	Relatively simple operation	
	Usually not sensitive to corrosion problems	
	Can handle gas streams which contain	Significant water usage and generation of
	flammable and explosive dusts with low risk	waste water. The higher the efficiency of
	Reasonable size of the equipment	abatement, the higher the consumption of water
	Can handle both gaseous and particulate	and energy
Wet dust	pollutants	High maintenance costs due to corrosion and
scrubber	Good efficiency of abatement for particles	erosion issues
	below 10 μm	Risk of plugging for treatment of high
	Possibility to collect sticky particles	concentration of particles in the flow
	Provides cooling for hot gases	High pressure drops required for an efficient
	Corrosive gases can be neutralized	treatment

Waste (or by-product if reused or recycled)
collected wet
Protection against freezing required
Collected PM may be contaminated and/or not
recycled
Off-gas may require reheating to avoid visible
plume
It tends to minimize the risk of explosion or
even eliminate the risk of fire and explosion,
unless of course dust is reactive with the liquid
phase such as some metallic dust that may form
hydrogen in the presence of water.
V C P C C C C P It t e u u P