



Katherine Gobey

Investigation of an Atmospheric Pressure Plasma device for
reduction of water use in sustainable cleaning of concentrating solar
power mirrors

School of Aerospace, Transport, and Manufacturing
PhD in Manufacturing

Doctor of Philosophy
Academic Year: 2019 - 2023

Supervisor: Dr Peter King
Associate Supervisor: Professor Chris Sansom
June 2023



School of Aerospace, Transport, and Manufacturing
PhD in Manufacturing

Doctor of Philosophy

Academic Year 2019 - 2023

Katherine Gobey

Investigation of an Atmospheric Pressure Plasma device for
reduction of water use in sustainable cleaning of concentrating solar
power mirrors

Supervisor: Dr Peter King
Associate Supervisor: Professor Chris Sansom
June 2023

© Cranfield University 2023. All rights reserved. No part of this
publication may be reproduced without the written permission of the
copyright owner.

ABSTRACT

Concentrating Solar Power (CSP) is a method of renewable electricity generation that uses large areas of mirrors, that reflect and focus the sun's energy onto a receiver which is then used to heat water to power a conventional steam turbine, generating electricity.

These plants are typically located in areas with consistently high levels of sunlight which are typically arid desert areas where sand and dust is deposited onto the mirrors, reducing their reflectivity and thus the plant's output. Conventional mirror washing consumes huge quantities of water, which is costly and incurs ethical and environmental concerns in areas already experiencing water scarcity.

This work investigates the use of an atmospheric pressure plasma to induce a super-hydrophilic surface on the soiled mirrors which are then able to be cleaned with significantly lower quantities of water. Characterisation of the plasma torch is conducted, and surface energy modification effects investigated with regards to water spreading, evaporation, and travel. For cleaning trials, solar type mirrors were artificially soiled with sand gathered from a CSP plant, then plasma processed before being conventionally washed with water. Mirrors that were subject to soiling were successfully washed, as determined by reflectance measurements, with up to 87.5% less water than mirrors exposed to the same artificial soiling procedure but without plasma processing prior to washing. Plasma processed samples also exhibited self-cleaning properties when subject to condensation trials, mimicking overnight dew formation. There was no observed effect in either reduction or exacerbation of subsequent resoiling of plasma processed samples.

Fundamental processes behind these effects are discussed and the application and implication of the work are considered.

Keywords:

Plasma processing, surface energy modification, hydrophilic, nitrogen plasma, dielectric barrier discharge, heliostats, mirror soiling, renewable energy, solar thermal, anti soiling, self cleaning.

ACKNOWLEDGEMENTS

This work was supported by the UK EPSRC under grant EP/K503241/1 (Centre for Doctoral Training in Ultra Precision Engineering) and EP/L016389/1 (Centre for Doctoral Training in Sustainable Materials and Manufacturing).

Thanks to my supervisors Dr Peter King and Professor Chris Sansom for their guidance over the project and for giving me the opportunity to undertake this PhD.

Thanks to ADTEC Plasma Technology & ADTEC Europe for providing financial and technical support and bespoke plasma equipment. Particular thanks to Mary, Sam, and Konstantinos for their friendly and encouraging support, and Taku for technical support and advice.

Thanks also to Dr Adam Bennett of Cranfield Plasma Solutions for consultancy for the project and enthusiastic help, guidance, and support, professionally and personally, and for introducing me to the CDT Programme. Without him I would never have considered myself capable of a PhD.

Thanks to my internal reviewer Jeff Rao for constrictive feedback and academic guidance over the course of the project, and to Sharon McGuire for administrative help and support.

The practical work completed would not have been possible without the help and guidance of laboratory staff and technicians, especially Alan Heaume and Kane Murrell, who provided invaluable technical support as well as much needed good humour.

Thanks also to all the friends and family who supported me along the way.

This thesis is dedicated to the memory of my grandparents, Joan Skinner and Reg Gobey, who always encouraged and supported me in all aspects of life.

TABLE OF CONTENTS

ABSTRACT	i
ACKNOWLEDGEMENTS.....	iii
LIST OF FIGURES	vii
LIST OF TABLES	xiv
LIST OF EQUATIONS.....	xv
1 Introduction.....	1
2 Literature Review	7
2.1 Introduction	7
2.2 Concentrating Solar Power	8
2.2.1 Parabolic Dish	10
2.2.2 Parabolic Trough	11
2.2.3 Linear Fresnel	13
2.2.4 Solar Tower	14
2.3 Photovoltaic	17
2.4 Mirror Materials	17
2.4.1 Glass	18
2.4.2 Aluminium.....	18
2.4.3 Novel Materials.....	19
2.5 Soiling	19
2.5.1 Composition of Soiling.....	20
2.5.2 Mechanisms of Soiling	21
2.5.3 Effect of Soiling on Mirrors	25
2.5.4 Soiling Prevention	26
2.5.5 Current Cleaning	27
2.5.6 Cleaning Frequency	31
2.5.7 Novel Cleaning	33
2.6 Summary	36
2.7 Plasma.....	37
2.7.1 Plasma Parameters.....	39
2.7.2 Plasma Criteria.....	42
2.8 Plasma Generation	43
2.8.1 Direct Current.....	43
2.8.2 Alternating Current Plasma	48
2.8.3 Beam Plasma.....	52
2.8.4 Shock Wave Generated Plasma	54
2.9 Plasma Tuning.....	55
2.10 Dielectric Barrier Discharge	57
2.10.1 Volume Discharge (VD).....	58
2.10.2 Surface Discharge (SD)	58
2.10.3 Coplanar Discharge (CD)	59

2.10.4 Packed Bed Reactor	59
2.10.5 Plasma Jet.....	60
2.11 Plasma Formation.....	60
2.11.1 Avalanche Phase	61
2.11.2 Streamer Phase	61
2.11.3 Decay Phase.....	61
2.12 Advantages and disadvantages of Dielectric Barrier Discharges.....	63
2.13 Dielectric Barrier Discharge Design Examples.....	64
2.13.1 Treatment of a Surface.....	64
2.13.2 Production of Ozone.....	65
2.13.3 Decontamination of Gas.....	66
2.13.4 Plasma Screen Televisions	67
2.14 Plasma for Cleaning.....	68
2.14.1 Etching	69
2.14.2 Drying.....	69
2.14.3 Electrostatic.....	70
2.14.4 Biological	70
2.15 Plasma Treatment of Glass	70
3 Plasma Torch Summary	73
3.1 Sairem S-Wave.....	73
3.2 Adtec M-CCMD Torches.....	75
3.2.1 M-CCMD 1	75
3.2.2 M-CCMD 2	76
3.2.3 M-CCMD 3	77
3.2.4 Generator	78
3.2.5 Torch Characterisation	80
4 Plasma Characterisation	85
4.1 Plasma Characterisation.....	86
4.1.1 Optical Emission Spectroscopy	86
5 Methodologies	99
5.1 Pre-cleaning.....	100
5.2 Plasma Processing	100
5.3 Surface Energy Modification	102
5.4 Soiling	105
5.5 Reflectance	108
5.6 Water Washing	111
5.7 Condensation Trials.....	115
6 Surface Energy Modification.....	119
6.1 Theory.....	119
6.2 Methodology	119
6.3 Sairem Microwave Trials.....	119
6.4 M-CCMD Trials	123

7 Plasma Only Cleaning	131
7.1 Theory.....	131
7.2 Methodology	132
7.3 Results.....	133
8 Hybrid Cleaning.....	137
8.1 Theory.....	137
8.2 Methodology	138
8.3 Mist Trials	141
8.4 Spray Trials.....	149
8.5 Jet Trials	157
8.6 Complete Cleaning Trials.....	163
9 Anti-Soiling	170
9.1 Theory.....	170
9.2 Methodology	170
9.3 Results.....	172
10 Self-Cleaning.....	175
10.1 Theory.....	175
10.2 Methodology	178
10.3 Results.....	179
11 Discussions and Conclusion.....	184
12 Future Work.....	189
REFERENCES	191

LIST OF FIGURES

Figure 2-1 Flow diagram of typical parabolic trough concentrating solar power plant [10].	7
Figure 2-2 Diagram of Mouchot's solar engine [11].	8
Figure 2-3 Details of John Ericsson's Solar Engine [11].	9
Figure 2-4 a) diagram and b) photograph of parabolic (Stirling) dish solar collector [19].	10
Figure 2-5 a) diagram and b) photograph of parabolic trough solar collector [19].	12
Figure 2-6 a) diagram and b) photograph of linear Fresnel solar collector [19].	14
Figure 2-7 a) diagram and b) photograph of a solar tower plant [19].	15
Figure 2-8 Calculated solar flux of a solar tower receiver. Flux of over 50 kW/m ² is dangerous to animals [20].	16
Figure 2-9 Cross sections of glass based mirror construction, layers are not to scale.	18
Figure 2-10 Cross section of an aluminium mirror construction.	18
Figure 2-11 Dust intensity measured by concentration in µg/m ³ of particles with diameter < 10 µm (PM ₁₀) [40].	21
Figure 2-12 Worldwide map of direct Normal Irradiation (DNI) [42].	21
Figure 2-13 Adhesion forces experienced by soiling particles of different sizes [35].	23
Figure 2-14 Diagram showing forces experienced by a particle of soiling on a flat surface [35].	24
Figure 2-15 Photographs showing soiling of mirrors at IMDEA Energy, Spain (Left), and Green Energy Park, Morocco (Right) [46].	25
Figure 2-16 Typical equipment for manual cleaning of mirrors. Items are labelled by: 1: pressure washer with handheld nozzle, 2: water-fed horsehair bristle brush attachment, 3: steam cleaner, 4: demineralised water tank, 5: detergent tank [3].	28
Figure 2-17 Conventional semi-autonomous cleaning of parabolic trough (left) and flat heliostat (right) mirrors [55].	29
Figure 2-18 Photograph of HECTOR robot undertaking heliostat cleaning at the Gemasolar solar plant in Andalusia, Spain [58].	30
Figure 2-19 Effect of natural cleaning events on specular reflectance of mirrors [60].	31

Figure 2-20 Specular reflectance of mirrors subject to varying durations of cleaning cycles [60].	32
Figure 2-21 Photographs of experimental ultrasonic mirror cleaning device, showing application on (L-R) horizontal, oblique, and vertically oriented mirrors [61].	34
Figure 2-22 Diagram of working principle of an Electro Dynamic Screen incorporated into a solar mirror [63].	35
Figure 2-23 Relationship between T_e and T_g in a plasma at increasing pressure [89].	42
Figure 2-24 Current-Voltage profile of a DV plasma discharge [73].	44
Figure 2-25 Schematic of regions within a DC glow tube (a) and their associated properties (b) [95].	46
Figure 2-26 Diagram of a plasma plume produced during laser ablation of a solid [117].	53
Figure 2-27 Diagram of a volume discharge (VD) configuration [130].	58
Figure 2-28 Diagram of a surface discharge (SD) configuration [130].	59
Figure 2-29 Diagram of a coplanar discharge (CD) configuration [130].	59
Figure 2-30 Diagram of a packed bed reactor configuration [130].	59
Figure 2-31 Plasma jets created via different electrode end dielectric configurations (a) and schematics of coaxial configurations that may facilitate these (b) [130].	60
Figure 2-32 Current (left) and voltage (right) profiles of a microdischarge [135].	62
Figure 2-33 Evolution of a discharge with time [133].	63
Figure 2-34 Diagram of a DBD system designed for plasma treatment of a film [130].	64
Figure 2-35 Cavity surrounded with dielectric for the purpose of ozone generation [146].	65
Figure 2-36 Packed bed DBD for processing of gas [152].	67
Figure 2-37 Mesh electrode DBD for removal of pollutants from a gas, shown in details (left) and in situ as part of the dielectric barrier discharge (right) with direction of gas flow indicated by arrows [153].	67
Figure 2-38 . Schematic of a section of rough design for plasma display, this design features carbon nanotubes (CNT) in the dielectric layer to reduce required sustain voltage [156].	68

Figure 2-39 Molecular structure of sodium silicate glass (above), and the result of plasma exposure on this structure (below) [170].	72
Figure 3-1 Sairem S-Wave torch [173].	73
Figure 3-2 Processing of a mirror sample using the Sairam torch.	74
Figure 3-3 Plasma generation pattern of the M-CCMD 1.	76
Figure 3-4 Processing of a mirror sample using the M-CCMD 1.	76
Figure 3-5 Plasma generation pattern of the M-CCMD 3.	77
Figure 3-6 Processing of a mirror sample using the M-CCMD 3.	78
Figure 3-7 Photograph of generator used for the M-CCMD torches.	79
Figure 3-8 Close up detail of generator display panel.	79
Figure 3-9 XCT image of M-CCMD1.	81
Figure 3-10 Details of stacked electrode structures in the gas channels.	82
Figure 4-1 Experimental setup showing: a, generator; b, mass flow controller; c, plasma generating device (torch); d, motion stage; e, spectrometer.	88
Figure 4-2 Emission spectrum of air plasma using spectrometer USB2H115902.	89
Figure 4-3 Emission spectrum of Nitrogen plasma.	90
Figure 4-4 Emission spectrum of Nitrogen Plasma in the UV-C region.	90
Figure 4-5 Emission spectrum of Oxygen Plasma.	91
Figure 4-6 Emission spectrum of air plasma with relative humidity of 39%.	92
Figure 4-7 Emission spectrum of a nitrogen plasma with a relative humidity of 36%.	92
Figure 4-8 Details of OH peak evident as widening of the 315.9 nm nitrogen triplet.	93
Figure 4-9 Temporal stability of 337 nm peak in plasma generated from clean dry air.	94
Figure 4-10 Detail of initial ramp up of air plasma, where the plasma was ignited at 0.2 minutes.	94
Figure 4-11 Spatial mapping of air plasma at a. 60 L/min 0.9 A, b. 10 L/min 0.9 A, c. 60 L/min 0.2 A, d. 10 L/min 0.2 A.	95
Figure 4-12 Intensities of air plasma at 60 L/min with varied generator current.	96
Figure 4-13 Intensities of air plasma at 0.9 A with varied gas flows.	97

Figure 5-1 Photograph of the M-CCMD 3 torch during processing of a mirror.	101
Figure 5-2 Stock photograph of a Theta Lite optical tensiometer of the same model used in this work [193].	103
Figure 5-3 Optical Tensiometer setup showing components: a, light source; b, water droplet and mirror sample on stage; c, camera; d, computer and software analysis.	103
Figure 5-4 Screenshot of software analysis of a 2 μ L droplet of deionized water on a clean mirror surface prior to plasma processing.	104
Figure 5-5 Example of a 2 μ L droplet of water on a plasma induced superhydrophilic surface, which was not possible to measure with the software.	105
Figure 5-6 Photograph of soiling chamber.	106
Figure 5-7 Photograph of sample mounted inside inner soiling box.	107
Figure 5-8 Schematic of detector apparatus for Condor SR-6.1 reflectometer showing components: 1, mirror; 1', reflecting surface; 1'', glass; 2, LED; 3, detector; 4, reference detector; 5, diaphragm; 6, lens; 7, optic edge [196].	109
Figure 5-9 Measurement rig showing cradle in which the reflectometer sits above mirror placed in recess.	110
Figure 5-10 Diagram showing the locations of 9 reflectance measurement points on each sample, split into three rows. All dimensions are in millimeters.	111
Figure 5-11 Photograph of the washing rig.	112
Figure 5-12 Detail of a mirror sample passing through the washing jet.	112
Figure 5-13 Diagram showing position of water jet across mirror sample relative to the 9 reflectance measurement points.	114
Figure 5-14 Photograph of condensation chamber.	116
Figure 5-15 Photograph of two mirror samples on the condensation block.	117
Figure 6-1 Graph showing the area covered by a 2 μ L droplet of water with relation to its Water Contact Angle.	120
Figure 6-2 A graph showing how the water contact angle of a water droplet influences its area and also the time it takes to dry.	121
Figure 6-3 Graph of the area of a 2 μ L droplet of water and its contact angle, after processing using the M-CCMD 3.	124
Figure 6-4 Graph showing the water contact angle achieved after plasma processing at different speeds.	125

Figure 6-5 Graph showing the daily ageing of the surface after plasma processing.	126
Figure 6-6 Photograph of a water droplet on a mirror surface showing contamination.	127
Figure 6-7 Graph showing ageing of a sample for 18 days after plasma processing.	128
Figure 6-8 Graph showing the water contact angle before (red) and after (blue) reprocessing samples.	129
Figure 7-1 Chart showing plasma only cleaning methodology steps.	133
Figure 7-2 Reflectance of mirror samples subject only to plasma cleaning. ...	134
Figure 8-1 Chart showing hybrid washing methodology steps.	138
Figure 8-2 Diagram showing position of water jet and measurement points. .	139
Figure 8-3 Photographs of one set of samples subject to the same washing procedure after plasma processing (left) or without plasma processing (right) at washing speeds of a = 20 m/min, b = 15 m/min, c = 10 m/min, d = 5 m/min, e = 2.5 m/min.	142
Figure 8-4 Average reflectance values for the samples in mist trials.	143
Figure 8-5 Reflectance values of samples with (red) and without (blue) plasma processing prior to water washing.	144
Figure 8-6 Change in reflectance of samples with (red) and without (blue) plasma processing prior to water washing.	145
Figure 8-7 Image of samples processed at 15 m/min washing speed, showing measurement of washed area width, tracks (♦) and completed tracks (*), the non plasma processed sample on the right has no width and no tracks..	147
Figure 8-8 Average number of tracks on samples with (red) and without (blue) plasma processing.	147
Figure 8-9 Width of mist washed area on samples with and without plasma processing.	148
Figure 8-10 Photographs of one set of samples subject to the spray washing procedure after plasma processing (left) or without plasma processing (right) at washing speeds of a = 20 m/min, b = 15 m/min, c = 10 m/min, d = 5 m/min, e = 2.5 m/min.	150
Figure 8-11 Average reflectance of samples with and without plasma processing.	151
Figure 8-12 Reflectance values of samples with (red) and without (blue) plasma processing prior to spray washing.	152

Figure 8-13 Change in reflectance of mirror samples with(red) and without (blue) prior plasma processing.....	153
Figure 8-14 Number of started and completed tracks on washed mirror samples.	154
Figure 8-15 Width of spray washed area on samples with and without plasma processing.	155
Figure 8-16 Reflectance values of rows A, B, and C (blue) and the average value for each (red) for the 2.5 m/min washing speed spray trial set.	156
Figure 8-17 Photographs of one set of samples subject to the jet washing procedure after plasma processing (left) or without plasma processing (right) at washing speeds of a = 20 m/min, b = 15 m/min, c = 10 m/min, d = 5 m/min, e = 2.5 m/min.....	158
Figure 8-18 Average reflectance of samples with and without plasma processing.	159
Figure 8-19 Reflectance values of samples with (red) and without (blue) plasma processing prior to jet washing.	160
Figure 8-20 Change in reflectance of mirror samples with(red) and without (blue) prior plasma processing.....	161
Figure 8-21 Number of started and completed tracks on jet washed mirror samples.	162
Figure 8-22 Width of jet washed area on samples with and without plasma processing.	163
Figure 8-23 Reflectance values of plasma processed samples in complete cleaning trials.....	165
Figure 8-24 Reflectance values of non-plasma processed samples in complete cleaning trials.....	166
Figure 8-25 Average reflectance of samples in complete cleaning trials against the equivalent Water Consumption Rate.	168
Figure 9-1 Chart showing anti-soiling methodology steps.	171
Figure 9-2 Average reflectance of samples with and without plasma processing prior to washing.	172
Figure 9-3 Average reflectance of samples with (red) and without (blue) plasma processing prior to washing.	174
Figure 10-1 Flow chart showing self cleaning trial methodologies.....	178
Figure 10-2 Mirror samples that have (left) and have not (right) been plasma processed, after being in the condensation chamber for 30 minutes.....	179

Figure 10-3 Mirror samples that have (left) and have not (right) been plasma processed, after being in the condensation chamber for 60 minutes.....	180
Figure 10-4 Mirror samples that have (left) and have not (right) been plasma processed, after being in the condensation chamber for 90 minutes then allowed to dry completely.	181
Figure 10-5 Reflectance values of plasma processed (red) and unprocessed (blue) samples after self-cleaning.....	182
Figure 10-6 Reflectance values of plasma processed (red) and unprocessed (blue) samples throughout the self-cleaning testing procedure.	183

LIST OF TABLES

Table 2-1 Summary of current and novel mirror washing technologies.	37
Table 8-1 Hybrid washing trial water flow parameter grouping.	139
Table 8-2 Water Consumption Rate of mist washing trials.	141
Table 8-3 Average reflectance (%) of samples with and without plasma processing prior to mist washing. Cells shaded in green indicate areas considered “clean” by the criterion of above 90% reflectance.	146
Table 8-4 Water consumption rates of spray washing trials.	149
Table 8-5 Average reflectance (%) of samples with and without plasma processing prior to spray washing. Cells shaded in green indicate areas considered “clean” by the criterion of above 90% reflectance.	151
Table 8-6 Table showing equivalent water consumption rates of jet washing trials.	157
Table 8-7 Average reflectance (%) of samples with and without plasma processing prior to jet washing. Cells shaded in green indicate areas considered “clean” by the criterion of above 90% reflectance.	159
Table 8-8 Water consumption rates for complete cleaning trials.	164
Table 8-9 Average reflectance (%) of samples with and without plasma processing prior to complete washing. Cells shaded in green and blue indicate average reflectance values of higher than 90% and 93% respectively.....	167
Table 8-10 Speed and water consumption of washing to meet cleanliness criteria.	168
Table 9-1 Average reflectance (%) of samples with and without plasma processing prior to washing.	173
Table 10-1 Average reflectance of samples after self-cleaning trials.	181

LIST OF EQUATIONS

(2-1).....	42
(2-2).....	42
(2-3).....	43
(2-4).....	51
(2-5).....	54
(2-6).....	54
(2-7).....	55
(2-8).....	55
(2-9).....	56
(2-10).....	56
(2-11).....	56
(2-12).....	56
(2-13).....	56
(2-14).....	56
(2-15).....	57
(2-16).....	66
(2-17).....	66
(2-18).....	66
(4-1).....	90
(5-1).....	102
(5-2).....	102
(5-3).....	113
(5-4).....	113
(5-5).....	113
(5-6).....	113
(5-7).....	113
(6-1).....	121
(6-2).....	121

(8-1).....	140
(8-2).....	140
(8-3).....	140
(10-1).....	176
(10-2).....	176
(10-3).....	176
(10-4).....	176
(10-5).....	176
(10-6).....	177
(10-7).....	177
(10-8).....	177
(10-9).....	177

1 Introduction

Fossil fuels have played a significant part in human history, powering the world through the industrial revolution and remaining a major source of energy today, with coal alone providing 27% of the total global energy production in 2022 [1], however there is an increasingly urgent impetus to move away from polluting and non-renewable energy sources. Climate change, environmental degradation due to mining and drilling, and pollution from combustion are all significant issues caused or exacerbated by fossil fuel use, and as such most of the world is actively working towards reducing their use. However, electricity demand continues to rise as more of the world's population becomes developed, requiring electricity to power their homes, gadgets, and increasingly, cars. In 2010 the global electricity demand was 18,548 TWh and in 2021 this rose to 24,700, with it predicted to rise further under all models studied by the International Energy Agency for their 2022 World Energy Outlook report [1], potentially with energy demand set to grow another 25% by 2040 [2].

To make up for the gap, renewable electricity sources are increasing their share of the energy generation market, in 2021 renewable sources provided 28% of the worldwide electricity demand, up from 20% the previous year and projected to reach 43% in 2030 [1]. Wind and solar take most of this sector, and solar photovoltaic is predicted be the largest contributor of electricity from the 2030s [1], however all renewable energy generation methods have their own advantages and limitations and so no single source can be a solution alone.

Solar power is one such source that can contribute to the electricity generation mix, and is split into two main categories: photovoltaic (PV) and concentrating solar power (CSP).

Concentrating solar power, as the name suggests, uses mirrors to focus and concentrate the sun's energy onto a receiving medium which then acquires significant heat, hence CSP's alternative designation of Concentrating Solar Thermal. The heat can then be used directly, in industrial or domestic heating applications, or used to boil water and generate steam to power a steam turbine,

generating electricity in much the same way as in a fossil fuel power station, but without the harmful emissions or combustion of a finite resource.

CSP is a relatively under-developed resource however is undergoing considerable growth in its contribution to global energy supply, rising from only 2 TWh in 2010 to 15 TWh in 2021, with this growth predicted to continue up to 329 TWh in 2050 [1].

In order to be adequately efficient, these plants must be located in areas of consistently high levels of sunlight, typically with a minimum Direct Normal Irradiance (DNI) between 1700 and 2000 kWh/m² per year [3]. For context, the UK receives between 400 kWh/m² in the north and up to 1100 kWh/m² in the south each year, compared with Morocco which receives between 1800 and 2500 kWh/m² a year [4]. Locations that meet this criterion generally do so because they are arid regions with little cloud cover and therefore rainfall, and as such the ground is dry and dusty. For example, in 2020 the top five producers of CSP were Spain, the United States, China, Morocco, and South Africa [5], with China in particular installing significant CSP capacity, and is rapidly developing its energy base centre in the Gobi desert region [6]. The dust prevalent in these CSP locations can become airborne and settle on the mirrors in a process of soiling, which reduces the mirrors' reflectance and therefore the energy transferred into the heat medium, and ultimately reduces plant output. Mitigation strategies against this generally consume vast quantities of water during washing of the mirrors, which whilst an effective technique in removing soiling from the mirrors, can be costly and is itself not environmentally sustainable as water scarcity becomes increasingly problematic. Typical water consumption for CSP mirror cleaning is around 20 – 40 gallons/MWh (75-152 L/MWh) [7], and so as more electricity is demanded and generated, more water is required also. Considering the case of the Crescent Dunes solar plant in Nevada, US, which generated 100,666 MWh in 2022, this could result in a demand 7.5 – 15.3 million Litres a year for one plant alone. Access to water is already a concern, with some estimates predicting 1 billion people will be in absolute water scarcity by 2025, mostly in areas of north Africa, China, and India [8], all areas with high solar

capability. Indeed, the lack of a reliable water supply in such areas has been known as a significant constraint on the growth of CSP [9].

Therefore, reducing the water consumption of such CSP plants increases their feasibility as a significant contributor to renewable electricity generation, with the environmental and socio-economic benefits that come with this.

This thesis will discuss in detail the background of the issues highlighted here, the current state of research, and the potential application of a novel plasma device to reduce the water consumption of CSP plants.

First is presented a review of literature for the topics covered, including concentrating solar power and plasma technology, both generally and the specific technologies studied in this work. The state of the current mitigation strategies and water reduction research is discussed, and from here a solution proposed.

Work conducted as part of this thesis is then discussed, starting with characterisation of a plasma torch, including x-ray computed tomography (XCT) and extensive optical emission spectroscopy (OES) which together help explain how the torch works to generate plasma, and the nature of that plasma produced.

Methodologies of the work conducted are then presented, followed by results and discussion of these. Discussion of the surface energy modification effect of the plasma is presented alongside the implications of this with regards to solar mirror soiling and washing. The mirror washing work is split into three primary sections: plasma only cleaning, hybrid plasma cleaning, and self-cleaning. In each of these sections the specific methodology is recalled, the results presented and discussed along with their implications and applications to concentrating solar power washing and water use.

An overall discussion of the research presented is then made, as well as suggestions of the potential future investigations that could build upon the results and understanding developed during this work.

The contribution to knowledge of this work is in the application of atmospheric pressure plasma to modify the surface of solar mirrors, with the view to reduce water consumption of conventional cleaning processes. Such application of plasma has not been attempted before, and therefore the effects of such application were not previously known.

With the above in mind, the project was undertaken with the following overall aim:

Aim:

Investigate an atmospheric pressure plasma system that can be used in situ to reduce water consumed during cleaning of Concentrating Solar Power mirrors.

This is split further into the following objectives:

Objectives:

- Investigate the temporal and spatial stability of the produced plasmas.
- Determine if plasma can be used to remove soiling from CSP mirror segments.
- Determine if plasma can modify surface energy of CSP mirror segments.
 - And what effect this has on washing efficiency, anti-soiling, and water use
- Understand the fundamental processes behind observed cleaning and water behaviour effects.

Investigation of the stability of the plasma is necessary to ensure any processing is predictable, homogenous, and repeatable, which are vital to industrial and commercial processes.

Determination of whether the plasma alone can be used for mirror cleaning was the next objective as this would mean a 100% reduction in water consumption, therefore would have been the most ideal solution.

In conjunction with this objective, determination of the surface energy modification effects of the plasma on the mirrors was carried out to investigate the effect this would have on water applied to the mirrors, which was utilised in the hybrid cleaning trials.

Understanding the fundamental processes behind the observed effects is important to fully comprehend the causes and implications of the effects, and how these may be optimised.

Data generated in this work has shown that a dielectric barrier discharge generated plasma can successfully and significantly modify the surface energy of solar type glass. Importantly, this work has also shown the effects this surface energy modification has on the behaviour of water subsequently applied to the mirror surface, and how this behaviour change results in more efficient washing of the mirrors. From a water saving perspective, plasma processed samples required less water to reach a satisfactory level of cleanliness than those that had not been plasma processed, as determined by mirror reflectance measurements.

The implications of this on future soiling adhesion and also potential self-cleaning effects is also investigated and discussed.

2 Literature Review

2.1 Introduction

Concentrated solar power (CSP), is a method of renewable energy generation whereby the sun's energy is concentrated using reflective surfaces to a focal point at which the energy can more easily be converted to electricity, either directly using Stirling engines at each focal point, or more commonly using a heat transfer fluid (HTF) such as a molten salt or high temperature oil which is then transported away from the mirrors to heat water to power a steam generator much like in traditional energy generation. Figure 2-1 shows a flow diagram of a typical 30 MW plant which utilises a field of parabolic trough solar collectors to heat a heat transfer fluid which then travels through a heat exchanger to provide super heated steam to a turbine which in turn is connected to the electricity grid.

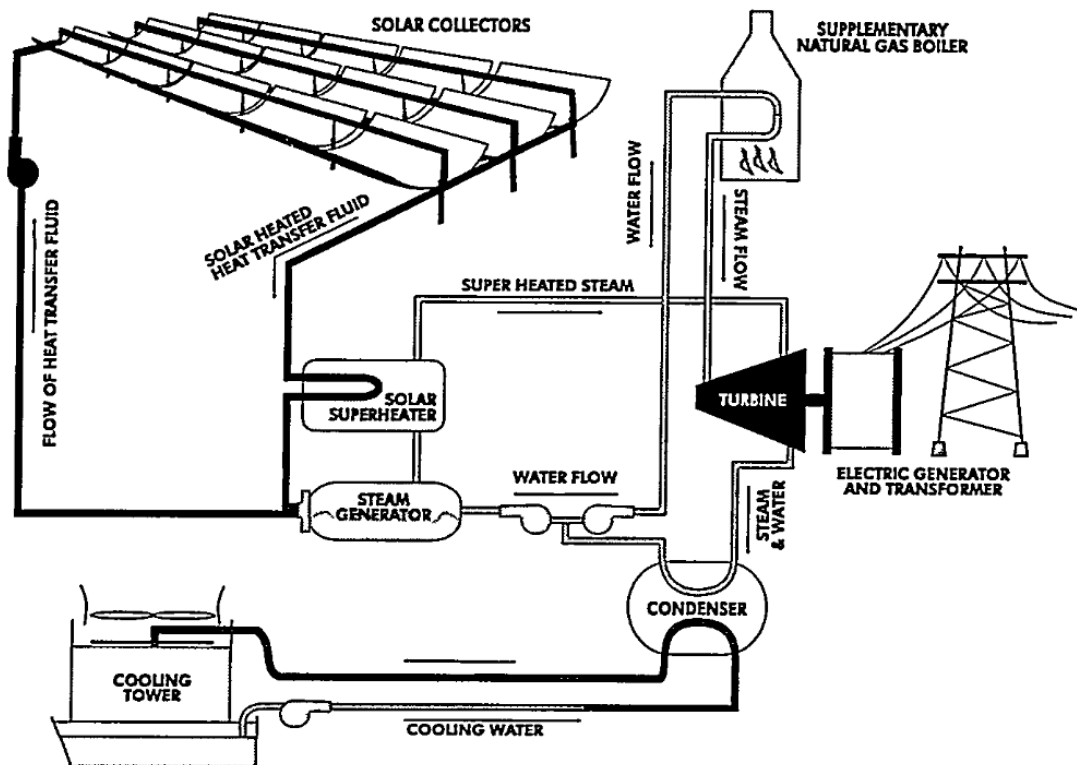


Figure 2-1 Flow diagram of typical parabolic trough concentrating solar power plant [10].

2.2 Concentrating Solar Power

CSP is a relatively new technology in the renewable energy field, with the first recorded experiments into converting solar energy into mechanical energy occurring in the late 19th century when in 1865 Augustin Mouchot developed a solar collector shown in Figure 2-2, which used mirrors arranged in a cone around a central cavity in which water was heated to generate steam which was then diverted to power a steam engine [11].

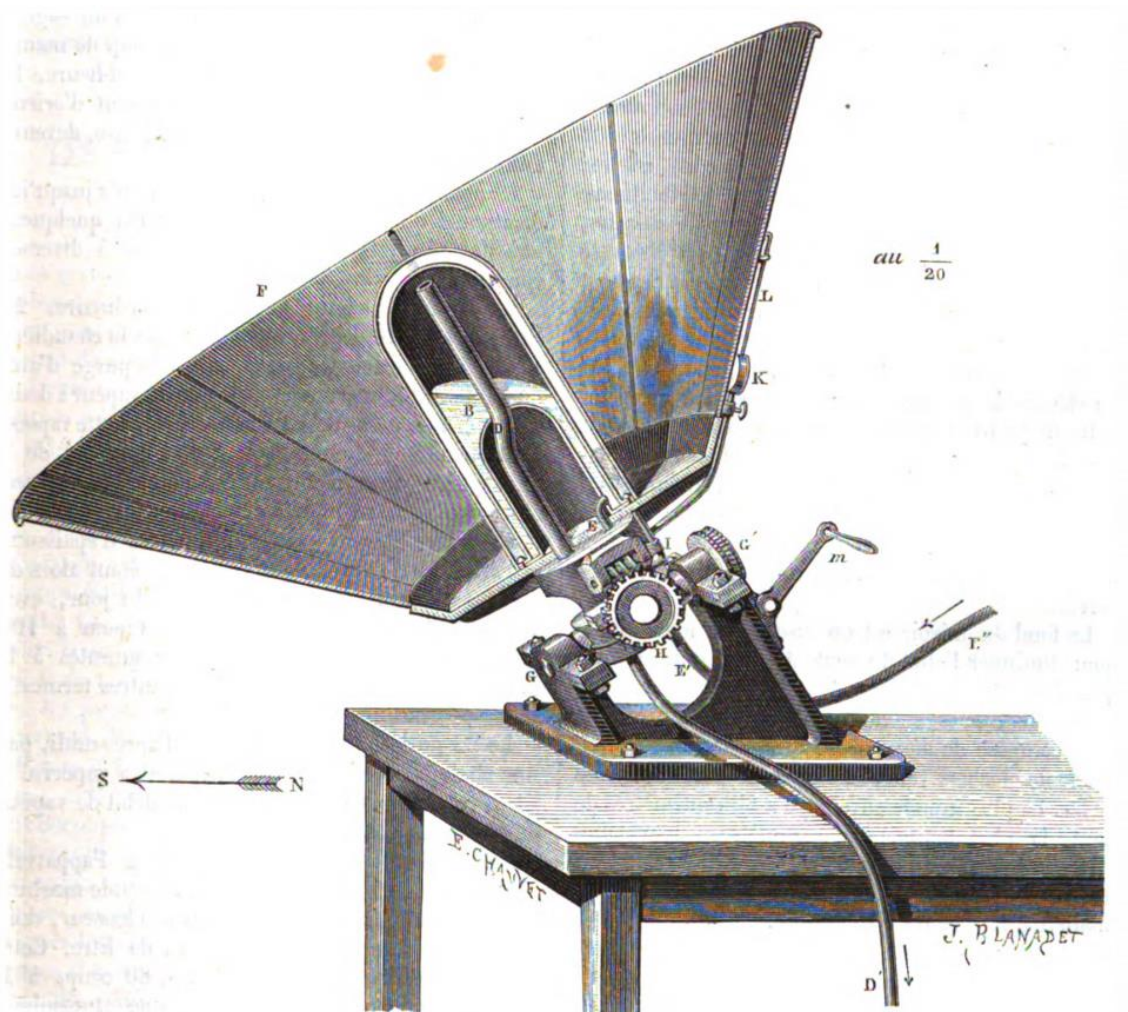


Fig. 4. — Générateur solaire de M. Mouchot.

Figure 2-2 Diagram of Mouchot's solar engine [11].

At around the same time, John Ericsson also developed a solar engine, this time of the parabolic trough type shown in Figure 2-3, which used an evacuated glass

tube to focus the sun's energy onto water, creating steam that directly entered a steam turbine, producing 240 rpm under optimal conditions [12].

CSP research and development was then largely neglected until the 1970s when the global oil crisis spurred interest in alternative energy sources, and investigations into large scale concentrated solar energy began, becoming commercially available in the 1980s [13].

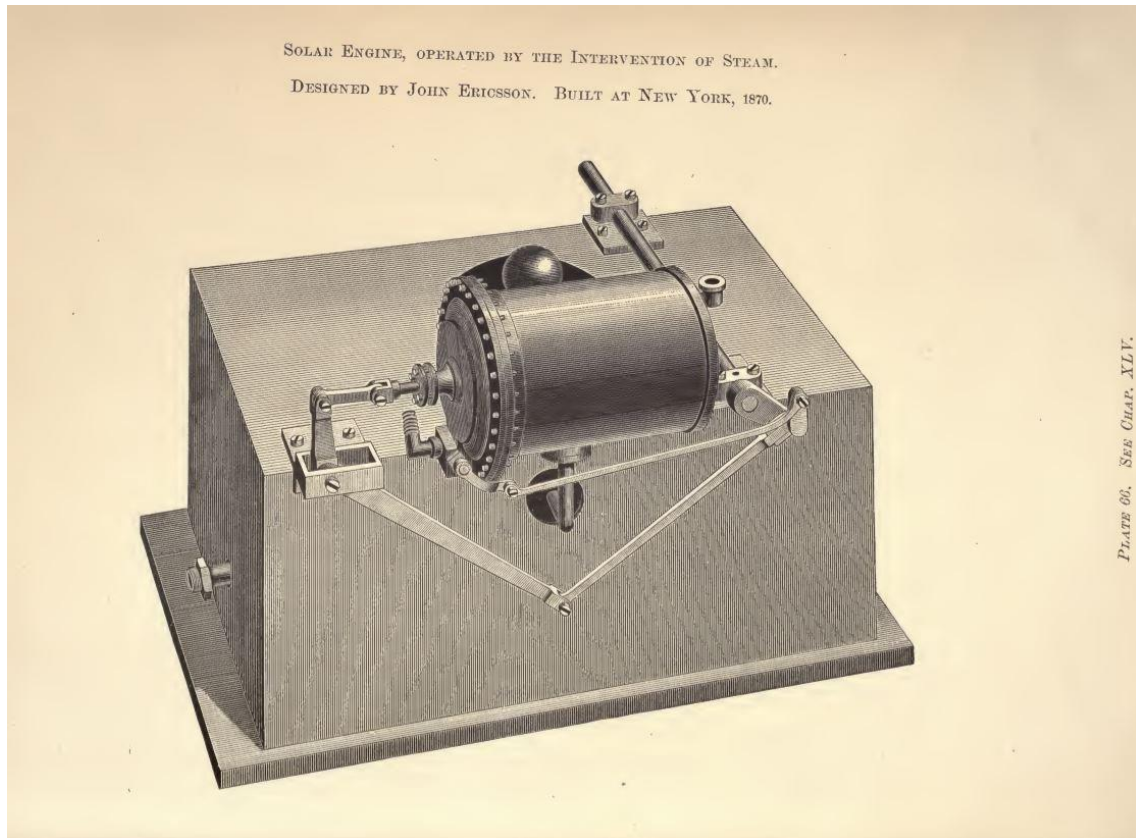


Figure 2-3 Details of John Ericsson's Solar Engine [11].

CSP is still lagging globally, and produced less than one percent of the world's electricity in 2015 [14], however costs are already reducing dramatically. In the decade between 2006 and 2017, bids for CSP generated energy dropped by two thirds from 31 pence per kilowatt hour kWh from the world's first commercial CSP plant in Spain, to 9.4 pence kWh [15]. In the following six months the price dropped by another half to 5 pence per kWh. Such drastic drops in price put CSP costs on par with more conventional forms of energy generation and prove highly promising for increased production of CSP plants.

There are numerous forms of CSP electricity generation, with primary differences being in the method used to focus the solar energy towards a central point or points.

2.2.1 Parabolic Dish

Also known as the Stirling Dish, the parabolic dish is the most efficient of CSP types, and can achieve efficiencies of around 23%- 29% [16], however initial costs are far higher than for other installation types, often as much as two or three times, and operational costs remain higher than for its competitors [17], and as such only 0.1% of CSP generated electricity is provided by dish type installations [18].

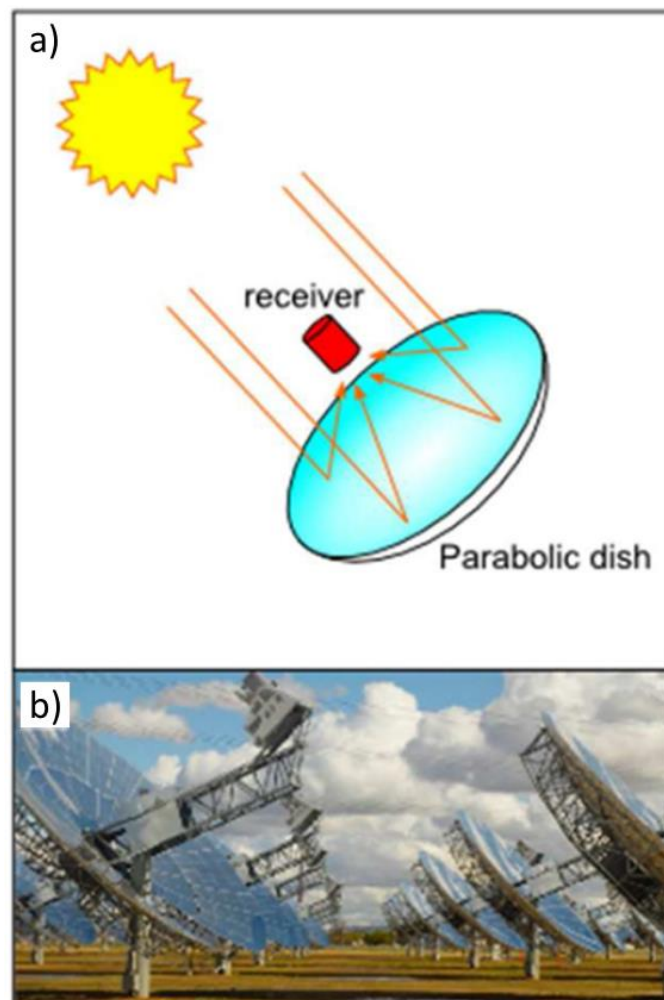


Figure 2-4 a) diagram and b) photograph of parabolic (Stirling) dish solar collector [19].

As shown in Figure 2-4, the parabolic dish differs to other methods of CSP generation in that rather than use the sun's energy to heat a medium to power a steam turbine, most parabolic dish installations utilise individual Stirling engines at the focal point of each dish. This in part is responsible for higher capital costs and increases the maintenance costs owing to increased risk of failure at each Stirling engine. The use of direct energy transfer from the incoming radiation to the Stirling engine also means there is no energy storage, which exists to some extent with installations using a heat transfer medium.

An advantage of parabolic dish installations however is that they are able to be deployed on a much smaller scale than the other methods, as each dish is a standalone electricity generation plant, not requiring any of the ancillary network components seen for the trough collector plant in Figure 2-1 such as insulated pipes to transfer heat transfer fluid to a central turbine, nor the central turbine itself.

2.2.2 Parabolic Trough

The parabolic trough setup inhabits the largest share of CSP electricity generation with 96.3% of total annual production [18]. Curved troughs focus the sun's energy onto a central receiver tube that is filled with the heat transfer fluid, shown in Figure 2-5. The fluid is then directed to a steam turbine electricity generator.

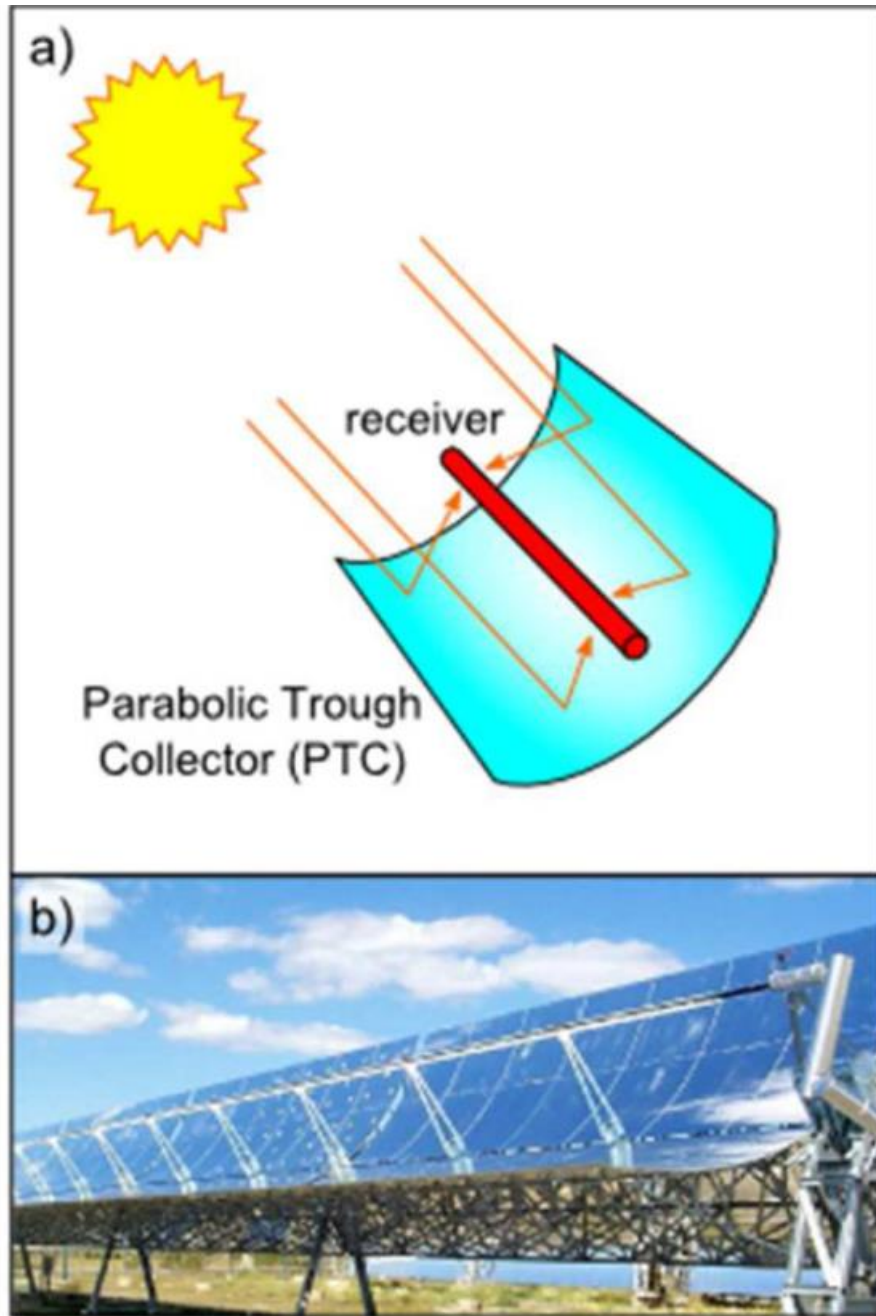


Figure 2-5 a) diagram and b) photograph of parabolic trough solar collector [19].

Parabolic trough systems exhibit moderate efficiencies of around 15% and lower cost capitals and maintenance costs than other systems [17], which is in part responsible for its prevalence. The troughs are usually mounted on motors that allow the mirrors to track the sun's path through the sky, resulting in higher efficiencies than stationary mirrors.

2.2.3 Linear Fresnel

Similar to the parabolic trough system, the linear Fresnel reflector (LFR) uses mirrors in long thin strips, seen in Figure 2-6, that reflect and concentrate light onto a central receiver or in some cases multiple receivers. The name comes from Augustin-Jean Fresnel, a French physicist who designed lenses for lighthouse beacons that allowed for significant reduction in weight and volume compared to traditional lenses. The same benefits apply when used for CSP generation. LFR plants have low capital and maintenance costs but also has lower efficiencies of around 10% [17]. They are also more inefficient to wash as there is not one continuous mirror surface, instead cleaning needs to be focussed on the mirror strips, or a blanket cleaning of the area undertaken, resulting in considerable wasted water that does not make contact with any mirrors, instead falling through the gaps. They produce only 0.5% of the world's annual CSP generation [18].

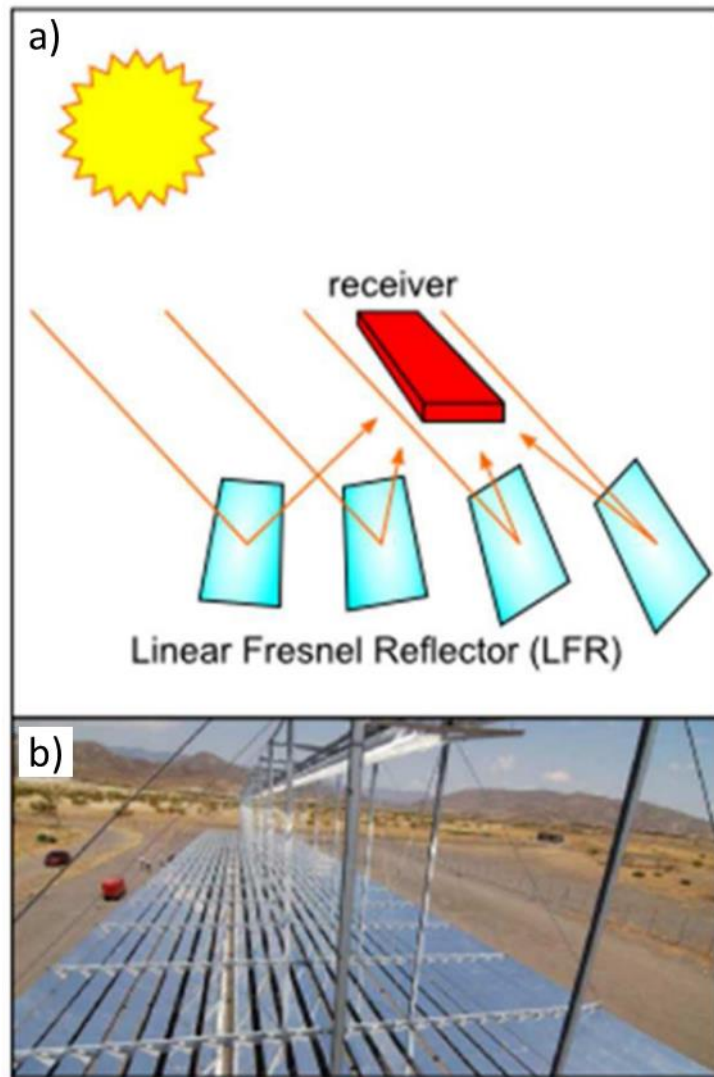


Figure 2-6 a) diagram and b) photograph of linear Fresnel solar collector [19].

2.2.4 Solar Tower

Unlike the other systems, in power tower configurations the mirrors (heliostats) and receiving unit are completely separate. A circular array of heliostats focus sunlight onto a central receiver atop a tower, seen in Figure 2-7. It is in the tower where the energy is transferred to a HTF which goes off to produce steam to power a turbine in a similar fashion to the Linear Fresnel and Parabolic Trough systems. As with linear and trough systems, the mirrors are usually mounted on motors to track the sun, to increase efficiencies. Solar Tower plants are generally

very large, with thousands of individual mirrors, the largest of which currently in operation is the Ivanpah plant in California, which has a total of 173,500 heliostats spread over one field of 53,500 and two fields of 60,000, each field focused onto one of three receiving towers 137 m tall. Each heliostat is 15m^2 , resulting in a total area of $2,602,500\text{ m}^2$.

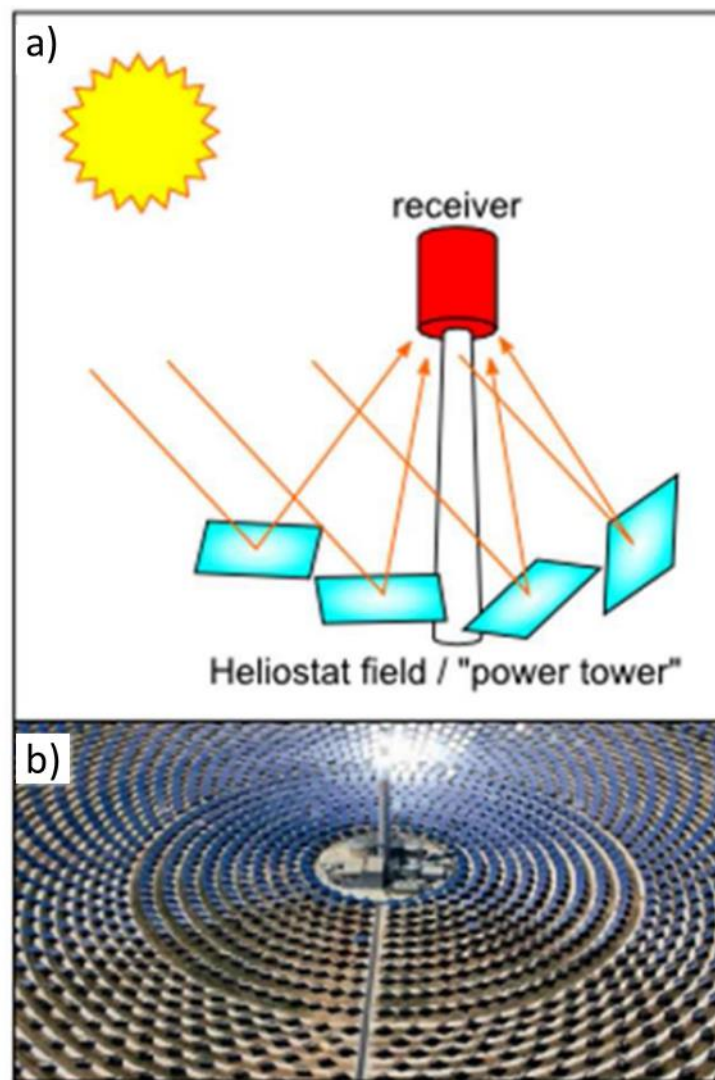


Figure 2-7 a) diagram and b) photograph of a solar tower plant [19].

As solar tower plants focus all the light onto one area, the energy incident on this relatively small area is very high, shown in Figure 2-8, and as such has additional safety and environmental risks not seen in other plant types.

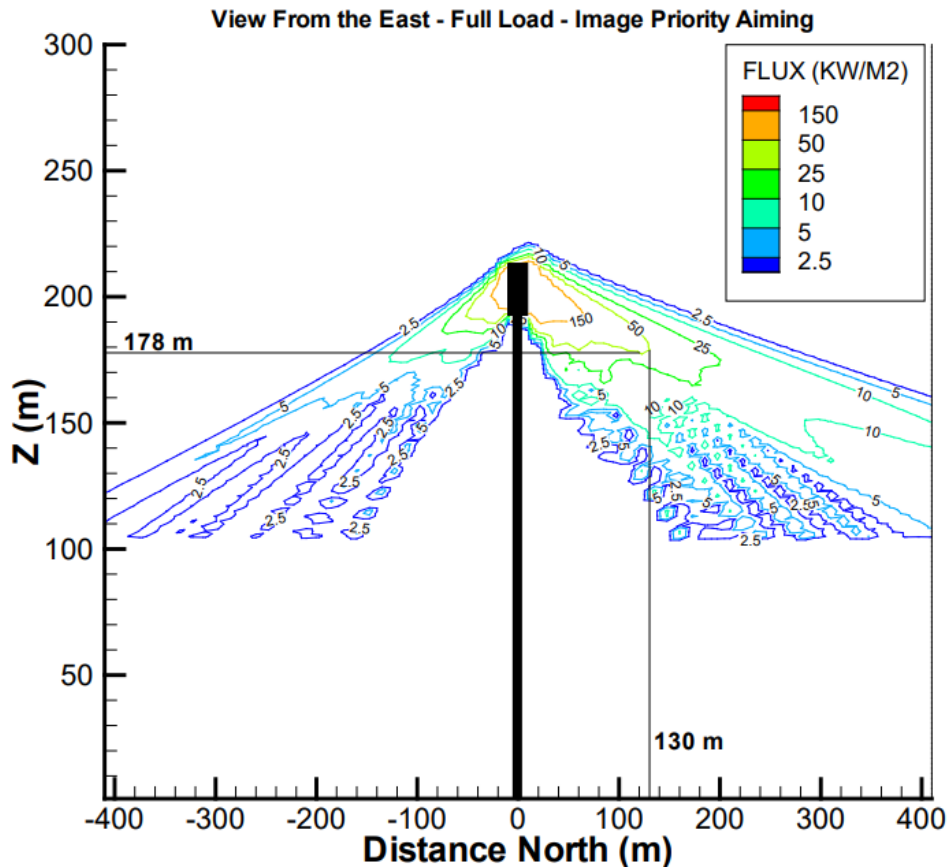


Figure 2-8 Calculated solar flux of a solar tower receiver. Flux of over 50 kW/m² is dangerous to animals [20].

For example, in May 2016 the aforementioned Ivanpah facility suffered a fire to one of the receiving towers when mirrors were mistakenly aligned onto a tower that was offline for maintenance.

Environmental concerns have also been raised with regards to birds and bats flying into the path of concentrated light, resulting in their burning and usually death. Mitigation strategies such as ensuring the mirrors are not aligned to a central point in the air during maintenance can reduce these risks, such that a CSP plant presents no significant increase danger than any other large structure [21].

Solar tower holds only a 3% share of total CSP generated power [18],

2.3 Photovoltaic

Photovoltaic (PV) solar systems are not the subject of this thesis and as such will not be discussed in detail, however they do share some characteristics and problems with CSP and therefore it is beneficial to have a degree of knowledge as to their operation. Also, as PV panels are also subject to soiling, plasma processing may also be beneficial in this application.

The principle of operation of PV is entirely different to that of CSP, it is a much more direct harvesting of electricity via the photovoltaic effect that occurs when a photon strikes an electron imparting energy upon it such that it become excited and raises from a valence band to a conduction band, creating an electron-hole pair. This electron hole is filled by an electron from a neighbouring atom, which itself creates an electron hole that is in turn filled by a neighbouring atom's electron, continuing as the hole ripples through the medium [22]. This creates a direct current (DC) throughout the cell generating a potential difference of a few volts, with large arrays of cells generating significant quantities of electricity. In the UK a domestic rooftop installation may generate up to 4 kW [23], whereas commercial PV plants have generating capacities of over 70 MW [24].

Unlike CSP, PV can operate under fairly low direct normal irradiation (DNI), and as such can be deployed really anywhere there is a moderate amount of sunlight. Consequently, although soiling of PV can be an issue just as in CSP [25], they are often situated in regions where there is lower levels of airborne dust and adequate rainfall such that active cleaning it not necessary.

2.4 Mirror Materials

The physical composition of mirrors varies, however all materials consist of a reflective layer, often silver

There are two dominant mirror materials used in CSP: glass and aluminium, in addition to novel materials in various stages of development and deployment.

2.4.1 Glass

Much of CSP power generation relies on standard back-silvered low-iron float glass as the mirror material of thicknesses between 1 mm and 5 mm, with thinner layers held usually on a supportive plastic backing. Glass is advantageous as it has a relatively low initial cost, it is widely available from multiple suppliers, it has proven durability of up to 25 years and, when properly maintained, retains high reflectivity throughout its life [26].

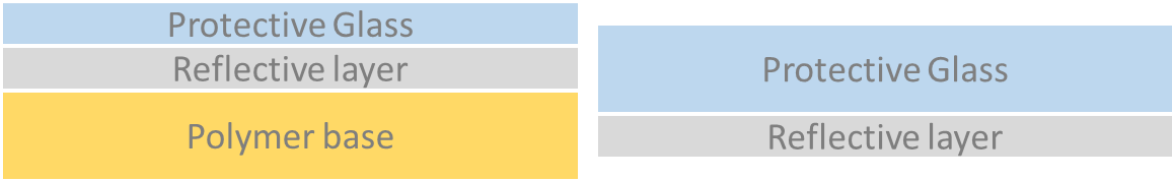


Figure 2-9 Cross sections of glass based mirror construction, layers are not to scale.

The drawback of glass is primarily its weight, it necessitates large rigid structures to hold and support the mirrors, and sagging and physical distortion of the mirrors can impact each mirror's focus and can result in unnecessary energy losses [27][28]. The fragility of glass also increases the risk of mirror breakage, increasing maintenance costs. To mitigate these, the glass layer can be minimised and a polymer base added to add sturdiness, as shown in Figure 2-9.

2.4.2 Aluminium

Front surface aluminised mirrors typically consist of a polished aluminium substrate with an enhanced reflective layer, oxidation of which occurs to produce a protective layer of Al_2O_3 [29], as seen in Figure 2-10.

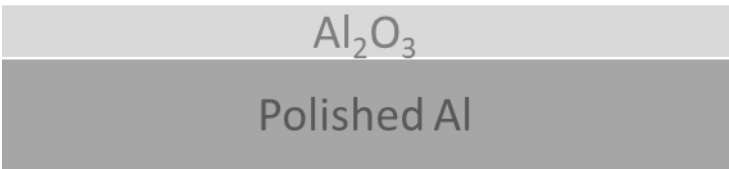


Figure 2-10 Cross section of an aluminium mirror construction.

Aluminium can have lower initial costs than glass and is more lightweight and easier to handle, however it is more susceptible to erosion than glass resulting in an irreversible long term reduction in reflectivity [30]. To protect against this the mirror may be coated with a transparent protective polymer later, however this too is subject to degradation and will also require periodic replacement.

2.4.3 Novel Materials

An emerging material for CSP mirrors are polymers such as polymethylmethacrylate (PMMA) or polyethylene terephthalate (PET) onto which a thin layer of silver is applied to produce a reflective surface [31]. Polymers have the advantage of being thin, lightweight, and flexible, however they must be carefully selected to ensure they are resilient to UV exposure and harsh desert environments. There have also been reported issues with delamination of the reflective silver layer from the polymer substrate. As a relatively new technology, quality and suitability of polymer mirrors varies wildly and it is not widely employed in commercial CSP generation.

2.5 Soiling

A problem for all solar electricity systems is the accumulation of dust and other contaminants on the mirror surfaces, thus reducing reflectance and in turn power generation. Mitigation of soiling requires active plant maintenance and can be a significant financial liability, as not only does the cost of water have to be considered, but also that of equipment and labour that is needed for the cleaning process. As such research into its prevention and alleviation is extensive and ongoing [32], with initiatives such as WASCOP (WATER Saving for CONcentrating solar Power, spearheaded by The French Alternative Energies and Atomic Energy Commission and funded by the European Union's Horizon 2020 research and innovation programme. This programme gave almost \$5million for research towards the reduction of water use in CSP plants, working with institutions from academia, government, and the commercial sector [33].

2.5.1 Composition of Soiling

Soiling is a broad term that refers to any kind of unwanted particles on the mirror surfaces, the origin of which can include combinations of biological, agricultural, geological, industrial, and meteorological. Composition can also vary greatly depending on location, and within each location there can be variations in soiling depending on weather, mirror orientation, and season. A frequent categorisation of soiling is by particle size, in which soiling can be grouped in three distinct categories depending on their diameter: clay, below 2 μm ; silt, between 2 μm and 63 μm ; and sand above 63 μm [34]. Particles are considered an issue when they are in the clay and silt regions as larger than this they are generally too heavy to be carried by winds and thus do not have the opportunity to settle on solar collectors except during considerable desert storms [35]. An analysis of over 60 samples collected worldwide found the primary component of dust in arid regions is SiO_2 (quartz) and CaCO_3 (calcite) [36], however this can vary greatly, for example plants situated near major highways may experience soiling containing rubber from vehicle tyres [37] whereas those located near agricultural activities may be subject to crop or feed dust [38]. Biological matter such as pollen, lichen, or fungi can also be present soiling issues in less arid areas [39]. Whilst the soiling can vary enormously not only within regions but even within the same plant, there are regions of the world in which climate and environment result in higher airborne particles and consequently higher rates of soiling [40]. Figure 2-11 shows a map of the world split into zones depending on the average airborne concentration of PM_{10} , particles that are fewer than 10 μm in diameter and large constituent of soiling. This can be compared to Figure 2-12 which shows a world map in terms of Direct Normal Irradiance (DNI), a measure of the sunlight (power per unit area, W/m^2) that is frequently used when considering suitable locations for new CSP plants [41]. It can be seen that areas with a high DNI and thus most desirable for concentrating solar power are also often areas with high PM_{10} concentration, demonstrating the largely unavoidable and inherent nature of soiling of mirror surfaces in CSP plants.

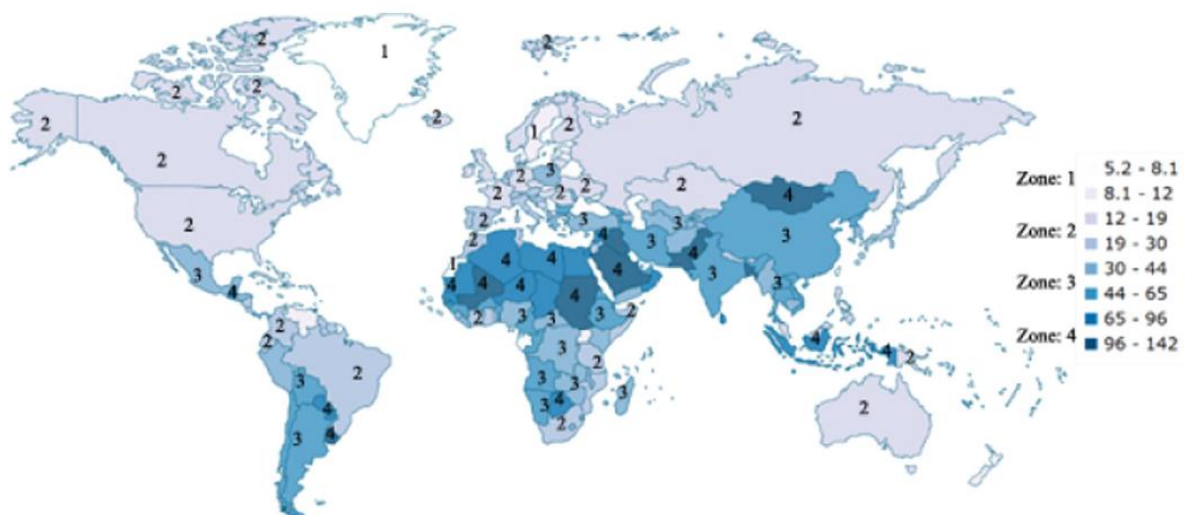


Figure 2-11 Dust intensity measured by concentration in $\mu\text{g}/\text{m}^3$ of particles with diameter $< 10 \mu\text{m}$ (PM₁₀) [40].

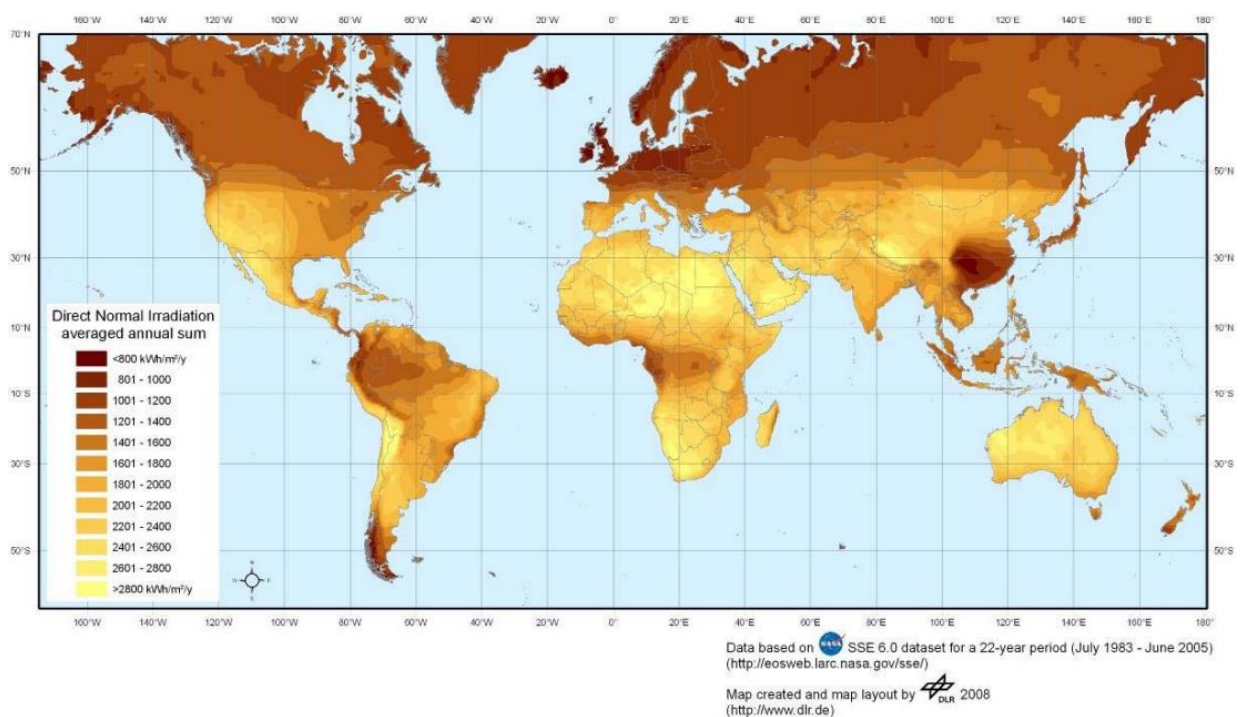


Figure 2-12 Worldwide map of direct Normal Irradiation (DNI) [42].

2.5.2 Mechanisms of Soiling

When a particle strikes a surface, known as deposition, it may immediately be deflected without becoming adhered via a process known as rebound.

Alternatively, it can become attached to the surface but removed later by the wind, known as resuspension. The net result of these processes is known as accumulation and represents particles of soiling that remain attached to the surface until active removal with cleaning [43]. Deposition of particles can be further classified by the method of contact with the surface, which can occur through Brownian motion, sedimentation, or inertial deposition. Brownian motion is applicable to only the smallest of particles of less than 1 μm diameter, where their random diffuse motion may lead them into contact with the mirror surface. Sedimentation is settlement of particles due to gravity and occurs mostly with regards to the much larger particles above 100 μm . Inertial deposition is responsible for soiling of mid-sized particles of the order of $\sim 10 \mu\text{m}$ and is a result of a rapid change in air flow such as around an object which causes particles to deviate from the stream and deposit upon it, although at low wind speeds mid-sized particles also experience sedimentation [43].

Once deposition of a particle has occurred it can be held on the surface via a complex combination of adhesion forces, the main three of which are van der Waals, capillary, and electrostatic [34].

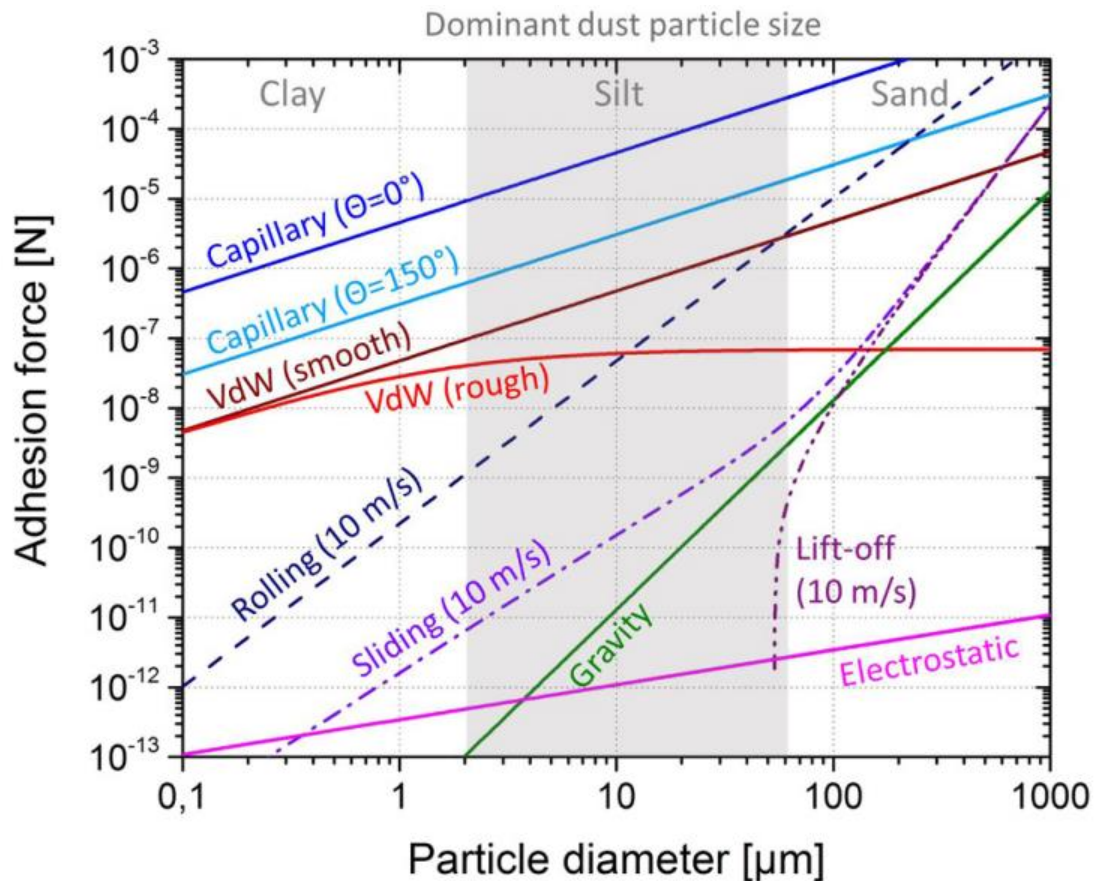


Figure 2-13 Adhesion forces experienced by soiling particles of different sizes [35].

Van der Waals forces are an electromagnetic radiation between the surface of two dipoles, either fixed or induced, and are most prominent for smaller particles ($< 10 \mu\text{m}$). Capillary forces occur at larger separation distances when two wet bodies are in contact via the condensation of humidity existing in the local atmospheric environment. They are most prominent at a relative humidity of 40-60 % and when present are the dominant adhesion force in soiling [34]. Electrostatic forces occur as a result of electromagnetic attraction of charged particles to the mirror surface.

Figure 2-13 displays these forces in relation to the particle sizes, and further differentiates forces of Van der Waals into those on a smooth and rough surface,

and the capillary forces for hydrophilic ($\theta = 0^\circ$) and hydrophobic ($\theta = 150^\circ$) surfaces. The dotted lines denoted rolling, sliding, and lifting, show the minimum net force required to overcome the adhesion force and move the soiling particle on the surface. This is further displayed in Figure 2-14 which also shows visually the action of the capillary (F_C) and Van der Waal (F_{VdW}) at the surface, as well as the gravitational (F_G) adhesion force.

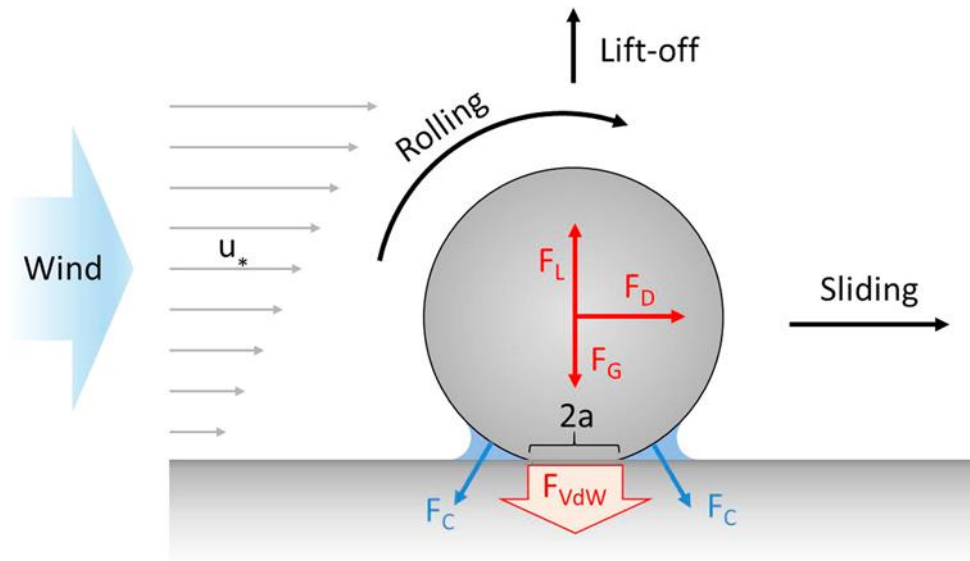


Figure 2-14 Diagram showing forces experienced by a particle of soiling on a flat surface [35].

An external influence such as wind, denoted in the figure as u_* , can result in the particle experiencing lift (F_L) and drag (F_D), which can result in the aforementioned Rolling, Sliding, and Lift Off movements.

Deposited soiling may then be further adhered to the surface via the process of cementation, which occurs when levels of high humidity, such as in the instance of morning dew, react with the water-soluble particles of soiling resulting in a salt solution and an insoluble particle. When humidity decreases the salt precipitates, anchoring the now insoluble particle to the surface [44]. Cementation is a significant issue as it results in particles that are not easily removed via standard washing, instead requiring soaking time or even use of solvents. Additionally, cemented particles provide a rough surface onto which further soiling can more

easily attach, which if left results in multiple layers of cementation and considerable decrease in reflectance.

2.5.3 Effect of Soiling on Mirrors

Soiling can have noticeably detrimental effects on performance in CSP plants, with even relatively light soiling being visibly noticeable on mirrors, as can be seen in Figure 2-15. The standard measure of cleanliness of mirrors for CSP is by measuring specular reflectance, which is a ratio of light arriving at the surface to light being reflected from that surface, usually expressed as a percentage. A theoretically perfectly clean mirror would have a value of 100%, however mirrors in plants are generally considered clean at values of reflectance above 90% [45].



Figure 2-15 Photographs showing soiling of mirrors at IMDEA Energy, Spain (Left), and Green Energy Park, Morocco (Right) [46].

Rate of soiling is not constant as it is highly dependent on weather conditions which are often inherently erratic in locations where CSP is deployed. Daily drops in reflectance as a result of soiling can vary from less than 0.5% for calm weather conditions, to up to 19% following a dust storm [10]. A complete avoidance of cleaning could result in a 70% loss of reflectance in one year [47]. Losses in reflectance translate to reduced power output, a 1% drop in reflectance can cause a 1.2% drop in power output [10], and as such financial implications of mirror soiling can be significant.

2.5.4 Soiling Prevention

As with most things, it is preferable to prevent a problem arising rather than allowing it to become an issue that requires remediation, and as such the CSP industry employs a number of preventative measures in an attempt to reduce soiling of mirrors. The most basic of these is, where mirrors are on movable mountings, to turn them away from the source of soiling. Many plants will have a pre-set dust storm position for mirrors, where they will be turned to point to the ground in order to shield against the worst soiling effects of the storm [48]. This is generally an effective technique however means that the plant is unable to generate any electricity for the duration of the storm, and also requires accurate forecasting of dust storms as motors for moving the mirrors are generally designed for slow movement for tracking the sun's path across the sky and as such may not be able to move the mirror quickly enough to provide protection from sudden unexpected dust storm events.

Some research has focussed on mirror coatings which aim to reduce the adherence of soiling to the mirror surface, typically composed of fluoropolymers, occasionally with embedded nanoparticles such as silica to create a structured surface [49]. Some coatings work to achieve a hydrophobic surface with low surface energy, allowing water during cleaning or naturally occurring dew to form beads on the surface which then drag particles of soiling away when they roll off [49]. Others such as investigated by Hunter et al. utilise a hydrophilic surface with a high surface energy, which encourages water to form a film over the entire surface, allowing it to soak into soiling particles to facilitate their removal, as well as overcoming electrostatic adherence forces. It is also possible that some coatings (namely WO_3 or TiO_2) can provide a photocatalytic benefit, enabling organic matter to decompose on exposure to sunlight [50]. Coatings can be effective in preventing soiling and aiding its removal; however they suffer from damage and degradation upon exposure to repeated contact cleaning cycles as well as surface scratching from dust and sand in desert winds. Longevity of anti-soiling mirror coatings of unspecified composition was investigated by Wette et al. who found that after 6 years in situ in Plataforma Solar de Almería (PSA) the coated mirrors had a loss of up to 3.5% in specular reflectance, compared to a

change of +0.2% for the uncoated mirrors. Further investigation using Taber abrasion testing showed the coated mirrors initially suffered a significant reduction in reflectance of approximately 20% after 20 Taber cycles as the coating is scuffed. There is then a gradual restoration in reflectance as the coating is removed almost entirely after 100 cycles. Similarly, Sansom et al. found that manual washing even with soft brushes caused degradation of the polymer coating investigated [51]. This can result in a permanent loss in reflectivity that can only be rectified by removal and reapplication of the coating, incurring financial expense and taking mirrors out of service during the process.

Dust barriers are also an area of increasing interest, where they work mainly to disrupt the flow of winds carrying soiling particles over and onto the mirrors, however design and placement of dust barriers must be carefully considered. King et al. investigated a range of dust barrier shapes and porosities using both Computational Fluid Dynamics (CFD) analysis and experimental techniques and found that a solid barrier increased turbulent flow immediately after the barrier that can pick up ground dust and may actually increase the rate of soiling, whereas barriers made of a mesh of 15 – 50% porosity resulted in 48.5% of airborne particles being deposited within a meter of the barrier, preventing their potential adhesion to the mirrors beyond [52].

2.5.5 Current Cleaning

Currently, the most common method of controlling soiling effects for CSP is a rudimentary physical washing with demineralised water and brushes [53]. Whilst effective, restoring mirrors to near original reflectivity, it has high consumption of both time, labour, and water which are costly resources, and also risks scratching and damaging the surface of the mirror which can permanently reduce reflectivity.

Cleaning methods are often categorised by their level of autonomy, being either manual, semi-autonomous, or autonomous.

2.5.5.1 Manual Cleaning

Manual cleaning is the most basic and time consuming, and involves personnel washing each mirror by hand, usually with a water sprayer and a brush mounted

on a long pole, such as shown in Figure 2-16. It is generally only employed where the cost of labour is very low or there are a small number of mirrors, but can also be employed supplementary to more regular cleaning methods to remove stubborn areas of soiling that remain after routine washing [10].



Figure 2-16 Typical equipment for manual cleaning of mirrors. Items are labelled by: 1: pressure washer with handheld nozzle, 2: water-fed horsehair bristle brush attachment, 3: steam cleaner, 4: demineralised water tank, 5: detergent tank [3].

2.5.5.2 Semi-autonomous

The most frequently employed methods of cleaning are semi-autonomous, often requiring just a driver who controls a specially adapted truck featuring a water tank, pump, and arm(s) onto which cleaning apparatus is mounted. The cleaning can be either contact, where brushes work to physically remove soiling from the mirrors, or non-contact, which utilises the force of water spray to dislodge soiling. Contact cleaning is generally more effective in restoring reflectance however introduces a risk of damage to the mirror surface resulting in irreparable reflectance losses.

Washing of flat heliostats in solar tower plants is a more simple operation, as a single flat arm can wash the entire surface, however curved mirrors such as in parabolic trough plants require more considerably engineered tools, as shown in

Figure 2-17, that can effectively clean the surface without damaging either the mirror itself or the receiver apparatus [54].



Figure 2-17 Conventional semi-autonomous cleaning of parabolic trough (left) and flat heliostat (right) mirrors [55].

Water consumption of typically employed semi-autonomous washing varies, but is generally between 0.5 to 1.0 L/m² [54][56] or 20-40 gallons per MWh [7]. Given the large size of many commercial CSP plants, this adds to a considerable demand for water, a precious resource already scarce in the sunny and dry environments where CSP is typically deployed which not only has significant financial implications, as de-mineralised water of sufficient quality and quantity can be costly in these locations, but also presents an ethical conundrum, as clean water is a vital resource necessary for life. Indeed the Crescent Dunes Solar Energy Project, a solar tower installation in Nevada, USA, drew the ire of local residents when it applied to divert 0.2 million litres of demineralised water a day to clean its 10,347 heliostats [57].

2.5.5.3 Autonomous

Rarely, cleaning of mirrors is undertaken autonomously, where negligible human labour is involved. An example of an autonomous cleaning device utilising conventional washing techniques is HECTOR (Heliostat Cleaning Team-Oriented Robot), shown in Figure 2-18. This device is a small robot that utilises a roller brush and wiper to clean the surface of heliostats, aided by demineralised water stored onboard the robot in a small tank [58]. Human intervention is low although not zero, as the robot requires initial positioning on each heliostat as well as frequent refills of the water tank.



Figure 2-18 Photograph of HECTOR robot undertaking heliostat cleaning at the Gemasolar solar plant in Andalusia, Spain [58].

Autonomous mirror mounted robots have the advantage of significantly lower labour requirements, as well as avoiding the creation of airborne dust and sand that is created by trucks travelling between mirrors for cleaning. However initial costs are high and as a very new technology uptake amongst commercial CSP plants is low. They are also only able to operate on flat surfaces and therefore are unable to be utilised in parabolic trough or dish installations.

Another autonomous cleaning method is the installation of large roller brushes or wipers that span the entire height of the mirror, which periodically sweep across the mirror surface to remove soiling. These have high initial costs as a cleaning unit needs to be installed on each mirror, and also in the case of roller brushes are most often used without water in a dry cleaning process meaning their risk of causing surface damage is comparatively high, and as such they are not widely used in CSP applications although have found use for PV installations in high soiling environments [38].

2.5.6 Cleaning Frequency

Frequency of washing varies between plants and seasons, and can be between 5 or over 30 days, however cleaning routines themselves can take up to a week for large plants and thus in some cases cleaning is a constant endeavour [59]. Scheduled cleaning cycles are often adjusted ad hoc in response to incidences of heavy soiling such as after dust storms, or when mirrors are cleaned naturally by rainfall. Figure 2-19 shows the specular reflectance (where a value of 1.0 is equivalent to 100% reflectance) of mirrors in Albuquerque, NM, exposed to soiling for 480 days without any active cleaning. Increases in specular reflectance are as a result of natural cleaning events such as rain and even snow. Figure 2-20 shows specular reflectance of mirrors at the same location with cleaning cycles of two, six, and twelve days, showing that whilst soiling and natural cleaning may be erratic, more frequent cleaning results in a higher average reflectance.

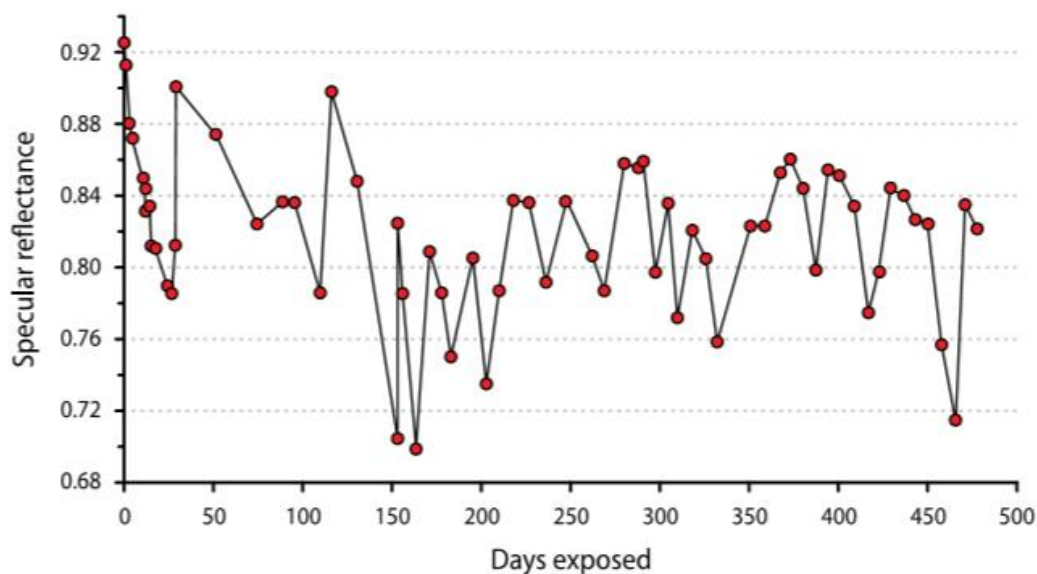


Figure 2-19 Effect of natural cleaning events on specular reflectance of mirrors [60].

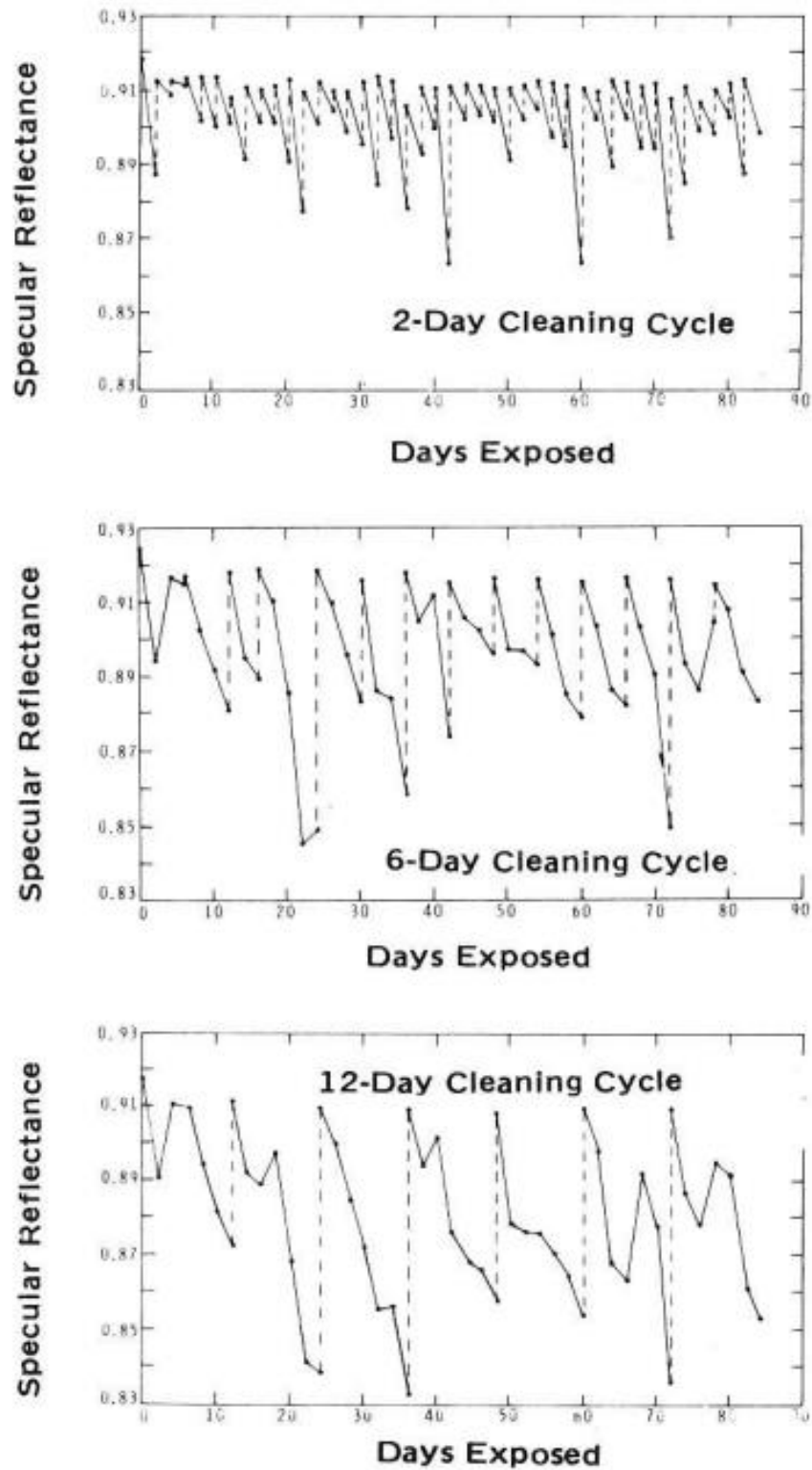


Figure 2-20 Specular reflectance of mirrors subject to varying durations of cleaning cycles [60].

2.5.7 Novel Cleaning

Conventional cleaning methods of mirrors often have numerous drawbacks, they can be time consuming, costly, require significant labour, and consume vast quantities of expensive and precious water. Consequently, there is an effort to conduct research into novel cleaning techniques. Presented below are a select number of novel cleaning techniques and devices in various states of research maturity.

2.5.7.1 Ultrasonic Cleaning

Sometimes known as acoustic cleaning, ultrasonic cleaning still requires water although at a lower rate than traditional cleaning, up to 600 times less water according to one investigation by Sarasua et al. [61]. It works by applying a high frequency electric field across piezoelectric crystals which then vibrate, generating ultra-sonic waves as they do so. These waves travel through the water resulting in cavitation bubbles within the liquid that then undergo asymmetric implosion, creating microscopic jets of water that dislodge soiling particles [61]. One such novel device is shown in Figure 2-21, which utilises an ultrasonic head that applies vibrations along a 300mm long metal bar, which when placed in close proximity (1-3 mm) to a wetted mirror surface induces ultrasonic cleaning. Ultrasonic cleaning can be effective in restoring mirror cleanliness, with some devices, such as that being described in a patent filed by Bru et al., claiming to achieve up to 99% of initial reflectance values [62] with water consumptions of only 0.025 L/m² when washing horizontally positioned mirrors.

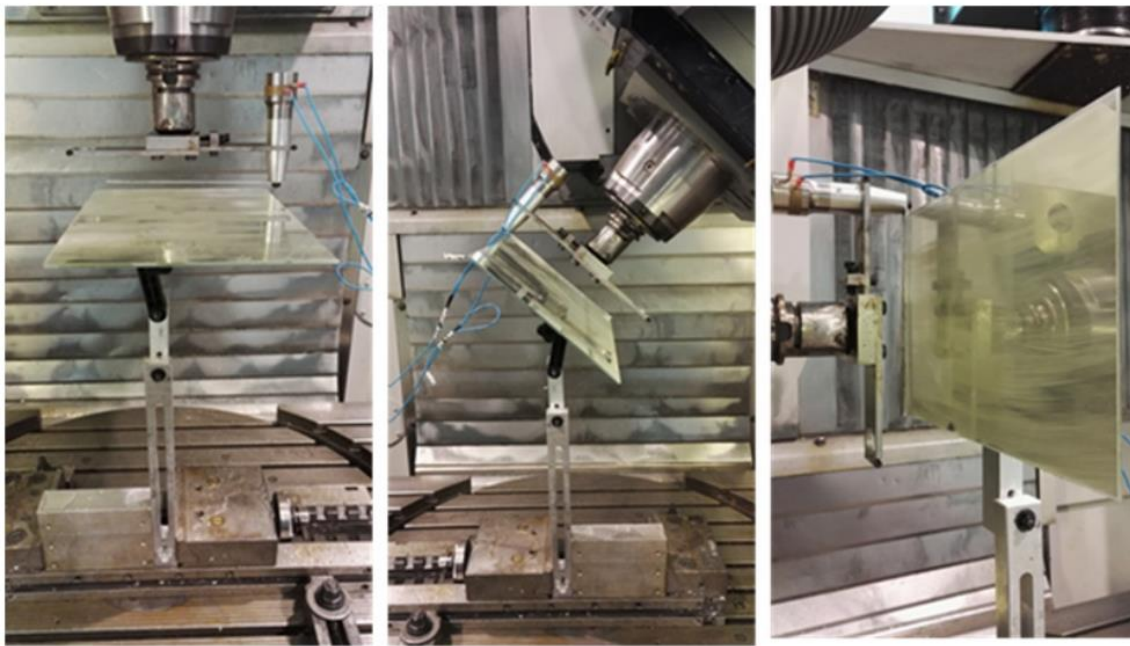


Figure 2-21 Photographs of experimental ultrasonic mirror cleaning device, showing application on (L-R) horizontal, oblique, and vertically oriented mirrors [61].

2.5.7.2 Electrodynamic Removal

Perhaps also considered a method of soiling prevention in addition to cleaning, mirrors can be constructed or retrofitted with transparent electrodes integrated into a thin dielectric layer on the glass surface to create an electrodynamic screen (EDS). The electrodes are typically only 50 to 100 μm wide and placed at intervals of 500 to 800 μm across the entire mirror surface. A three phase AC voltage is applied across the electrodes which results in electrostatic charging of the soiling particles which are then pushed and pulled along the mirror surface with the alternating electric fields, until they eventually reach the edge and are removed from the mirror.

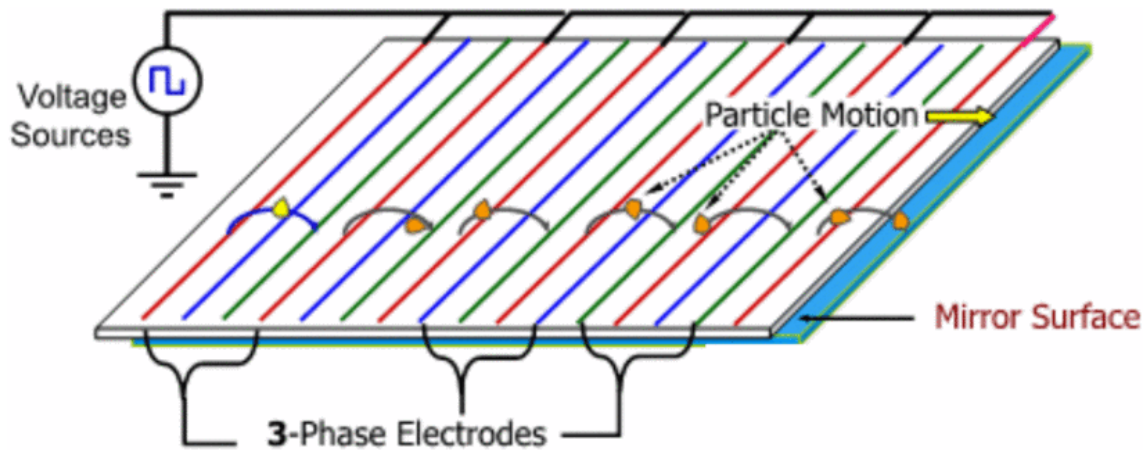


Figure 2-22 Diagram of working principle of an Electro Dynamic Screen incorporated into a solar mirror [63].

A review of these technologies and investigation into one such device by Stark et al. showed that on a back silvered glass mirror onto which electrodes were deposited using manual screening, EDS was able to maintain spectral reflectance of $>90\%$ when the mirrors were exposed to soiling [63]. The energy required to run EDS cleaning was calculated at $3.6 \times 10^3 \text{ J/m}^2$ per three week cycle, compared to energy losses of $1.08 \times 10^5 \text{ J/m}^2$ per three weeks due to mirror soiling. This method of soiling mitigation is promising in that it requires nil water, an attractive prospect in CSP, however soiling removal is not as successful as with other methods, for example it is not effective for particles of less than $2 \mu\text{m}$ diameter or at humidities higher than 50% , and as such returns mirrors to reflectance of only a little over 90% [54], in some instances requiring additional water based washing. Additionally, the integrated electrodes are not 100% transparent, so there are inherent losses of reflectance even if the surface is entirely free from soiling. As a novel technology there is no available information on cost, however authors of the above reports claim the money saved in water use easily eclipses the cost of fitting the electrodes into the mirrors, and the electricity consumed in powering them.

2.5.7.3 Plasma Cleaning

A proposed solution to the above issues is the utilisation of plasma to reduce or potentially even eliminate use of water for cleaning in CSP plants. Plasma is a state of matter in which electrons are stripped from the nucleus resulting in a

substance of overall neutral charge but consisting of charged ions. Depending on plasma parameters such as feed gas, power, and surrounding atmospheric conditions, plasmas can be tailored to different processing tasks making use of plasma constituents such as reactive species, particle bombardment, UV emissions, and heat. Plasmas are already in use to clean and modify surfaces during manufacture and processing such as to increase adhesion between layers or to make more efficient use of processing liquids.

It is therefore proposed that plasma could play a role in reducing water consumption of plants for mirror cleaning, through both reduction of soiling adhesion and in reduced water use during washing.

2.6 Summary

In Table 2-1 the above methods are listed in terms of their average costs and consumptions. It can be seen that no one solution is ideal across all categories, and hence no one solution is solely deployed across all plants. Each cleaning approach has its own positives and negatives that make it more or less attractive a solution to individual plants. Traditional cleaning methods of water jets with or without brushes are fast, simple, and quick to deploy, so hold the largest share of cleaning strategies, however the water consumption rate is high. Novel technologies show promise in lowering water consumption however are often slow and expensive and so have not seen deployment in commercial plants.

It is anticipated that use of plasma will have an overall favourable profile, being fast and efficient in cleaning, with a significant reduction in water consumption. The initial cost may be higher, however with use of plasma generated from air or nitrogen pulled from the air, its running cost may be low, and plasma surface processing deployed in other industries has shown it can have a high processing speed.

Table 2-1 Summary of current and novel mirror washing technologies.

Cleaning method	Initial cost	Running cost	Speed	Water use	Readiness
Water spray	Medium	Medium	Fast	High	Deployed
Roller brushes	Medium	Medium	Fast	High	Deployed
Wipers	High	Medium	Fast	Medium	Not widely deployed
Robot cleaning	High	Low	Slow	Medium	Not widely deployed
Ultrasonic	High	Low	Slow	Low	Early research
Electrodynamic	High	Low	N/A	Very low	Early research
Plasma *Anticipated	Medium	Low	Fast	Low	Not investigated for application, deployed in other industries

2.7 Plasma

Although not particularly prevalent on earth, plasma is the most abundant state of matter in the universe, in fact it is considered that 99.999% of all observable matter in the universe is plasma [64]. It constitutes celestial bodies such as stars and nebulae, there is even growing support for plasma cosmology: an alternative theory that suggests that plasma, not gravity, is the most important formative ‘force’ in the universe [65]. Plasma cosmology aims to explain formation and existence of the universe without the theorised unknowns of dark matter and dark energy that the widely accepted Big Bang theory relies upon.

On earth plasmas are most spectacularly observed naturally in lightning and via the aurora borealis and aurora australis, which occurs when the solar wind, a hot

stream of plasma from the sun, interacts with the magnetic field of the earth [66]. Plasmas are also harnessed in consumer goods such as fluorescent lamps [67] and television screens [68], as well as in multiple industrial applications [69–72].

Although there are many methods that can be used to create a plasma, they all adhere to the same principle: giving a gas enough energy such that it becomes ionised.

A gas consists of a quantity of molecules moving freely in space, during their travel these molecules interact with each other via collisions which can either be elastic or inelastic in nature. During elastic collision, both momentum and kinetic energy are maintained, the particles are deflected in their trajectory but otherwise remain the same. In the case of a collision between an electron and an ion or atom, as the difference in masses is so large there is negligible transfer of energy [73]. During inelastic collision, momentum is still maintained however there is a significant transfer of the internal energy of the particles. When enough energy is transferred into an atom or ion excitation, and eventually ionisation, can occur as the electrons rise through the energy levels of the atom before detaching from it entirely.

Collisions of electrons with other particles (A) in the gas occur frequently and can have a number of outcomes. Elastic collisions result in scattering ($e + A \rightarrow A + e$), when the direction of motion of the atom is changed however internal energies of both particles remain mostly unchanged. When electrons collide with particles at higher energies inelastic collisions begin to occur, such as Excitation ($e + A \rightarrow A^* + e$), when a considerable portion of the incoming electron's kinetic energy is transferred to an electron residing in the inner shell of the atom or ion which is consequently raised to a higher energy level (A^*). Excitation is quickly followed by de-excitation, also known relaxation by spontaneous emission as the electron releases its excess energy in the form of a photon when it decays back to its original level. With enough incident energy, ionisation can occur ($e + A \rightarrow A^+ + 2e$), and an electron will escape the bounds of its original ion or atom (A^+), and is then able to itself collide with other ions and atoms. It is also possible for the incoming electron to be captured by the ion with which it collides, resulting in

recombination ($e + A^x \rightarrow A^{x-1} + (h\nu)$) when it occupies a vacant energy level and releases its excess energy as a photon ($(h\nu)$, where h is Planck's constant and ν is the frequency). If ionisation occurs at a higher frequency than recombination, an electron avalanche is produced and a plasma may be formed.

There is also the possibility of interaction without collision, as in the case of Bremsstrahlung or “braking” radiation. This occurs when an electron's trajectory is altered when it passes a positively charged ion. As it decelerates it loses part of its kinetic energy in the form of a photon, sometimes known in plasmas as free-free radiation as the electron is free of any atom or ion both before and after the interaction [74].

The probability of any of the above outcomes can be understood by considering the collision cross section, σ . For neutral particles this can be simplified as relating only to the area of the particle ($\sigma = \pi(2r)^2$), however interactions between charged particles can also be predicted using a more complex formula that takes into account coulomb force [75].

The above interactions are happening constantly within any gas; however, to create a plasma a number of criterion need to be fulfilled, in order to understand these we must first examine some properties of plasma and a few select parameters.

2.7.1 Plasma Parameters

Plasmas are incredibly complex and their physics and dynamics have been subject to extensive study [69,74–77]. Giving an adequate definition of each process, parameter and interaction would be enough to fill an entire thesis itself, indeed many a PhD has been focused entirely on this. Instead defined here is a small number of parameters that aid in basic understanding of the plasma medium, as well as the three main criteria for classification of a plasma.

2.7.1.1 Debye Shielding

Considering a section of plasma within a bulk that is not constrained by any walls, its population of positive ions and negative electrons are roughly equal and will be distributed evenly such that the plasma overall is considered “quasi-neutral”.

Now consider a sudden local change in charge that may be as a result of recombination or ionisation. The charged particles within the nearby vicinity of this new point charge will experience either repulsion or attraction to this depending on their charge, which in turn creates movement towards or away from it. The distance over which ions experience this attraction or repulsion to a non-negligible degree is known as the Debye length, λ_D , after German physicist Peter Debye. Debye shielding is the term for the sphere of radius λ_D which shields the bulk of the plasma from these electrostatic disturbances [78]. Debye lengths can range between a few meters for low density space plasmas such as solar winds, down to nanometers for imploded fusion plasmas, for typical lab made plasmas the range is around 10^{-4} to 10^{-6} m [79].

2.7.1.2 Plasma Frequency

Owing to the considerable disparity in mass between the electrons and the ions, when movement occurs as a result of changes in local charge the electrons travel so at a much higher speed than the heavier particles. They will in fact, within the Debye sphere as described above, overshoot the position of charge neutrality resulting in a further charge imbalance, when again they move to rectify this and again they overshoot. This results in an oscillation of the plasma known as the plasma frequency, ω_p , which can be further classified into the electron frequency ω_{pe} , and the ion frequency ω_{pi} [80]. This oscillation also results in a neutralising effect to applied electric fields of frequency less than the plasma frequency as the electrons can quickly move to neutralise the field.

2.7.1.3 Frequency of Collisions

As the plasma is a highly energised medium, movement of the particles within is prevalent and collisions inevitable, however there will be time between collisions when electrons are travelling. The mean free path, λ , is a measure of the average distance travelled between collisions, which in turn defines the mean free time, τ , the average time between collisions [81]. In vacuum or low pressure plasmas, the mean free path is large, as the distance between particles themselves are large, therefore it is more likely that particles will travel further before colliding with another particle. At atmospheric or high pressure plasmas particle density is

considerably higher, and so the mean free path reduces greatly as collisions occur much more frequently as particles are already in close proximity. The difference can be as great as 0.3 m at 10^{-1} Torr to just 4×10^{-6} m at 10 bar (7500 Torr) [82]. In plasmas interaction between particles is dominated by coulomb forces which provide a level of protection against direct impact collisions [83].

2.7.1.4 Temperature

When discussing the temperature of a plasma, it's important to consider that different components of the plasma can have vastly different temperatures. When creating a plasma via an applied electric field, electrons gain energy, and thus heat, during their mean free path. Upon collision with a heavy particle such as an ion or atom the disparity in mass means only a small percentage of their energy is transferred through the process of Joule heating ($J \cdot E$) [84], resulting in the electron temperature, T_e (usually expressed in units of eV), initially being much greater than the temperature of the ions or atoms, T_i (or often referred to as gas temperature, T_g) [85]. Consequently plasmas where $T_e \gg T_g$ are often called non-equilibrium plasmas, and can also be considered to be nonthermal (NTP), as the ion temperature may be not significantly higher than room temperature [86]. Nonthermal plasmas are of considerable interest as the low gas temperature means they can be utilised in processes where a high temperature would be dangerous or detrimental, such as in medical applications [87] or processing delicate heat sensitive materials [88].

The relationship between T_g and T_e is strongly related to the pressure, as a lower pressure results in more sparse distribution of particles, which in turn results in fewer collisions and thus less transfer of energy from the electrons into the heavier ions. Figure 2-23 displays this relationship for a mercury vapour discharge at constant current and shows how T_e and T_g converge as pressure increases, to become roughly equal as the electron density reaches 10^8 to 10^{13} cm^{-3} . For arc discharges the gas temperature can reach 3000°C , whereas for nonthermal atmospheric pressure plasma jets this can be as low as room temperature up to approximately 200°C , with an electron temperature of 1-10 eV [89].

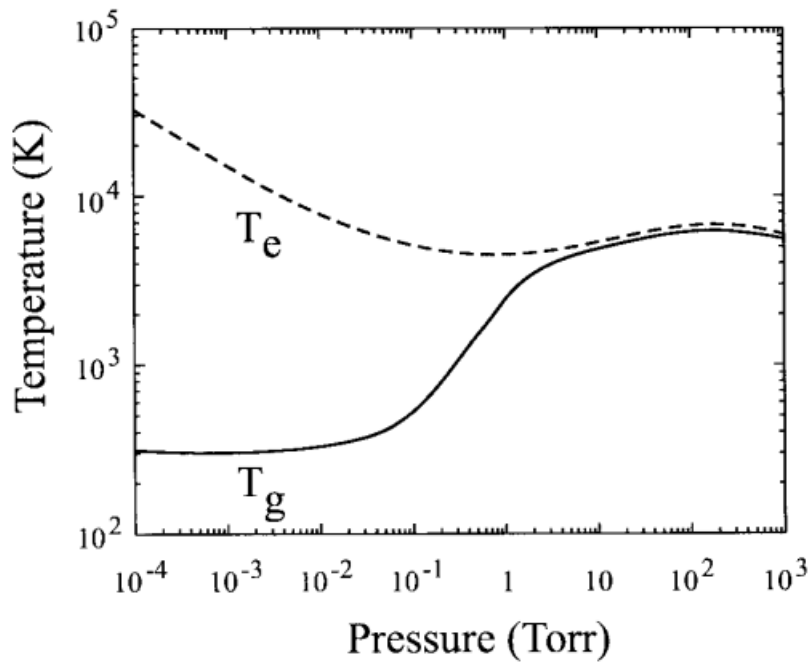


Figure 2-23 Relationship between T_e and T_g in a plasma at increasing pressure [89].

With enough time and energy, local thermal equilibrium (LTE) between the electrons and the heavier particles can be achieved. This is usually achieved when the E/ρ value is low, as in there is a low electric field (E) and/or high density (ρ) and thus high pressure (<10 kPa) [90].

2.7.2 Plasma Criteria

Considering now the above parameters, we arrive at three plasma criteria:

Firstly,

$$\lambda_D \ll L \quad (2-1)$$

Where L is the length of the plasma bulk. In effect this stipulates that local disturbances in charge do not affect the plasma as a whole.

Secondly,

$$N_D = \frac{4}{3}\pi\lambda_D^3 N \gg 1 \quad (2-2)$$

where N_D is the number of particles inside the Debye sphere, and N is the number density of the plasma as a whole. This criterion requires that the number of particles within the Debye sphere, and in turn the particle density of the bulk plasma, must be sufficiently high.

And the final criterion is

$$\omega_p \tau > 1 \quad (2-3)$$

which necessitates that particles in the plasma oscillate more frequently than they collide.

2.8 Plasma Generation

Plasmas can be created in either laboratory or industrial setting using a variety of principles and apparatus, depending on the desired plasma parameters and as always equipment and cost limitations. Presented below are the most frequently used methods of plasma generation, grouped by their method of energy application.

2.8.1 Direct Current

The application of a Direct Current (DC) voltage across a gas generally occurs in three distinct stages as shown in Figure 2-24, depending on the applied current: The corona discharge (sometimes known as the dark discharge or Townsend region) between 10^{-7} and 10^{-5} A; glow discharge between 10^{-5} and 1 A; and arc discharges above 1 A [73].

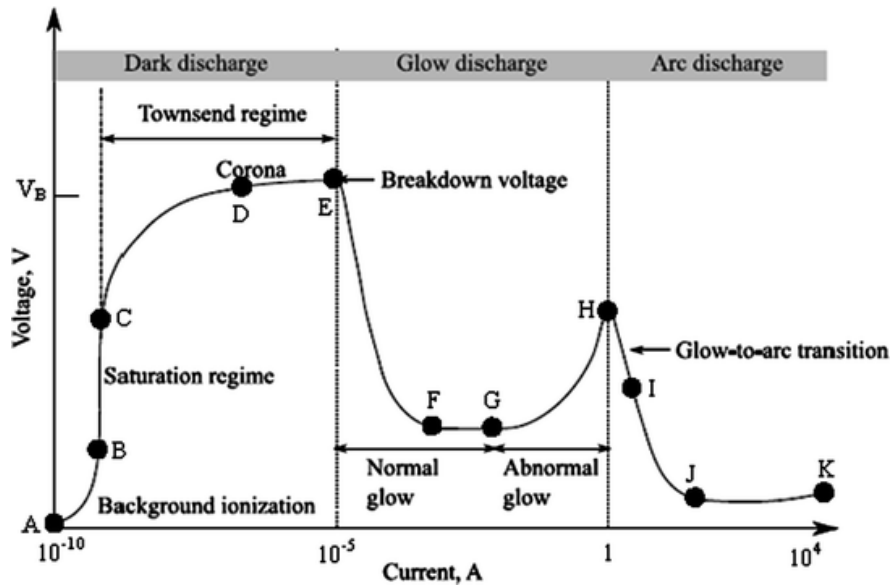


Figure 2-24 Current-Voltage profile of a DV plasma discharge [73].

2.8.1.1 Corona Discharge

At low currents, charges are produced as a result of background radiation or the photoelectric effect at the surface of the cathode due to UV radiation. Electrons released may be accelerated towards the anode if present, however with the low electric field collisions resulting in ionisation happen infrequently if at all, and as such the current is limited by the total number of initial electrons. With an increase in applied potential, acceleration of the electrons also increases and collisions resulting in excitation and ionisation can occur, creating new ions that enable an increase in discharge current. Subsequent recombination and de-excitation releases energy as photons and produces a glow which gives the corona discharge its name: Latin for “crown”, as past mariners observed glowing atop the masts of their ships during electrical storms [91]. If the potential is increased further, breakdown voltage (V_B) will be reached and an electrical discharge will be formed.

Corona discharges are often an unwanted effect of high voltage equipment such as power transformers, and as such steps are taken to eliminate or relocate corona glows for example by designing charged parts with large smooth surface areas, which works by reducing the field strength that would otherwise occur at points or corners, or with the use of corona rings, that divert the discharge away

from valuable equipment [92]. However corona discharges do have uses in industrial applications, the most common of which is in electrostatic precipitators (ESP), in which corona discharges are utilised as an ion source to charge particles of pollution and thus allowing them to be diverted and collected [93]. DC Corona discharges are also used in the industrial production of ozone [94].

2.8.1.2 Glow Discharge

Perhaps the most basic in construction and consequently of great historical importance in plasma research, DC glow discharges consist essentially of two electrodes between which is the gas to be ionised. Free electrons that exist in the gas are accelerated toward the anode by the electric field produced when a potential difference of sufficient magnitude is applied across the electrodes. These accelerated electrons collide with gas atoms in both elastic and inelastic collisions, with inelastic collisions having the potential of resulting in excitation leading to ionisation, further releasing electrons. Meanwhile, positive ions are propelled towards, and collide with, the cathode, releasing yet more free electrons through the process of ion-induced secondary electron emission. This combination of ionisation and emission provides new source of electrons, resulting in a self sustaining plasma [72]. De-excitation and recombination produces visible light, and as such these DC plasmas are often known as glow discharges. Glow discharge effects can also be enhanced by externally heating the cathode, such that the cathode emits electrons itself and ionic bombardment is no longer necessary for the plasma to self-sustain [73].

DC glow discharges are a useful education and research tool as they have vast local variations in charge and produce distinct areas of light and dark within the discharge tube that aid in demonstration and understanding of plasma generation, as shown in Figure 2-25.

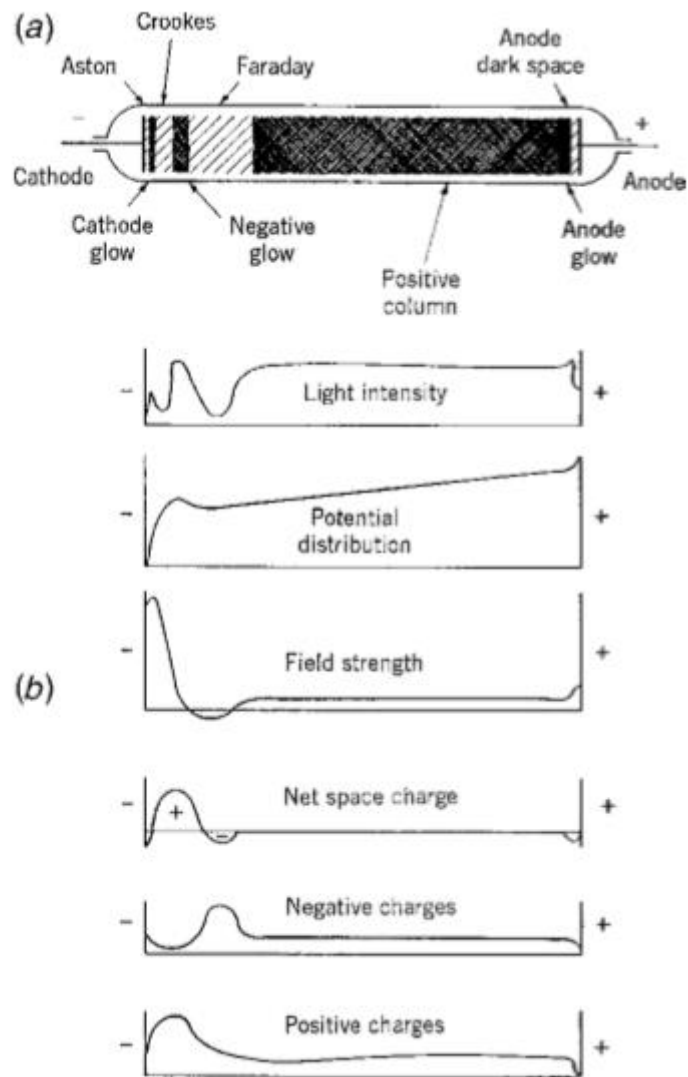


Figure 2-25 Schematic of regions within a DC glow tube (a) and their associated properties (b) [95].

The area at the cathode is known as the cathode fall space and exists of three distinct regions: the Aston dark space; the cathode glow; and the Crookes dark space. In this section the potential drops sharply resulting in a high electric field at the surface of the cathode causing energetic ionic bombardment and electron emission, creating a self-sustaining plasma [73]. The Aston dark space, named after physicist and chemist Francis William Aston [96], occurs as there exists a strongly positive cloud forming at the cathode that is of relatively low energy and consequently lacks luminescence. There is then a thin area of light known as the cathode glow followed by the Crookes dark space named for another physicist

and chemist William Crookes, where atoms gain enough energy to begin to ionise and the produced oppositely charged particles are repelled, resulting in a dark area where there is no immediate recombination of electrons to the nucleus and so no photons are emitted. Following this is the Negative Glow, where electrons from the Crookes dark space recombine with positive ions releasing energy as photons. As the electrons slow, the Negative Glow fades into another area of darkness, the Faraday Dark Space. There is then the Positive Column, the area of most prominent area of light creation, which can be either homogeneous or striated (standing or rolling). This region is considered the area of proper plasma: its longitudinal electric field is low and uniform, and it exhibits overall charge neutrality. The Positive Column ends with the Anode Fall area, first with the anode dark space, and then with the characteristic anode glow caused by acceleration of the electrons towards the anode and their subsequent bombardment of it.

Bombardment of the cathode with ions and fast moving atoms releases electrons not only from the gas but also atoms from the cathode material itself, a process known as sputtering. These sputtered atoms then join the plasma, undergoing the same processes of excitation, ionisation, and subsequent de-excitation and recombination resulting in energy release as photons that can be analysed via spectroscopy. Sputtering will degrade the cathode and is generally to be avoided, however it is desirable when utilised in DC plasma's widespread use as an analytical tool, known commonly as Glow-Discharge Optical Emission Spectroscopy (GDOES), whereby the sample to be analysed is used as the cathode, the sputtering and subsequent photon emission of which can be analysed through spectroscopy to determine its composition and layer profile [97].

Sputtering effects are also harnessed for removal of atoms from, and thus cleaning of, a surface, and also deposition of particles onto a substrate. In the case of cleaning, the sample to be cleaned is used as the cathode, and bombardment of the fast ions and atoms removes surface contamination such as oxides and organic molecules [98]. In the case of deposition, the cathode constitutes the material to be deposited, known as the target, the sputtered atoms and ions from which are directed towards the substrate along with the carrier gas.

The carrier gas is usually inert, commonly argon, resulting in deposition only of the target material onto the substrate, alternatively a reactive species such as oxygen can be selected to react with the target and/or substrate to produce the desired deposition [99].

2.8.1.3 Arc Discharge

When current exceeds 1A, the discharge undergoes a glow-to-arc transition, where the voltage across the electrodes drops below that of the glow discharge. For stability, arc discharges are usually operated at pressures higher than 10 torr, which ensures that the collision rate is high enough for the ions, electrons, and atoms, to reach local thermal equilibrium (LTE) with one another, resulting in a single temperature thermal arc. Non thermal arcs occur at lower pressures, when electrons are in thermal equilibrium at a higher temperature than that of the ions and atoms. The high current of the arc constricts its radius [100] resulting in a confined column of plasma. Owing to their high and homogenous temperature (around 20000 K [101]) , arc discharges are used industrially for welding, cutting, and in electric arc furnaces (EAF) [102] [103].

2.8.1.4 Pulsed Direct Current

Pulsed DC plasmas operate under the same principles as DC, however they do not operate continuously, instead plasma is created in short pulses. They are able to have far higher average charged particle density for the same average power [104]. This results in lower electron temperature during off time, and as such can reduce damage to the processed surfaces, allowing it to be used in processing of more delicate surfaces such a wafers and films. Pulsed DC is also employed to preventing arcing of the plasma by reducing build-up of charge [105].

2.8.2 Alternating Current Plasma

AC Plasmas require a signal generator that produces a current at the desired frequency and power, the fields produced by this current then give energy to the gas to incur ionisation. AC plasmas can be classified by many means, often with overlaps between categories, here they are grouped according to the frequency of their power source.

2.8.2.1 <1 kHz Low Frequency

Plasmas produced below 1 kHz are considered low frequency, as the periodic frequency of the field is much greater than the transit time for the ions to travel from anode to cathode, such that $\omega\tau > 1$, where ω is the field's angular frequency and τ is the electron transit time. At such low frequencies, discharges can be considered as separate DC plasmas of alternating polarity [73].

2.8.2.2 1 kHz – 300 MHz Radiofrequency

As the frequency increases, breakdown behaviour will change. Above 100 kHz, the frequency is sufficiently high as to enable a continuous discharge as opposed to periodically flipping DC discharges [72]. Additionally, breakdown voltage becomes lower: at around 1 MHz the frequency of field alternation is sufficient such that the majority of electrons will be reversed before they reach the anode. This significantly reduces or even entirely eliminates electron losses at this interface, as well as increasing ionisation in the gas. The majority of RF processes occur at 13.56 MHz, within the designated ISM (Industrial, Scientific and Medical) band, as this is the frequency permitted by communications authorities that will not interfere with other activities.

At RF frequencies, their vastly different masses mean electrons and ions exhibit very different behaviour, as whilst the light electrons can follow the rapidly alternating fields the heavier ions are able to follow only the time-averaged electric fields. The difference in mobility also results in self-bias, which occurs when the electrodes are not geometrically identical, resulting in a time averaged negative voltage on the smaller of the electrodes in order to preserve overall charge neutrality [106]. This self-bias is often harnessed in processing to enhance deposition or etching of a dielectric material, with the substrate mounted directly on top of the electrode such that it obtains a negative charge [107].

Plasmas generated by alternating current at radiofrequency can generally be sorted into two distinct groups: Capacitively Coupled Plasma (CCP) and Inductively Coupled Plasma (ICP), discussed further in sections 2.8.2.6 and 2.8.2.7.

2.8.2.3 300 MHz – 300 GHz Microwave

As frequency enters the microwave domain, the primary energy transfer into the plasma begins to shift from individual heating of particles as in as in RF and DC discharges, to collective absorption of energy by the electrons. The point at which an AC plasma becomes known as microwave rather than RF does not have a set definition and classification of microwave plasmas can vary from a few hundred MHz to 1GHz, however is generally considered to be when electron temperature (T_e) is roughly equal to neutral and ion temperature (T_n and T_i respectively, sometimes known collectively as T_g for gas temperature or T_h for heavy temperature) resulting in local thermal equilibrium (LTE). Hereon in a system will be described as microwave when its frequency is above 300 MHz. A common frequency for microwave plasma is 2.45 GHz, again within an ISM band set by the ITU (International Telecommunications Union).

Microwave plasma systems frequently employ a waveguide instead of a coaxial cable to reduce energy losses and promote effective coupling of energy to the gas, resulting in a higher efficiency system with less reflected power. These work to achieve a Voltage Standing Wave Ratio (VSWR) of 1, which would indicate perfect matching and nil reflected power, although in a reality no system has 100% efficiency [108].

Waveguide construction is typically a rectangular box around the plasma torch through which the gas passes. Microwaves are propagated through the box which can be tuned using a plunger to increase or decrease the cavity size [109]. Waveguides also necessitate the use of a mode converter, which ensures operation in the dominant TE₁₀ mode [110][111].

2.8.2.4 Surface Wave Discharge

Amongst the newest of plasma generation technologies, being described first in 1975 [112], in Surface Wave Discharge (SWD) systems (also known as Surface Wave Plasma (SWP) or Surface Launched), plasma can be generated and sustained via transfer of energy to the gas by waves that travel perpendicular to a dielectric enclosure within which the plasma is generated. SWPs are

considered electrodeless, with the electric field strength being greatest at the plasma dielectric boundary.

Surface wave plasmas hold an advantage over other methods of electromagnetic wave plasma production as the plasma volume is only limited by input power and not the resonant size of the coupling structure, enabling large columns of plasma to be produced [113].

2.8.2.5 Electron Cyclotron Resonance

Another method of wave heated plasmas, Electron Cyclotron Resonance (ECR) systems utilise the plasma parameter known as electron cyclotron frequency (ω_{ce}), an oscillation in which an electron of charge e and mass m_e in a static magnetic field of strength B will travel in a circle owing to Lorentz force, expressed as:

$$\omega_{ce} = \frac{eB}{m_e} \quad (2-4)$$

Upon application of an EM field at the same frequency as ω_{ce} , with the electric field being perpendicular to the magnetic, electrons are accelerated along a helix, creating an almost collision-less, low pressure plasma. Generally, the applied EM field is of microwave frequency 2.45 GHz, with the static magnetic field being tuned to achieve resonance and effective energy coupling [106].

AC Plasmas of both RF and Microwave frequency can also be defined by their two modes of operation, Capacitively coupled Plasmas (CCP), or E mode, and Inductively Coupled Plasmas (ICP) or H mode.

2.8.2.6 Capacitively Coupled Plasma

Much like in DC discharges, CCPs feature parallel electrodes between which the plasma is formed. The electrodes can be in direct contact with the gas or can be separated by a dielectric barrier. This will be discussed in more detail in section 2.10.

2.8.2.7 Inductively Coupled Plasma

In ICPs, energy is transferred into the gas via the electromagnetic field created by an induction coil (cylindrical solenoid or planar), with the plasma not in direct contact with the electrodes. A basic ICP setup consists of a dielectric tube, often quartz or ceramic, through which the gas flows, that is in turn surrounded by a solenoid connected to an AC supply [70].

Inductively coupled plasmas operate in two distinct modes: L mode (sometimes called E mode) and H mode[114]. At low powers, the plasma is actually coupled with the field capacitively in the direction of the separate E fields around the coils. In these conditions the plasmas is said to be in Low Confinement, or L-mode, and exists mostly towards the walls of the tubes. As the power increases, High Confinement, or H-mode, is achieved. The transition from L mode to H mode is distinct and abrupt, and occurs when coupling switches from capacitive to inductive coupling of the field produced by the solenoid. The precise nature of the E-H mode transition is not yet fully understood and is the subject of continuing study and discussion [115] [116].

Inductively Coupled Plasmas are frequently employed in the diagnostic technique of Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), where the material to be analysed is passed through the ICP torch along with an inert carrier gas, where it is ionised before being directed into a mass spectrometer where created ions are separated according to their mass to charge ratio as in conventional mass spectrometry.

2.8.3 Beam Plasma

Plasmas may be generated with application of a beam, commonly a laser or electron beam. In both cases, the beam is aimed upon the target which can be in any physical state (solid, liquid, or gas), in which it imparts significant energy upon the atoms of the target, resulting in excitation and ionisation.

The interaction of a laser with matter is complicated and extensively studied. It occurs essentially via energy transfer and excitation. Free electrons such as in metals absorb energy and accelerate, whereas electrons bound to an atom

absorb the photon's energy and excite to a higher energy band in the case where the photon energy matches the bandgap energy, E_g [117].

In the case of laser ablation of solids, each laser pulse that reaches the target surface produces a small plume of plasma as shown in Figure 2-26. This process starts with the laser photon energy exciting electrons resulting in the breaking of intermolecular bonds creating separate atoms. These atoms then become vaporised, resulting in the Knudsen layer, a layer of non-equilibrium gas of only a few mean free paths depth. After this is the plume core, which is the hottest and most dense section of the plasma, which gradually becomes cooler further from the target surface when ions begin to recombine to form neutral species. The rapid expansion during the plume process also creates a small shock wave front.

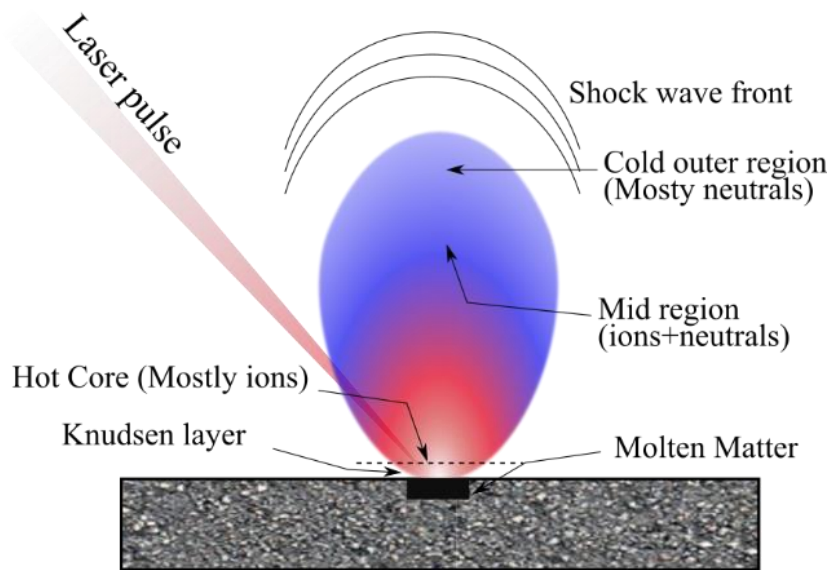


Figure 2-26 Diagram of a plasma plume produced during laser ablation of a solid [117].

Laser generated plasmas are often used industrially in the characterisation technique of Laser Induced Plasma Spectroscopy, where the light emitted from the plasma plume generated at the target can be analysed to determine its composition [118].

For plasma generated by electron beams the system consists of a cathode positioned within a strong magnetic field, producing electrons that are then confined and funnelled into a beam [119][120]. Much like in the laser induced plasma, this beam is directed to the target in any state where it is a source of energetic electrons that can then undergo any of the collisions mentioned previously (scattering, excitation, ionisation), which can create and sustain the plasma.

2.8.4 Shock Wave Generated Plasma

Rarely, plasmas are generated with the use of a shock tube, that utilises conservations laws in a shock wave to transfer energy into the gas via the relationship:

$$T_g \approx u^2 \times 10^{-9} \quad (2-5)$$

where T_g is the plasma gas temperature in Kelvin and u is the speed of the shockwave in centimetres per second, assuming a starting temperature of 300 K. This can also be expressed in terms of the Mach number, M , a ratio of the speed of the shockwave, u , and the speed of sound in the cold gas, c_s . In the case of hydrogen, ionisation begins at approximately $M \approx 20$, with the gas being fully ionised at $M \approx 70$, [121].

There are multiple designs of shock tube that can be utilised for this, the most basic of which being via a pressure-driven shock tube, which consists of two sections separated by a diaphragm. One section contains a driver gas of which pressure is increased until the diaphragm is broken, pushing the driver gas into the target gas like a piston.

Alternatively, there exist electromagnetic shock tubes that employ the z-pinch or θ -pinch of the gas, which use ohmic heating from the Lorentz force from an applied EM field. In this case the relationship is

$$p_2 = \frac{B^2}{2\mu} \quad (2-6)$$

where p_2 is the pressure of the target gas, B is the magnetic induction, and μ is the permeability.

A third method of shock wave generation is the coaxially driven shock tube, in which a discharge plasma is produced using a coaxial electrode as described previously. This plasma then acts as the piston as it travels through a tapered column, resulting in a shock wave as it reaches the target gas [122].

Pressure-driven shock wave systems are simple to construct however are limited in the strength of shock waves they can produce, typically $M < 50$, whereas electromagnetic and coaxially driven shock tubes can achieve much higher Mach numbers [121].

Shock wave generated plasmas are generally not stable either temporally or spatially, and have found only limited industrial applications [123], instead being primarily used for research purposes [124].

2.9 Plasma Tuning

Generation of plasma often requires additional equipment within the system, to enhance plasma coupling resulting lower reflected power and thus higher efficiency.

Impedance matching is an important aspect of system tuning, and works to match the impedance which is an evolved consideration of resistance in a circuit, also taking into account the reactance. The impedance of a plasma (Z_p) is given by

$$Z_p = X_p + jY_p \quad (2-7)$$

Where X_p is the resistive part, Y_p is the reactive part, and j is the imaginary unit [125].

The resistive part, X_p , can be further defined as

$$X_p = \frac{\lambda_p}{en_e\mu_e S_p} \quad (2-8)$$

Where λ_p is the plasma thickness, n_e and μ_e are the electron density and mobility respectively, and S_p is the average sectional area of the two electrodes of area S_1 and S_2 between which the plasma is generated

$$S_p = \frac{S_1 + S_2}{2} \quad (2-9)$$

The reactive part, Y_p is given as

$$Y_p = L_p \omega - \frac{1}{C_p \omega} \quad (2-10)$$

Where L_p is an inductive component due to electron oscillations between collisions, given as

$$L_p = \frac{X_p}{v_{eN}} \quad (2-11)$$

Where v_{eN} is the collision frequency between electrons and neutral particles, and C_p is a capacitive component due to the sheaths, approximated by

$$C_p \approx \epsilon_0 \left(\frac{S_1 S_2}{\lambda_{s1} S_2 + \lambda_{s2} S_1} \right) \quad (2-12)$$

Where ϵ_0 is the permittivity of free space, and λ_{s1} and λ_{s2} are the sheath thickness of the stressed and ground electrode respectively.

Impedance matching is achieved when the impedance of the circuit, which consists of the plasma and all ancillary parts and is given by

$$Z_{eq} = X_{eq} + jY_{eq} \quad (2-13)$$

equals the impedance of the generator.

This is satisfied when

$$X_{eq} = R_s \quad (2-14)$$

Where R_s is the output resistance of the generator, and

$$Y_{eq} = 0 \quad (2-15)$$

There are multiple ways in which this can be achieved or neared including both during the design and construction of the plasma system, and reactive tuning during plasma operation.

Manual tuners are generally of fairly rudimental design: the stub tuner is common and consists simply of 2 - 4 plunger screws that are raised or lowered in the chamber by hand, or alternatively they can be automatic for rapid and precise real time tuning of the plasma [71]. A sliding short can also be used to tune the power delivered to the plasma. Another active method of impedance matching is by adjusting the frequency outputted at the generator to reduce reflected power.

Tuning can also be done passively using physical components such as capacitors and inductors [126].

Systems are also often equipped with circulators, which protects the system from reflected microwave power by diverting it to a dummy load such as a reservoir of water away from both the plasma and the generator [127].

2.10 Dielectric Barrier Discharge

A popular method of plasma generation is using a dielectric barrier discharge (DBD), which similar to the ICP system makes use of a dielectric that separates the electrodes. The dielectric barrier, often quartz, glass, or in some cases a ceramic or polymer [128], works to prevent arcing between the electrodes upon application of an AC current, instead promoting formation of a number of micro-discharges or streamers, that produce plasmas in the gas flowing between [129]. Applied voltages generally range between 1 – 100 kV at frequencies in the kHz range, although research into higher frequencies of 1 MHz or higher is increasing [130]. Electrodes exist mainly in either planar format, where flat electrodes are parallel to each other, or cylindrical where the outer electrode radially encompasses the inner, typically with a discharge gap of 0.1 to 10 mm.

Further, DBD construction typically falls into three categories:

2.10.1 Volume Discharge (VD)

The most basic and thus frequently seen design, where two parallel electrodes are separated by a dielectric layer and a gas gap (Figure 2-27). The discharges are axially symmetric and distributed randomly in the gas layer which is generally no more than a few millimetres wide. For electronegative gasses such as air and oxygen their prevalence increases with an increase in applied voltage, however the amplitude of the current pulse per micro discharge is independent of this and thus charge is transferred in discrete quantities [131].

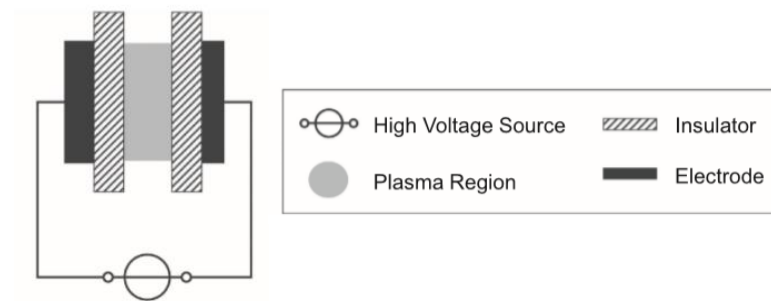


Figure 2-27 Diagram of a volume discharge (VD) configuration [130].

The majority of the work presented in this thesis was conducted with volume discharge dielectric barrier discharge torches. This is due to its simplicity and robustness of construction, favouring it to industrial applications, and also that the plasma is generated within the torch and expelled onto the surface via flow of gas, protecting the plasma generation region from adverse environmental conditions, such as in dusty desert environments.

2.10.2 Surface Discharge (SD)

In contrast to the case of the volume discharge, in a surface discharge there is no gas gap in between the electrodes separated by the dielectric barrier (Figure 2-28). Instead, one of the flat electrodes is replaced with a smaller elongated electrode that makes contact with the dielectric, with the discharges forming on the surface of the dielectric barrier around the smaller electrode.

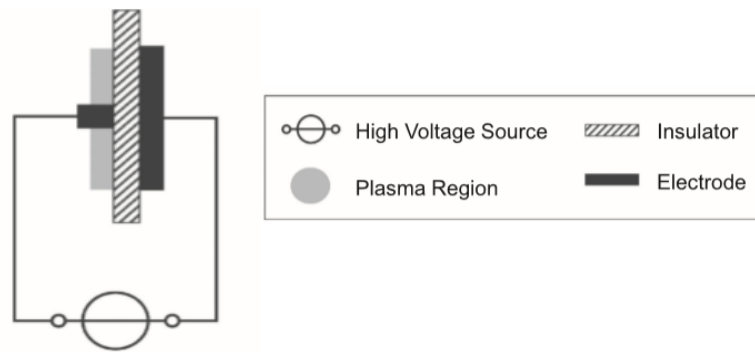


Figure 2-28 Diagram of a surface discharge (SD) configuration [130].

2.10.3 Coplanar Discharge (CD)

Occasionally, both of the electrodes are embedded within the dielectric, and the discharges form on the surface of the barrier (Figure 2-29).

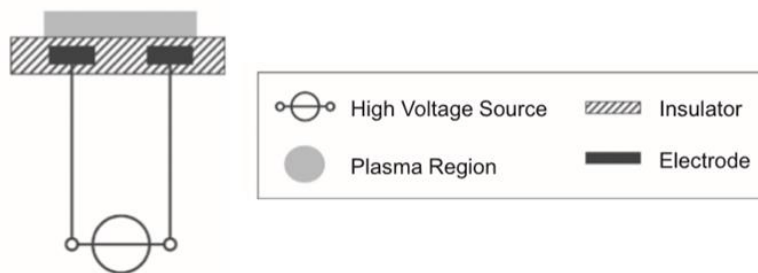


Figure 2-29 Diagram of a coplanar discharge (CD) configuration [130].

2.10.4 Packed Bed Reactor

For some applications the gas gap is filled with other materials such as glass beads or wool (Figure 2-30), which depending on composition and shape can have benefits such as enhancement of the electric field produced or increased catalytic reactions [132].

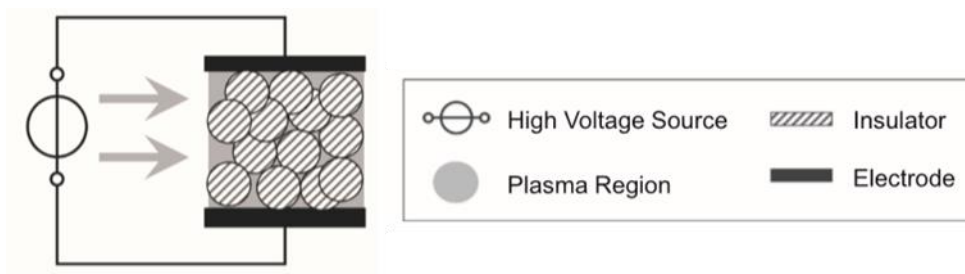


Figure 2-30 Diagram of a packed bed reactor configuration [130].

2.10.5 Plasma Jet

A variation of the Volume Discharge, it is possible to create a jet plasma with a DBD setup, this is usually achieved by flowing the gas through a coaxial electrode and dielectric arrangement at a sufficient rate such that the plasma extends out of the device, examples of which can be seen in Figure 2-31.

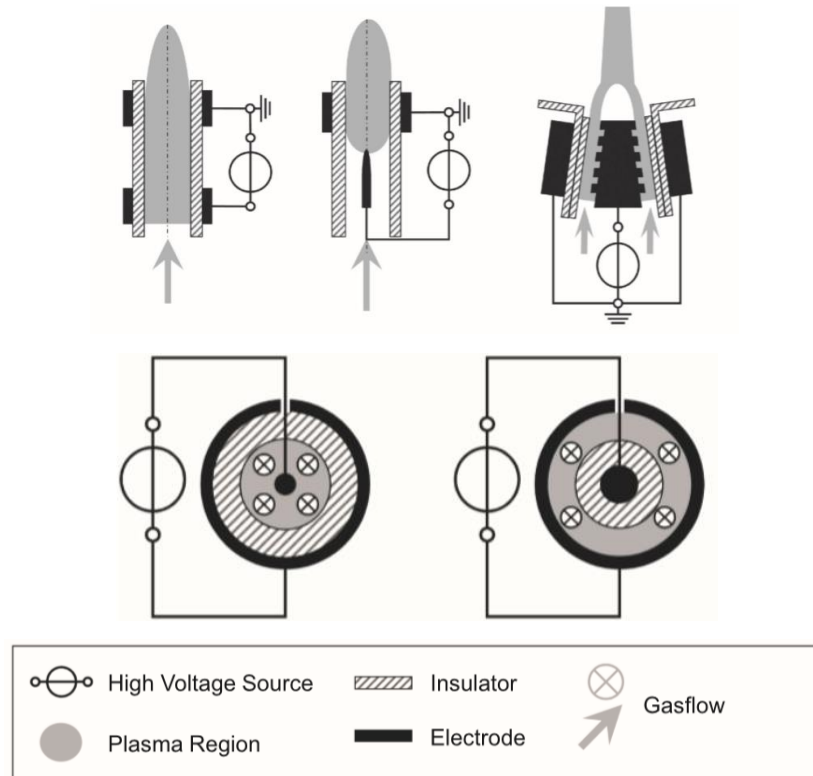


Figure 2-31 Plasma jets created via different electrode and dielectric configurations (a) and schematics of coaxial configurations that may facilitate these (b) [130].

2.11 Plasma Formation

The volume discharge is what is seen most frequently in practical applications, and is the type of torch used for the majority of the work here and so the subsequent writings are in reference to the VD setup.

Transport of charge across the gas gap during can be broken down into three distinct phases as described below and shown in Figure 2-32. All figures noted are for a DBD operating in atmospheric pressure.

2.11.1 Avalanche Phase

Seed electrons released from the cathode create an electron avalanche upon interaction with ions and atoms in the gas gap. Charge transfer between the electrodes during the avalanche phase is effectively nil due to negligible space charge effects. As the negatively charged electrons travel towards the anode, positively charged ions accumulate at the cathode producing a radial field strength. Eventually the induced electric field becomes great enough to initiate breakdown in the gas.

2.11.2 Streamer Phase

When the electron avalanche arrives at the dielectric shielding the anode, a streamer is formed. The streamers travel at high speeds of around 10^8 cm s^{-1} across the gas gap towards the cathode, during which the current transfer increases and the discharge voltage decreases [133]. Upon reaching the cathode the streamer creates a near cylindrical channel of around $200 \text{ }\mu\text{m}$ diameter [134] and electron densities of up to $10^{13} - 10^{14} \text{ cm}^{-3}$ [135] that connects the electrode with the dielectric at which point the electric field and discharge current reach their maximum, whilst the discharge voltage continues to fall as the barrier voltage increases.

2.11.3 Decay Phase

After around 10 ns when formation of the channel and transfer of charge is complete the streamer begins to decay. After a further 30 ns the electric field wanes and discharge current fall to zero.

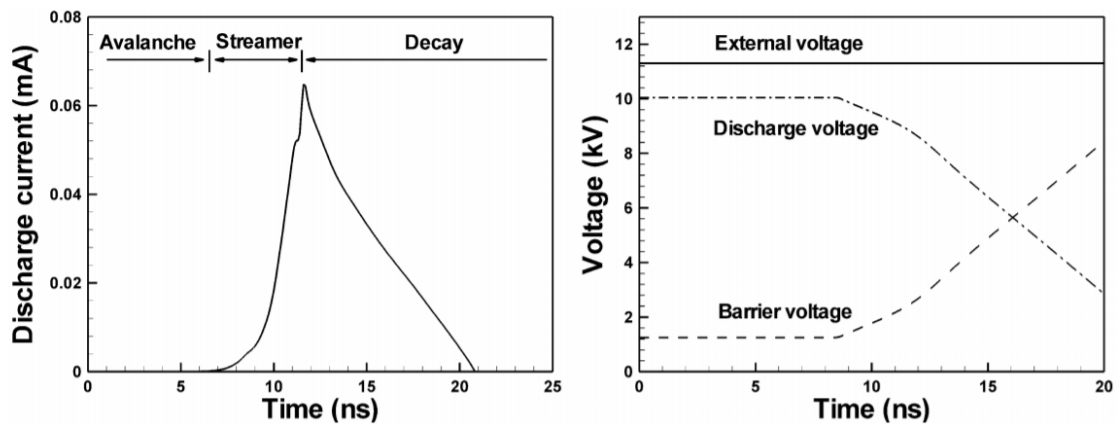


Figure 2-32 Current (left) and voltage (right) profiles of a microdischarge [135].

When considering only the electrons, the process of streamer formation and decay lasts only around 40 ns with each microdischarge capable of transporting around 100 pC of charge, however the heavier ions produced are slower to dissipate and can remain in existence in the gas gap for several microseconds [133]. It is also important to consider the heat created during discharge, as for an oxygen plasma a maximum temperature increase of 350 K may be achieved per microdischarge at the cathode layer, resulting in an average increase of 10 K across the gas gap [129]. Considering the vast number of microdischarges that will occur this creation of heat is likely to be problematic and as such DBD systems often necessitate the inclusion of a cooling system.

During the microdischarge process electrons from the avalanche are deposited onto the dielectric surface resulting in a local build-up of negative charge that momentarily prevents streamer formation in the immediate vicinity, this also results in the distribution of discharges over the entire area of the dielectric producing a “slab” plasma as opposed to the jets seen in other generation methods. Where a jet is required, the gas can be flowed through the gap at a higher rate, pushing the produced plasma out of the gas gap creating a torch device.

As DBDs are propagated via an AC power source, the voltage polarity will periodically be reversed and the deposited electrons now become a source for a new streamer travelling in the opposite direction, however it is often observed that after this switch in polarity, when it is now the cathode shielded by the

dielectric and the anode is in contact with the gas gap, that instead of discrete channels of discharge the charge transfer become a more homogenous stream of electrons between the surfaces [136] as shown in Figure 2-33.

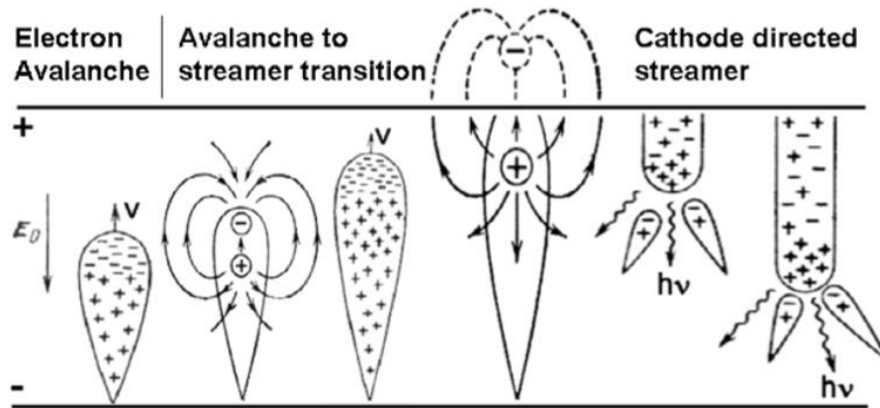


Figure 2-33 Evolution of a discharge with time [133].

2.12 Advantages and disadvantages of Dielectric Barrier Discharges

DBD systems are of great interest to industrial and research applications as they present many advantages over other methods of plasma generation.

A major benefit is that they can be operated with stability over a range of pressures from 10 kPa right up to 500 kPa, reducing the need for costly and time consuming vacuum formation. Similarly their range of operating frequencies is large, with ideal operation between 1 kHz and 10 MHz [134]. They additionally can produce larger areas of plasma owing to the protective effects of charge build-up on the dielectric, resulting in reduced processing time where the plasma is required to act upon an area and where arcing or temperature inhomogeneity may damage a workpiece [137]. DBD systems can exist individually at scales of a few millimetres, or can be scaled up in arrays of potentially thousands of devices or as large individual units [138].

The robust nature of DBD systems also enable ignition and generation of plasma without tuning elements such as waveguides or impedance matching, however a drawback of this is that the energy efficiency of DBDs is often low. To increase

efficiency, the torch design can be optimised such that the geometry is matched to the plasma generated, use of a generator with a tuneable frequency can also improve efficiency.

Another drawback of DBD technology is that the most active plasma region is within the torch itself, and whilst it is expelled in part through the torch opening, energy is lost in this process and so the desired processing may be less efficient in this afterglow area, with reactive species quenched before they exit the torch. Gas flow can be increased to increase the expulsion from the torch, however this also reduces residence time of the gas in the plasma region, so it gains less energy in doing so. A balance must be sought to allow sufficient energy in the plasma and also that the plasma is sufficiently ejected from the torch.

2.13 Dielectric Barrier Discharge Design Examples

DBD systems in essence all consist of the same basic components: electrodes of opposite polarity separated by a dielectric; however there are many variables within these components that can be tailored to produce a plasma most appropriate for its application. Discussed below are a number of DBD systems designed for specific industrial or research applications.

2.13.1 Treatment of a Surface

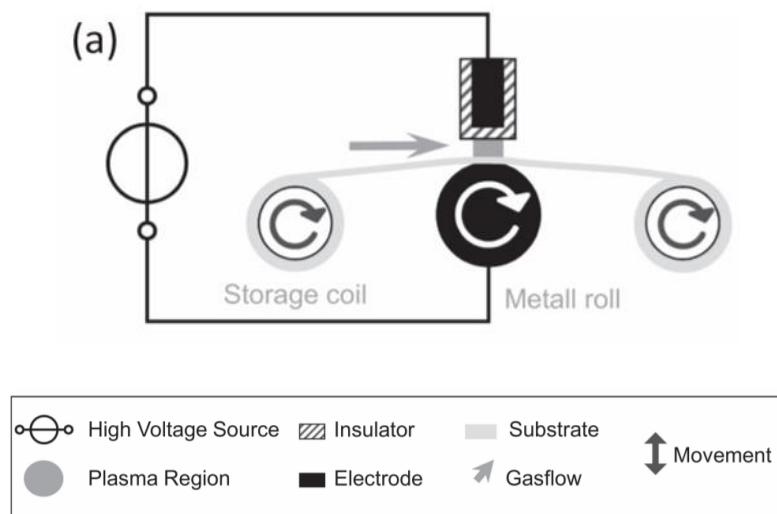


Figure 2-34 Diagram of a DBD system designed for plasma treatment of a film [130]

As discussed previously, DBD systems lend themselves to surface processing owing in part to their comparatively low gas temperatures and a larger area of plasma production. The system shown in Figure 2-34 utilises a metal roller as the ground electrode, over which the substrate passes. In setups such as this the dielectric can be either shielding the upper separate electrode, as in the diagram, or coating the roller [139]. The rollers enable considerable lengths of substrate to be processed continually, with exposure times being controlled via the speed of the rollers. Alternatively, for surfaces that are not suitable to be fitted on a roller, the substrate can be placed atop the lower electrode and will be subject to stationary exposure to the plasma. A limitation of this approach is that the substrate must be adequately conductive to allow the transfer of charge between the electrodes. In the case where the surface to be treated is metal, it can form the electrode itself [140]. DBD treatment of surface can be tailored to produce a range of desired effects including making a surface either more hydrophobic [141] or hydrophilic [142], to clean [143] and improve adhesion of a surface [144].

2.13.2 Production of Ozone

Ozone production is the earliest industrial application of the DBD system, with Werner von Siemens pioneering the technique as early as 1957, a diagram of the apparatus used is shown in Figure 2-35. [145].

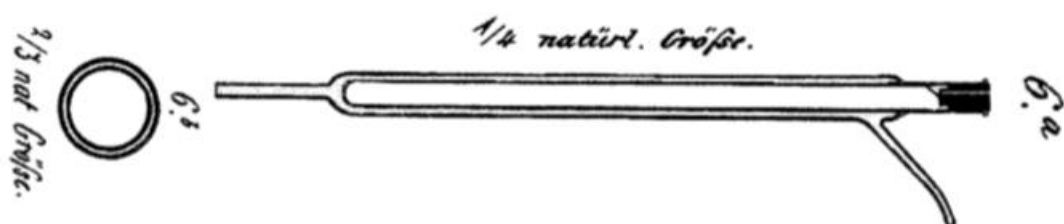


Figure 2-35 Cavity surrounded with dielectric for the purpose of ozone generation [146].

In typical industrial ozone production, air is fed between cylindrical glass tubes of diameters between 20 and 50 mm and from 1 to 3 metres in length which act as the dielectric between the two electrodes: an outer steel tube serving as the ground electrode and allowing around 1mm radial gap, and a special conductive

film applied to the inside of the glass that is connected to the high voltage supply [128].

When fed with air, ozone is produced via the following route, first with the creation of oxygen atoms, primarily through dissociation of O_2 molecules



But also through collisions of excited nitrogen molecules with oxygen



Oxygen atoms then readily combine with oxygen molecules to form ozone



Where M is a third-body collision partner [147].

Multiple of these individual units are stacked together in large chambers to enable production of vast quantities of ozone that can then be used in processes such as water treatment and bleaching.

2.13.3 Decontamination of Gas

DBDs have gathered attention for their use in removal of unwanted compounds from gasses, such as pollutants emitted by diesel engine exhausts or fossil fuel power stations [148] [149]. Typically these may make use of the packed bed type DBD as show in Figure 2-36, or feature a mesh electrode, shown in Figure 2-37, that can allow the contaminated gas to pass through whilst ensuring it comes into contact with the plasma for sufficient time [150][151]. The composition and geography of the medium with which the gas gap is filled in packed bed DBDs can be tailored to enhance the contaminant removal rate.

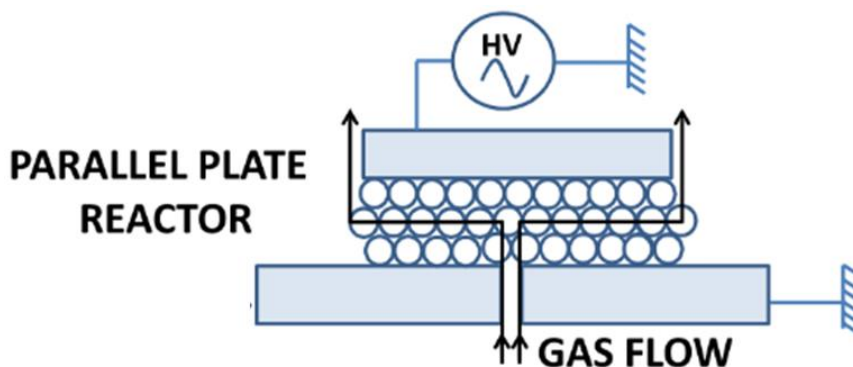


Figure 2-36 Packed bed DBD for processing of gas [152].

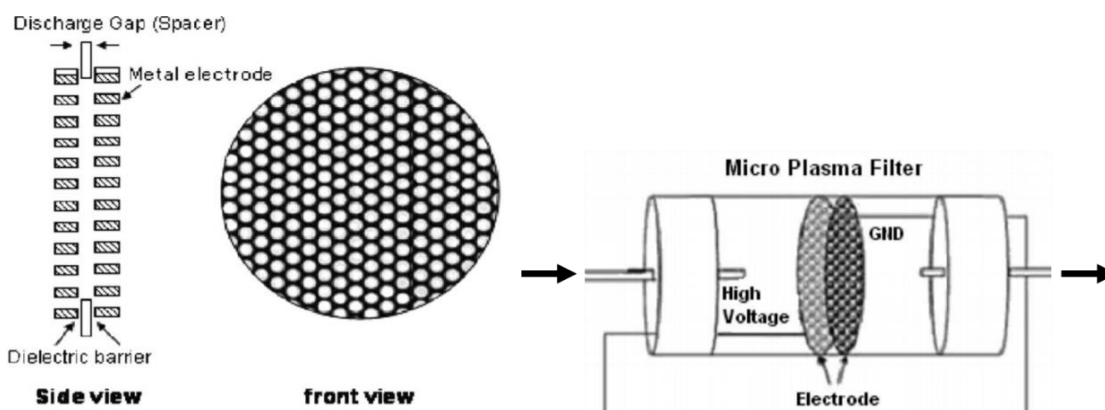


Figure 2-37 Mesh electrode DBD for removal of pollutants from a gas, shown in details (left) and in situ as part of the dielectric barrier discharge (right) with direction of gas flow indicated by arrows [153].

In these applications, pollutants are primarily removed not by the plasma itself, but instead upon reaction with species created by the plasma such as ozone or $N(^4S)$ [153] a technique that is often enhanced with the inclusion of a catalyst [154].

2.13.4 Plasma Screen Televisions

A frequently seen yet perhaps little appreciated application of the dielectric barrier discharge is in plasma screen technology. In this case, each pixel comprises of three separate cells, or occasionally long troughs, shown in Figure 2-38, filled usually with noble gasses and a small quantity of mercury. Each cell is lined with

a phosphor based coating of various compositions, and is bound at the rear by an electrode, and at the front by a dielectric layer and then a fine mesh or transparent electrode, followed by the glass [68]. Upon power up of each DBD cell, UV light is released by the mercury within the plasma which is then absorbed by the phosphor coating and subsequently re-released as either red, green, or blue visible light depending on the coating composition. Although plasma television screens have largely fallen out of favour having been replaced with OLED and LCD technology, DBD's use in plasma screen technology is testament to its commendable versatility, as each cell can be less than 0.5 mm across, a minute size that would be almost impossible for any other plasma generation method [155].

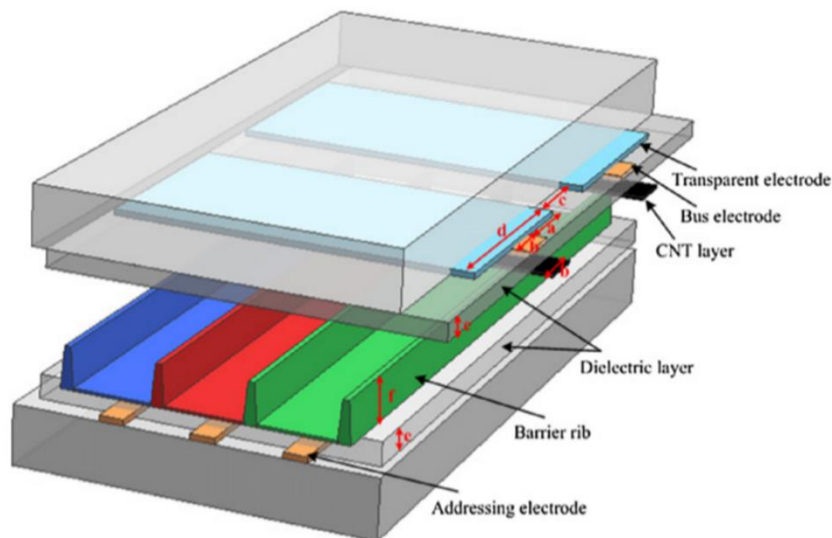


Figure 2-38 . Schematic of a section of rough design for plasma display, this design features carbon nanotubes (CNT) in the dielectric layer to reduce required sustain voltage [156].

2.14 Plasma for Cleaning

Plasma is a proven cleaning technology and has been utilised extensively for various cleaning applications. It is applied frequently to remove contaminants and thus improve adhesion between surfaces such as polymers [157], for the removal of photoresists in semiconductor manufacture (known as plasma ashing) [158] and to remove Volatile Organic Compounds (VOCs) and hydrocarbons from surfaces [159], amongst other applications.

Plasma cleaning has been the subject of study and investigation and has been found to work via multiple mechanisms:

2.14.1 Etching

In plasma, the term etching can refer to two processes: chemical and physical.

Chemical etching occurs when reactive species is generated inside the plasma which then react chemically with the contaminants on the surface to be cleaned, creating a detached particle that can then be removed, often by application of a vacuum. In order to remove only the contaminants whilst not reacting the surface, the plasma composition must be carefully controlled. Typically a plasma torch is fed with oxygen (O_2) or a fluorine bearing gas such as carbon tetrafluoride (CF_4) [160]. Oxygen plasmas are typically used for removal of hydrocarbon contamination, as the reactive oxygen species produced reacts readily with carbon and hydrogen to form CO , CO_2 , H_2O which can then be easily removed by an applied vacuum or airflow system [161].

Etching may also refer to the physical removal of material via sputtering. An example of this is the use of inert argon to remove naturally formed surface oxides from metals [98]. No chemical reaction take place in during this, rather the energetic ions produced in the plasma strike the surface transferring energy to the oxide layer allowing it to break free from the surface.

Both physical and chemical etching are usually carried out in a vacuum, allowing the dislodged species to be removed an preventing their resettling.

2.14.2 Drying

Where particles of soiling are held to the surface via capillary forces, drying of the area will remove this mechanism of adhesion. Gas temperature (T_g) of a typical non-thermal DBD air plasma can be between 90 and 230 K above ambient gas temperature, which would enable evaporation of water within these capillary bonds [162].

2.14.3 Electrostatic

Although exhibiting overall neutrality, plasmas are comprised in part of charged particles. The production of these particles is used in a process known as electrostatic precipitation, where the charged species attach to particles of pollution which are then diverted by an applied electric field and collected on electrodes where they can then be removed [163]. This technique is already widely in use industry for the cleaning of flue ash and exhaust gasses, and can remove a large variety of pollutants [93].

2.14.4 Biological

Plasma is of increasing interest to the medical field as a tool to clean wounds and sterilise equipment. Non-thermal plasmas have been found to be an effective tool to inactivate viruses, bacteria, fungi, and other biomolecules. They can also be used in the destruction of biofilms, to clean water, and sterilise surfaces [164]. A benefit of Cold Atmospheric Plasma (CAP) in particular is that the low gas temperature and operation at atmospheric pressure allows the plasmas to be used in-situ on wounds without damaging healthy tissue, helping reduce wound healing times and reduce the risk of infection and complications [165].

2.15 Plasma Treatment of Glass

There has been considerable research into use of plasma for the treatment of glass surfaces with research generally focussing on low temperature atmospheric pressure plasma as glass is susceptible to thermal shock damage and becomes soft at around 700 °C [166]. Plasma treatment is split mostly between cleaning of the surface and surface energy modification. Commonly, cleaning is seen as the precursor to a main manufacturing process such as attachment of a coating or adhesion of an additional layer, where impurities on the surface can result in delamination or uneven coating deposition [167].

Whereas on metals where a contamination is often comprised of an oxide layer, the composition of contamination on glass is frequently organic, in particular human sebum (oil) from manual handling, lubricating oils from instruments used during precious manufacturing or processing, and volatile organic solvents. A

DBD plasma device using nitrogen with the addition of small (<0.2%) amounts of oxygen was found to be effective at cleaning these contaminants from glass via a two-step mechanism of action, where first UV emission from NO generated in the plasma was found to weaken the C-C bond, and then the oxidising radical $O(^3P)$, from ozone produced within the plasma, reacted with the broken bond and the resultant product was carried away from the surface [168].

Another study found that using a Diffuse Coplanar Surface Barrier Discharge (DCSBD) also reduced the incidence of C-C bonds on treated glass, with an overall reduction in proportion of carbon on the sample from 14% to 5 % [169].

For surface energy modification, plasma is often used to produce a hydrophilic surface on glass. A study explored the effect of plasma generated from dry air and pure nitrogen on samples of sodium silicate glass. Here when the plasma is applied to the glass surface, electrons collide with and break the O-OH bond on the surface, resulting in polar groups of atomic O and radical OH, as shown in Figure 2-39. This increases the surface energy of the glass, resulting a hydrophilic surface with water contact angles of down to 3.3° in this study [170]. Another study also showed an increase in polar oxygen containing surface groups and corresponding decrease in C-C and C-H groups on glass samples when exposed to air plasma [171], which resulted in an increased wettability.

The effect is also seen when a glass surface is treated with a plasma generated using pure argon, where one study found an increase in polar C-O (+6.6%) and C=O (+1.9%) surface groups alongside a decrease in C-C (-4.5%) bonds [172]. As this work was conducted in a vacuum the effect is likely due to contaminant removal and surface reorganisation as a result of electron bombardment, rather than incorporation of atmospheric oxygen species, as there was only a minor decrease in the proportion of Si-O surface groups (-1.9%).

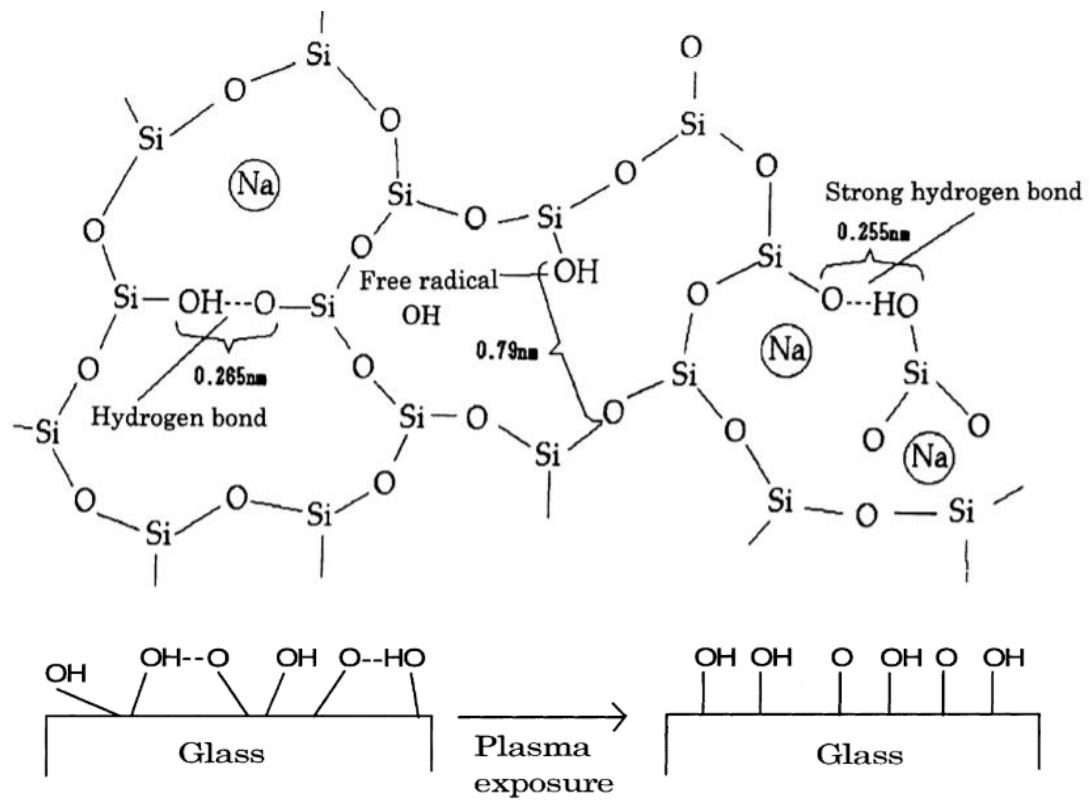


Figure 2-39 Molecular structure of sodium silicate glass (above), and the result of plasma exposure on this structure (below) [170].

3 Plasma Torch Summary

Multiple torches were investigated during this work, detailed here are the specifications and basic working principles behind each of the torches used.

All torches were non-thermal and operated at atmospheric pressure, as thermal plasmas would be unsuitable due to the risk of mirror damage, and vacuum or low pressure plasmas would be too impractical for CSP application.

3.1 Sairem S-Wave

Initial surface energy modification work was conducted using a Sairem S-Wave surface wave discharge torch, shown in Figure 3-1.

In this torch, power is transferred into the gas by microwaves from a generator, which travel along a coaxial cable into the torch before propagating longitudinally along the length of a dielectric tube, imparting energy into the gas as it flows through the tube. The plasma then flows out of the torch as a jet (Figure 3-2). Because of this, a raster pattern is necessary when processing areas greater than the jet footprint.

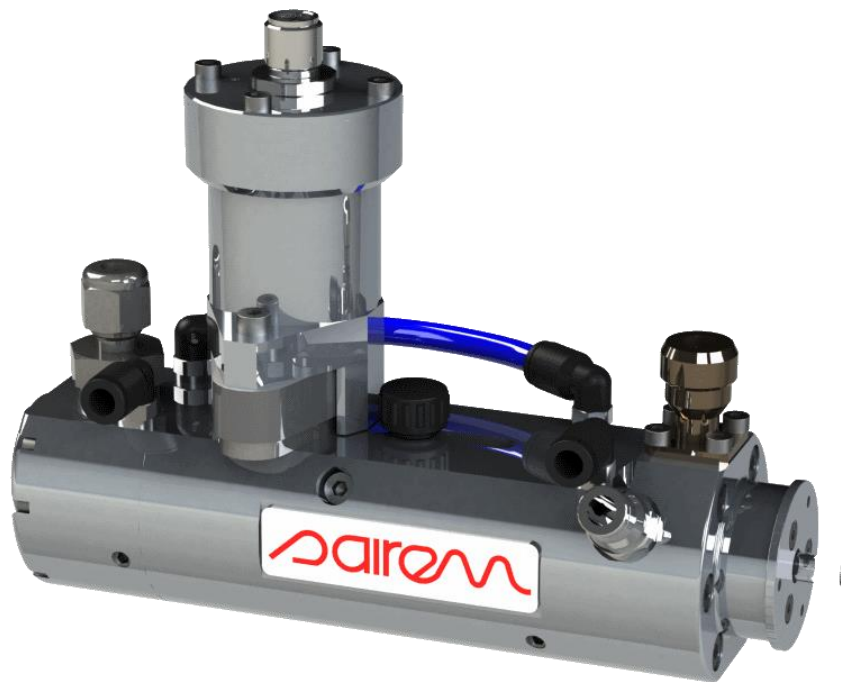


Figure 3-1 Sairem S-Wave torch [173].

Plasma tuning is achieved by two methods, autotuning of the frequency from the generator to reduce reflected power, and physical tuning of the cavity on the torch via a sliding short. These tuning methods allowed for effectively 0% reflected power returning to the generator.

The power was controlled via a microwave generator between 50 and 200 W and the gas was pure argon at 10 L/min. Frequency from the generator was approximately 2.45 GHz, varying slightly due to the autotuning.

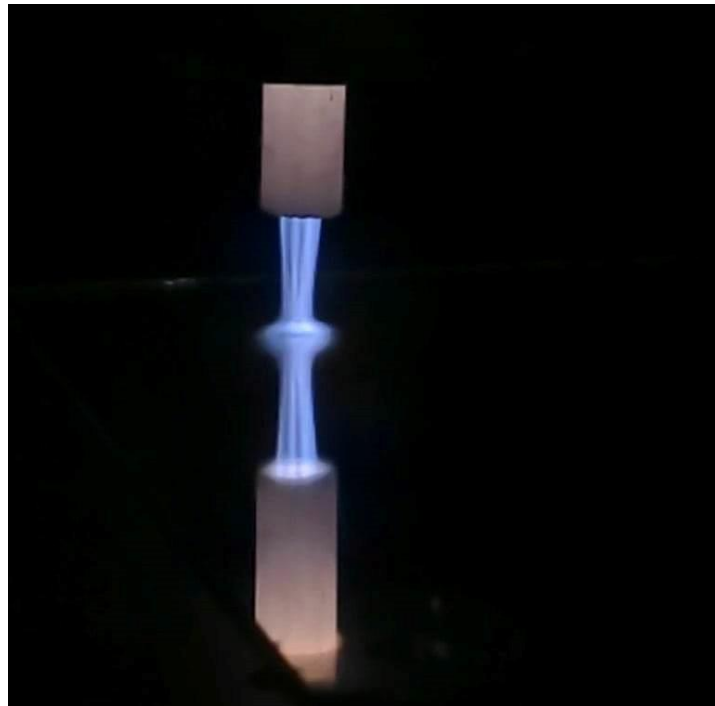


Figure 3-2 Processing of a mirror sample using the Sairam torch.

It is important to note that, whilst the Sairem torch was technically non-thermal in that the temperature of the electrons was much greater than the temperature of the heavy ions, it still generated significant heat and did result in the melting of some mirror samples during initial stationary dwell experiments. It is for this reason, and because the torch was a single point jet and therefore had a smaller footprint of processing, that it was only used for initial experiments and was not used for the main experimental work.

3.2 Adtec M-CCMD Torches

The bulk of the work conducted was with DBD type torches provided by Adtec Plasma Technology Co. Ltd., assigned the titles of “M-CCMD”, which stands for Multi – Capacitively Coupled Modified Discharge. There were three versions of the torch, designated here as M-CCMD 1, M-CCMD 2, and M-CCMD 3. The M-CCMD series of torches did not have any tuning mechanisms. Each torch was an improved version of the version that preceded it, with data and observations being reported back to the industrial sponsor Adtec Plasma Technology Co Ltd to allow them to update their designs with each iteration.

3.2.1 M-CCMD 1

The majority of the characterisation work was conducted on M-CCMD 1, where it was found to consist of a ceramic dielectric inside which 7 channels carried the flow of gas. Groups of electrodes were positioned inside the dielectric at the 7 channels to impart energy into the gas and produce the plasma, visible in Figure 3-3. These electrodes were connected via coaxial cable to a generator through which power was controlled via outputted current at 0.9 A. Gas flow was controlled independently of the plasma generating equipment via a Brooks mass flow controller. The torch did not have any cooling system and so could only be operated for a few minutes at a time before it had to be switched off and allowed to cool with the assistance of the unignited gas passing through the torch. Due to the segmented plasma generation, raster processing was necessary for large areas (Figure 3-4).

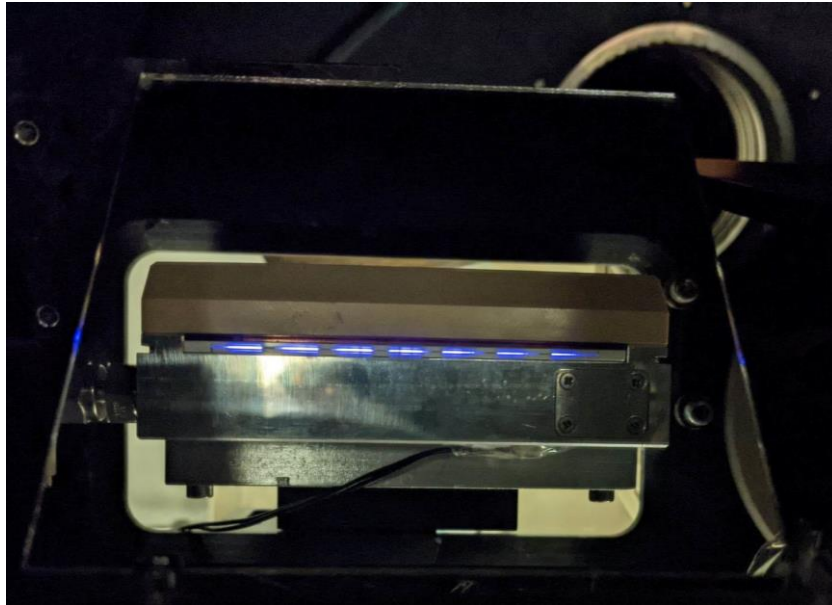


Figure 3-3 Plasma generation pattern of the M-CCMD 1.

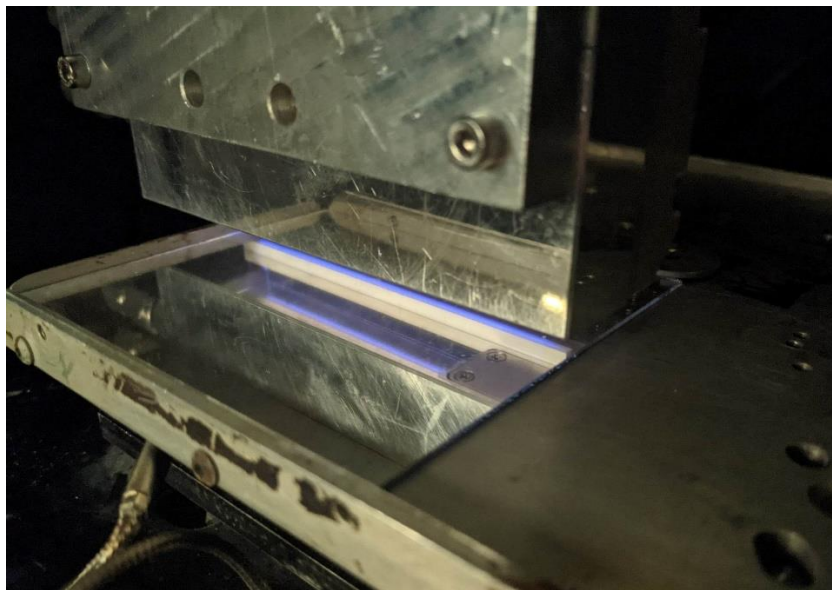


Figure 3-4 Processing of a mirror sample using the M-CCMD 1.

3.2.2 M-CCMD 2

This torch was not used extensively in this work. It was similar to the M-CCMD 1 in that it consisted of 7 gas channels inside a dielectric, however it featured a liquid cooling system, in which coolant was pumped through the torch by an external chiller unit, which allowed for the torch to be used continuously. This

allowed it to be used for optical emission spectroscopy that required longer running times, such as the temporal stability investigation.

3.2.3 M-CCMD 3

The majority of the hybrid washing and surface energy modification work was conducted with the final iteration of the torch, the M-CCMD 3. This was because, unlike the previous two versions, the third torch did not have the 7 channels, instead distributing the gas flow evenly across two separate ceramic dielectric plates as shown in Figure 3-5. This resulted in a wider area of processing per pass, and so removed the need for raster processing, allowing the mirrors to be processed in one motion.

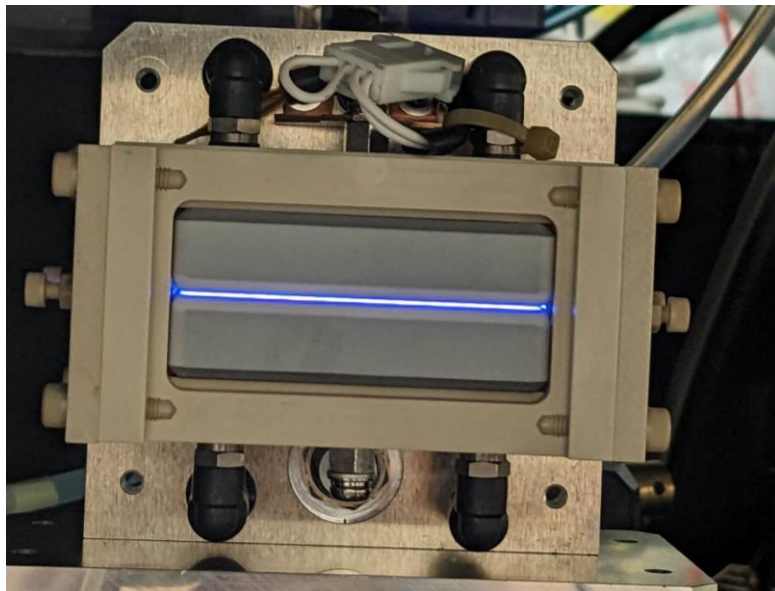


Figure 3-5 Plasma generation pattern of the M-CCMD 3.

Electrodes were still embedded into the dielectric plates and powered via the same generator, however the maximum current it would accept from the generator was significantly lower, at 0.33 A.

This torch also had a coolant system, this time using compressed air, however it was not used during processing work as it added instability to the dielectric plates.

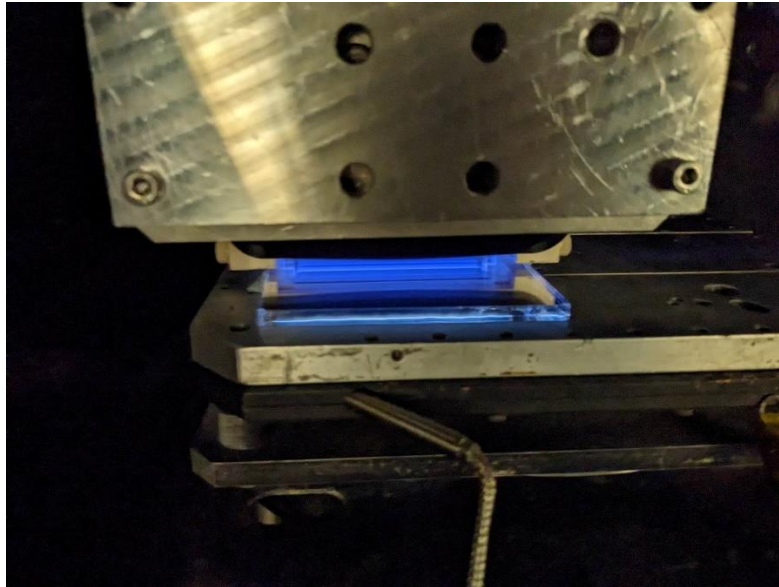


Figure 3-6 Processing of a mirror sample using the M-CCMD 3.

This setup produced a region of plasma approximately 60 mm wide, meaning the mirror samples did not need to be raster processed and instead could be processed in one single pass (Figure 3-6).

3.2.4 Generator

The generator used for the M-CCMD torches was also provided by Adtec Plasma Technology Co. Ltd, a photograph of which is shown in Figure 3-7. It had a maximum power of 300W and provided a 50 kHz output of 2.8 kV peak or 5.6 kV peak to peak. Power to the torch was controlled via output current which varied by torch type, the available range was 0.2 A for ignition and up to 0.9 A for torch running, in steps of 0.01 A. The generator also allowed for monitoring of the torch temperature via a sensor mounted in each torch. Figure 3-8 shows the display panel of the generator with the plasma running, where D1 is the Duty Cycle and I1 is the current, here 0.30A.



Figure 3-7 Photograph of generator used for the M-CCMD torches.



Figure 3-8 Close up detail of generator display panel.

The generator had safety cut outs when the duty cycle or temperature went beyond safe limits.

3.2.5 Torch Characterisation

3.2.5.1 Introduction

To better understand how plasma is generated within the torch, X-ray computed tomography (XCT) of the M-CCMD1 torch was employed to reveal the internal construction of the torch. Whilst not analysis of the plasma itself, knowing the physical layout and characteristics of the plasma generating device can help in interpreting data from the generated plasma.

3.2.5.2 Scientific Principle

XCT is an imaging technique whereby multiple 2D X-Ray scans of an object are obtained and collated such that a 3D image can be produced. X-Rays are produced by accelerating electrons through a high voltage and allowing them to collide onto a metal target, producing high energy photons. These photons are then directed towards the object of interest where they may interact with the object in one of three ways: primarily photoabsorption; although Compton scattering and Rayleigh scattering also occur. Photoabsorption is dependent on both the energy of the photons and the atomic number of the matter of the object, thus where the energy of the incident photons remains constant an image of shadows will be formed on the detector plate dependant on the elemental composition of the object. In industrial XCT systems the object is typically placed on a stage where it is rotated between image captures, creating a series of 2D images that can be used to produce a 3D map of the object [174].

3.2.5.3 Methodology

XCT images were obtained at the National Physical Laboratory (NPL) in London, UK, using a cone-beam X-Ray source with a beam energy of 170 kV, beam current of 80 μ A, and a power of 13.6 W. During imaging the M-CCMD1 torch was placed on its side onto a turntable within the machine enclosure between the X-ray source and the detector, which was connected to a computer with appropriate software. The turntable was rotated 45° between image captures.

3.2.5.4 Results

Figure 3-9 shows a single 2D image of the torch, rotated 90° clockwise to reflect the torch's position in operation, as it was stood on its side for image capture. The shadowing seen to the right is the turntable of the equipment upon which the torch was placed.

Most obvious in the image is a large rectangular area of shadow in the centre, where the photons were not able to pass through the material, indicating it consists of a high z-number element. This object appears to be connected to some wiring components that in turn connect to the power supply connection at the top of the torch. Thus it is likely that the material creating the shadowing is a copper component (atomic number 29) and part of the electrode system. Due to this significant shadowing it was not possible to create a 3D map of the torch and as such only 2D scans are presented.

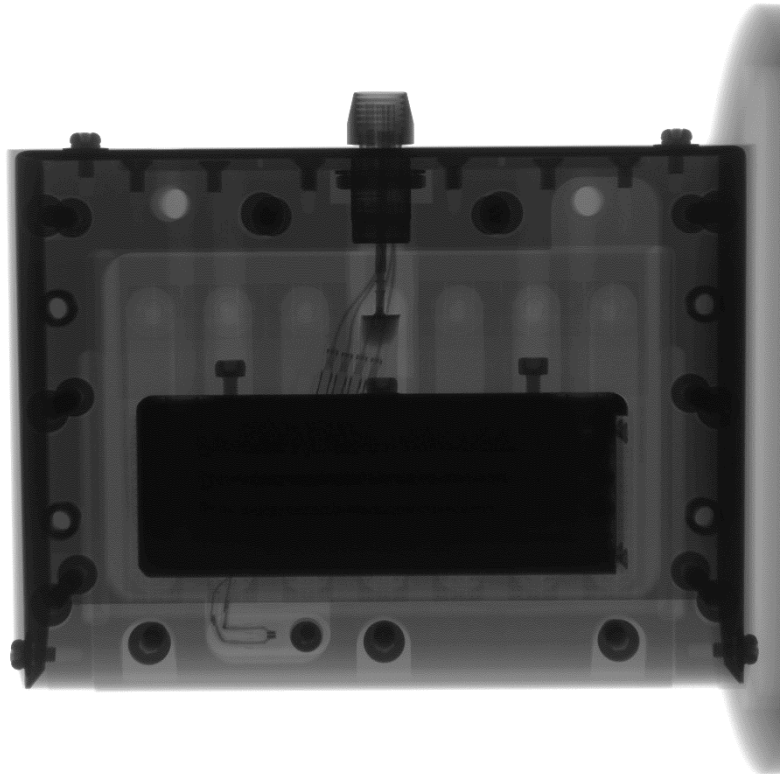


Figure 3-9 XCT image of M-CCMD1.

Also of importance on Figure 3-9 is the location of a thermistor type temperature sensor visible at the lower left, which is connected via cable to the generator where it triggers an automatic safety shutdown at 80 °C. This appears to be

independent of the electrode system, instead embedded in a material of low atomic number, therefore it is therefore likely that temperatures within the torch may exceed 80 °C before the safety threshold is reached at the sensor's location. Separately, there is evidence of 7 vertical channels, part of a lighter region that extends to the upper right hand side of the torch where the gas line enters the device (not visible on this image). Therefore, it can be assumed that these lighter regions are channels intended to distribute the gas from one side of the torch equally across the electrode area.

Of final note on the images were what appears to be arrays of small, stacked structures of a material of higher z-number than its surroundings (shown Figure 3-10, taken at a vertical rotation of 225° from Figure 3-9). These structures consist of three stacked layers of 4 points positioned within a square, and correspond with the position of the gas channels, suggesting they may form part of an electrode network.

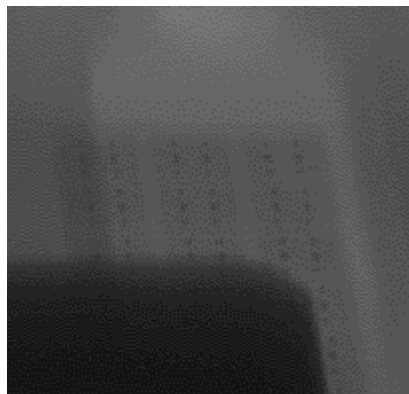


Figure 3-10 Details of stacked electrode structures in the gas channels.

3.2.5.5 Discussion

Whilst it was not possible to obtain a 3D scan of the torch using XCT techniques, the 2D images still provide beneficial information, for example on the potential electrode system of the torch, and also distribution of the gas flow once it enters the torch. The position of the temperature sensor means the temperature data obtained from the generator display should not be taken as plasma or electrode temperature, as it is located a significant distance from these. Care must therefore be taken to avoid overheating of the torch internals components, as it is not known what temperature is reached within the torch before the safety

threshold is reached at the temperature sensor. It is thus advisable that low gas flows are avoided for significant periods of time.

The suspected gas channels observed may help with even distribution of gas within the torch as the inlet gas line is positioned to the side of the torch, however there appears not to be any sort of chamber for mixing of these flows, and so it is likely the torch will not produce a homogenous region of plasma at its exit, which would significantly impact processing requirements.

4 Plasma Characterisation

Characterisation is a vital tool in all stages of processing and provides valuable information for understanding the fundamental science of processes, and in turn the ability to more accurately and precisely control the outcomes. For example, knowing the presence and relative abundance of species can provide information on potential interactions with the soiling or mirror surface. Knowing the spatial and temporal distribution of these species and the plasma as a whole can influence processing parameters and eventually improve torch design. For example, optical emission spectroscopy showed the uneven distribution of plasma in the MCCMD-1 and M-CCMD2 torches, and so for the M-CCMD3 torch the design and construction plasma generation region was significantly altered, to produce one homogenous region of plasma generation, which benefitted processing.

Characterisation of atmospheric pressure plasmas typically entails variations of spectroscopy, such as optical emission spectroscopy (OES) [111] or absorption spectroscopy [175], which can identify composition of species present and their abundance. Chemical composition of plasma can also be determined through the use of detectors and sensors [176]. Electrical characteristics such as voltage and current can be investigated to determine temporal patterns of plasma discharge [177], as well as high speed photography which can also be employed to monitor discharge morphology and streamer distribution and propagation [178]. Plasma temperatures can be measured directly with equipment such as Langmuir probe; which is able to measure characteristics such as electron temperature and density [179], or enthalpy probes, which calculate plasma enthalpy from the transfer of energy to the probe sheath [180][181][182]; or indirectly via the fitting of known curves to data obtained through OES [183].

In this chapter, characterisation of the plasmas produced are presented and discussed.

4.1 Plasma Characterisation

4.1.1 Optical Emission Spectroscopy

4.1.1.1 Introduction

Optical Emission Spectroscopy is perhaps the most widely utilised method of plasma diagnostics, here it is employed to provide information on the plasmas' composition, distribution, and temporal stability.

4.1.1.2 Scientific Principle

All matter is composed of atoms, which themselves are composed of a positively charged nucleus containing protons and neutrons, around which negatively charged electrons orbit in discrete shells referred to as energy levels. Electrons have the ability to transfer between shells, jumping further from the nucleus with an input of energy, or falling down towards the nucleus. When an electron drops an energy level it releases energy as photons, and as the shells are discrete and quantified, so too is the energy package released. In a plasma, processes of excitation, de-excitation, ionisation, and recombination occur constantly, and by measuring the wavelength and intensity of the photons released during the emission transitions it is thus possible to know the electrons transitions occurring and in turn the molecular and elemental composition of the plasma [184].

4.1.1.3 Methodology

For spectroscopy work, an OceanOptics HR4000 spectrometer (serial number HR4C24031) in the wavelength range 400-850 nm was used, with optical resolutions of 0.06 nm and 0.24nm (FWHM) respectively, as well as an OceanOptics USB2000 spectrometer (serial number USB2H115902) with the range 200-500 nm and optical resolution 0.16 nm. The USB2000 spectrometer was calibrated only in the range 200-400 nm and so the range 400-500 is excluded from data analysis. Both spectrometers are linear array 2048 element Charged Coupled Device (CCD) type spectrometers [185][186].

For the HR4000 spectrometers, a collimating lens of diameter 5 mm was placed below the opening of the dielectric at a distance of 10mm, which is the focal length of the lens. This lens was connected to the spectrometer via an optical fibre as

shown in Figure 4-1, and the spectrometer connected to a computer for data capture and analysis.

The lens was mounted onto a motion stage and for spatial mapping was moved beneath the plasma in x and y.

For the USB2000 spectrometer a cosine corrector was used in place of the collimating lens, and whilst this does not have a focal length as the collimating lens does, a height of 10 mm was maintained for consistency.

Data collection was controlled via OceanView software from the spectrometer manufacturer (OceanOptics, 2018).

Firstly, static spectra were obtained to ascertain the molecular composition of the plasma produced using feed gasses of oxygen, nitrogen, and air. For this, gas flow was set to 40 L/min and current from the generator at 0.9 A. The stage was moved such that counts were maximised, and a static measurement taken.

Temporal data was obtained similarly, with the lens remaining stationary beneath the plasma, and measurements taken once a second for one hour.

For spatial mapping, the stage was moved beneath the plasma at a speed of 100 mm/min with a measurement taken every 0.1 seconds, meaning each datapoint represented 0.167 mm. Each map consisted of 30 rows in the x axis at increments of 0.1 mm, covering a total range in y of 3 mm. To ensure the whole area was covered the distance travelled in the x axis was 120 mm, with either end trimmed during data processing to exclude datapoints where no plasma is generated

Owing to the physical dimensions of the torch it was not possible to position the lens horizontally to measure emissions at the opening of the torch and variations of these in the z axis.

Integration time was 100 ms throughout, with the exception of the oxygen static spectrum, which had an integration time of 500 ms for reasons discussed later.

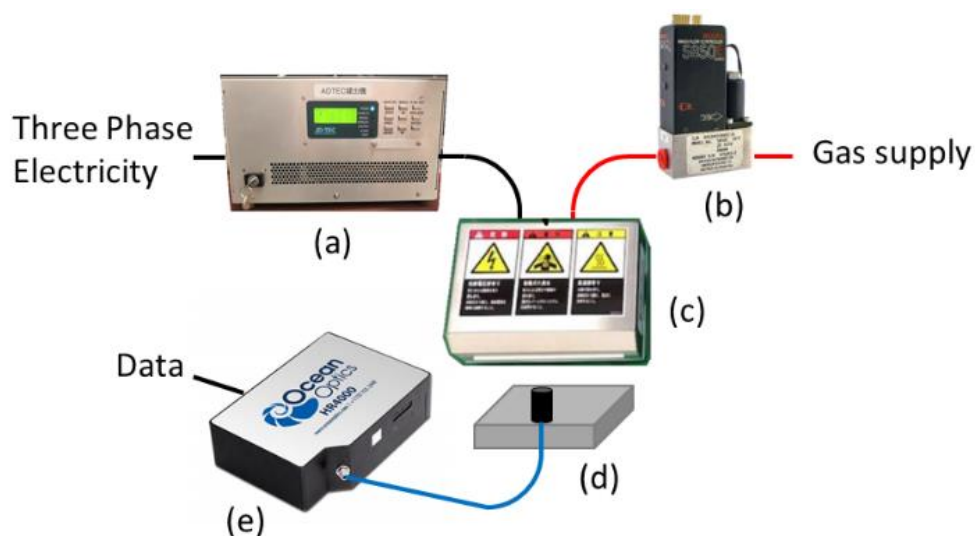


Figure 4-1 Experimental setup showing: a, generator; b, mass flow controller; c, plasma generating device (torch); d, motion stage; e, spectrometer.

An important caveat of presented data is that it is to be taken as relative intensities, not absolute, as whilst the USB2000 spectrometer was calibrated against a standard light source, the HR400 was not, and as such its data is only included in analysis of relative intensities. Similarly, repositioning of the lens beneath the plasma between periods of data collection and also the movement of the lens on the stage during spatial mapping has resulted in changes in relative intensity for identical sets of parameters. Such data is only used for identification of species, temporal stability, and spatial distribution, and not for quantitative analysis of species intensities.

4.1.1.4 Results

4.1.1.4.1 Static Spectra

Figure 4-2 shows the results from plasma where the feed gas is clean dry air (CDA) at 40 L/min and the current is 0.9 A.

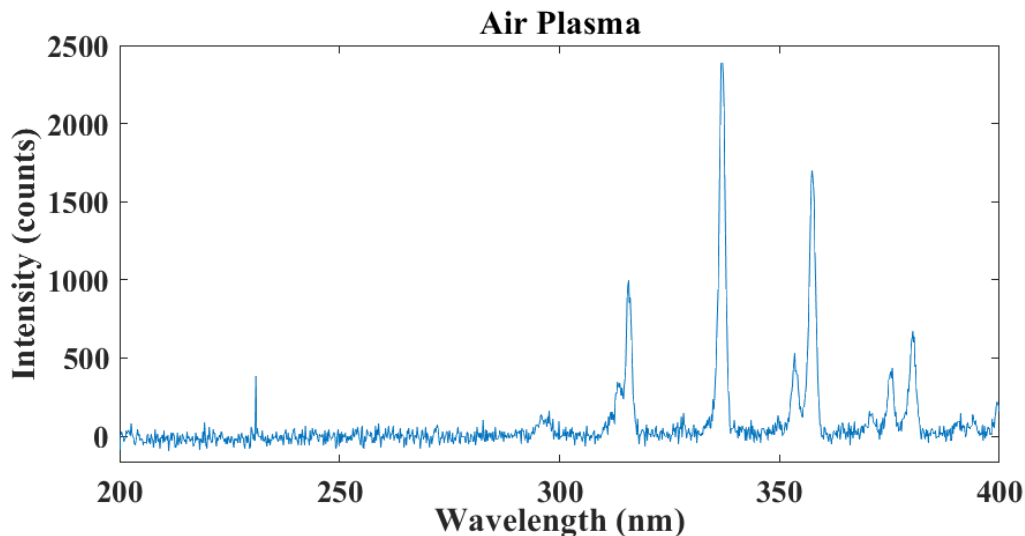


Figure 4-2 Emission spectrum of air plasma using spectrometer USB2H115902.

The static spectrum of the range 200 – 400 nm shows the characteristic triplets from the 2nd positive system of nitrogen [187] with band heads at 315.9 nm, 337.1 nm, 357.7 nm, and 380.5 nm. Smaller peaks at 297.7 nm and 399.9 nm, also from the nitrogen 2nd positive system, are also evident. These emission lines are from the $C^3\Pi_u - B^3\Pi_g$ transition [188] .

There is no evidence of oxygen peaks in the spectrum, indicating oxygen in the air does not undergo excitation or ionisation at significant quantities, and so whilst this is referred to in this work as an air plasma it is in fact a weaker nitrogen plasma, as considerable energy goes into species in the gas that are heated but do not undergo ionisation and do not constitute the plasma generated.

A static spectrum of plasma generated from nitrogen (Figure 4-3) showed the peaks from the second system of nitrogen as in the air plasma, however also exhibited peaks in the UV-C region, shown in detail in Figure 4-4, indicating the presence of Nitric Oxide, NO.

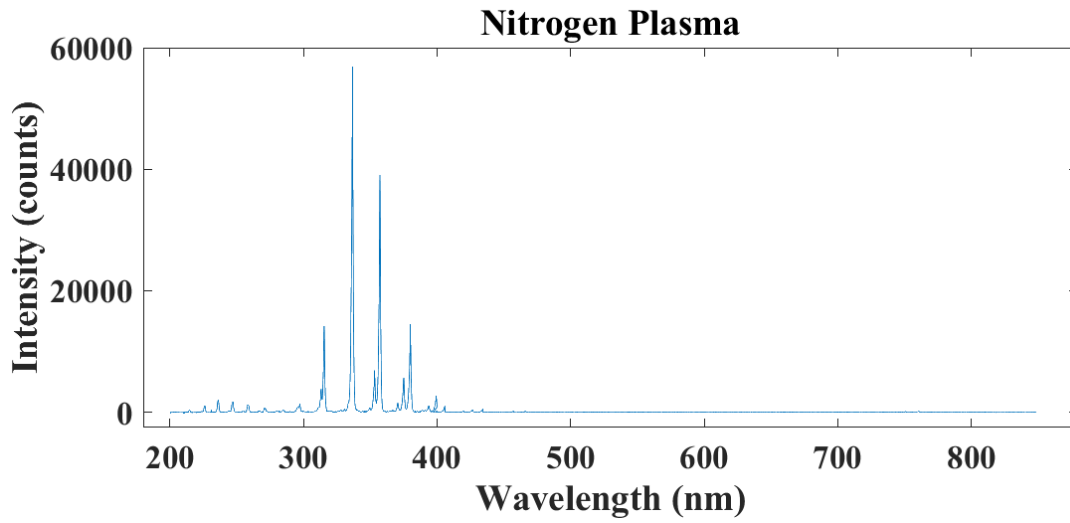


Figure 4-3 Emission spectrum of Nitrogen plasma.

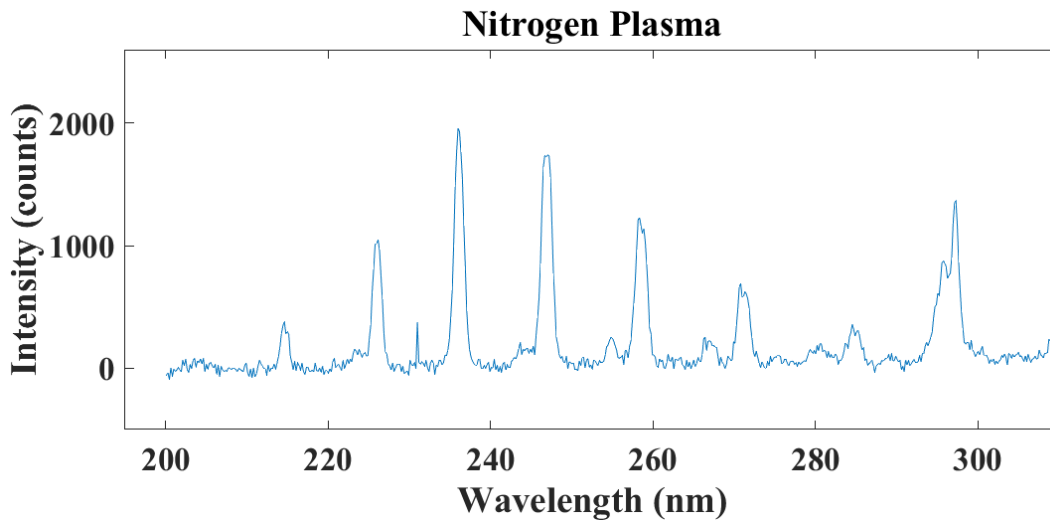


Figure 4-4 Emission spectrum of Nitrogen Plasma in the UV-C region.

These bands can be attributed to the gamma system of NO, produced in the plasma primarily by a reaction between the monatomic nitrogen and atmospheric oxygen [94]



For investigation of emission spectra from the plasma generated from oxygen, the integration time was set to 500 ms, to amplify the intensity of the lines (Figure 4-5).

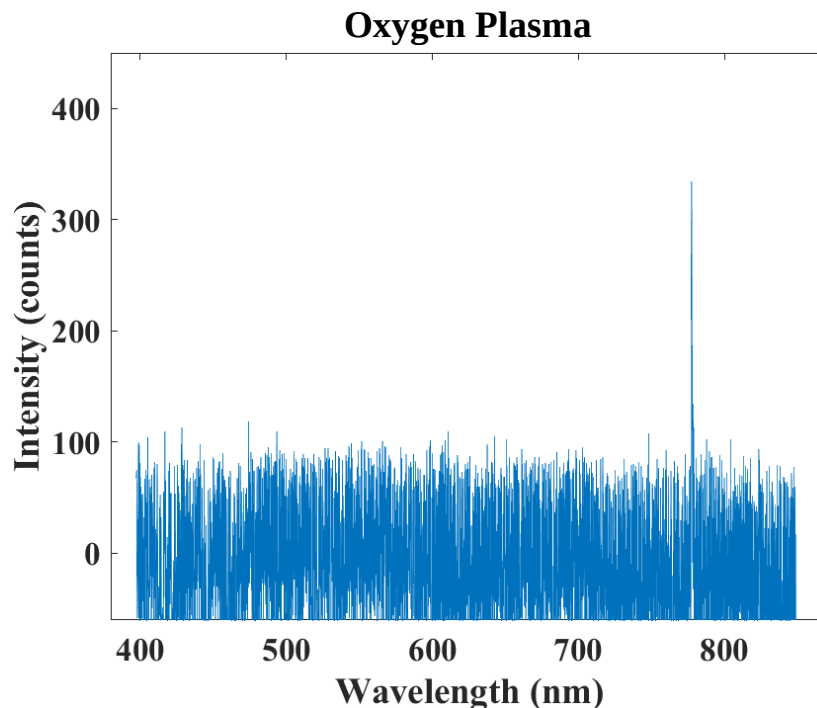


Figure 4-5 Emission spectrum of Oxygen Plasma.

The only significant peak is the characteristic 777 nm peak from oxygen $O(3p^5P \rightarrow 3s^5S)$, from dissociative excitation of molecular oxygen. Not evident is the peak to be expected at 844 nm, from the $O(3p^3P \rightarrow 3s^3S)$ transition, caused primarily by direct atomic excitation [189][190], although this transition may still be occurring and its peak being lost in the increased noise. The low intensity of the 777 nm peak, even with the fivefold increase in integration time, suggests very low levels of energy in the oxygen plasma. The majority of the oxygen flow appears to pass through the torch system without undergoing ionisation or excitation.

Also investigated were nitrogen and air plasmas where the feed gas was bubbled through deionised water, producing a humidified feed gas in comparison to the previously investigated dry gasses.

Emission spectrum from the humidified air plasma, shown in Figure 4-6, shows again the 2nd positive nitrogen system triplets between 300 and 400 nm, with no evidence of NO peaks, nor any derivative of the water molecules in the feed gas. The water molecules in the feed gas appear to pass through the torch system unaffected, as do the oxygen molecules as previously discussed.

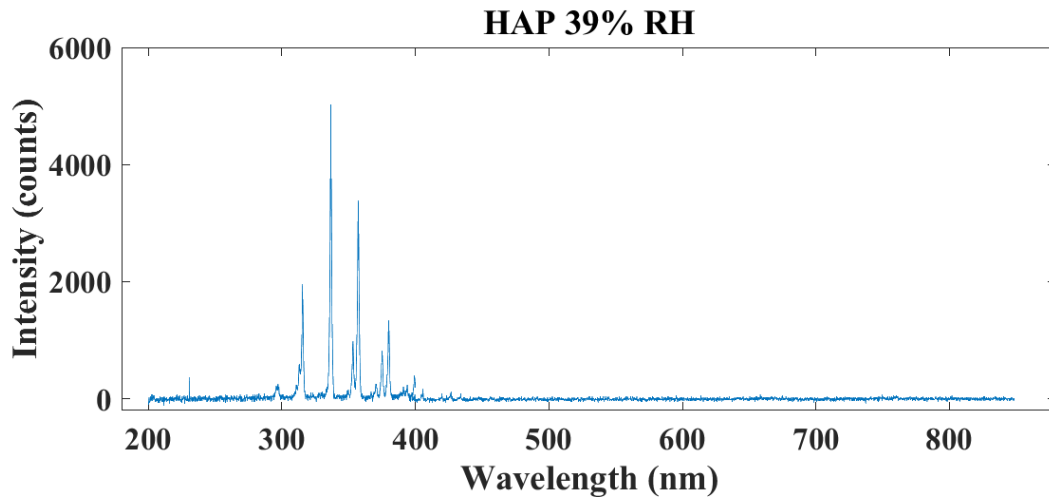


Figure 4-6 Emission spectrum of air plasma with relative humidity of 39%.

The humidified nitrogen plasma, however, exhibits both the 2nd positive nitrogen peaks seen previously, as well as the NO peaks in the UV-C range, shown in Figure 4-7. Also evident is a peak at 309 nm from $OH(A^2\Sigma - X^2\Pi)(0,0)$, causing a widening to the base of a nitrogen 2nd positive triplet of head band 315.9 nm (Figure 4-8).

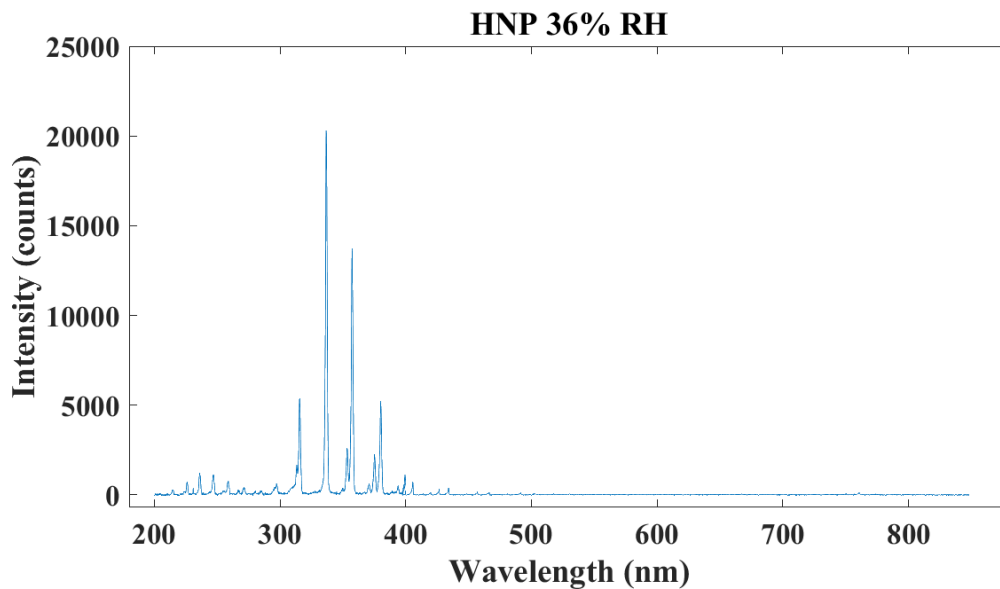


Figure 4-7 Emission spectrum of a nitrogen plasma with a relative humidity of 36%.

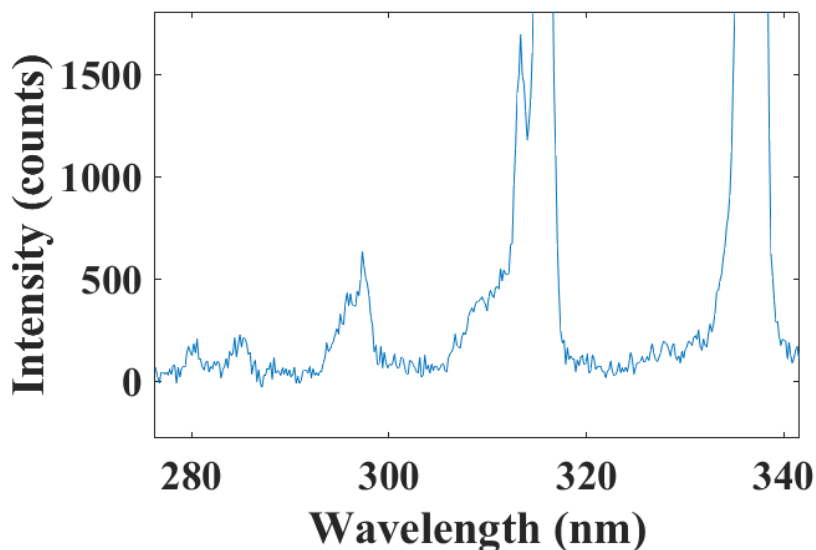


Figure 4-8 Details of OH peak evident as widening of the 315.9 nm nitrogen triplet.

These OH radicals are caused primarily by collisions between water molecules and high energy electrons [191], and thus indicate a higher level of ionisation in the nitrogen plasma than the air plasma, as the absence of this peak in the humid air plasma suggests there are inadequate electrons of sufficient energy to dissociate the H_2O molecules. Such OH radicals can also be produced on collision between $\text{O}(^1\text{D})$ and H_2O or O_2 and H, however the absence of any peaks attributed to oxygen, such as the 777 nm and 844 nm peaks mentioned previously, suggest this is unlikely to be a significant mechanism of OH production in these plasmas.

4.1.1.4.2 Temporal maps

For analysis of temporal stability, the 337 nm peak from the 2nd positive system of nitrogen was chosen owing to its higher intensity in comparison to other peaks. It also is present in all spectra obtained. Figure 4-9 shows stability over almost 2 hours for an air plasma generated with gas flow 60 L/min with current from the generator of 0.9 A, using the M-CCMD2 torch.

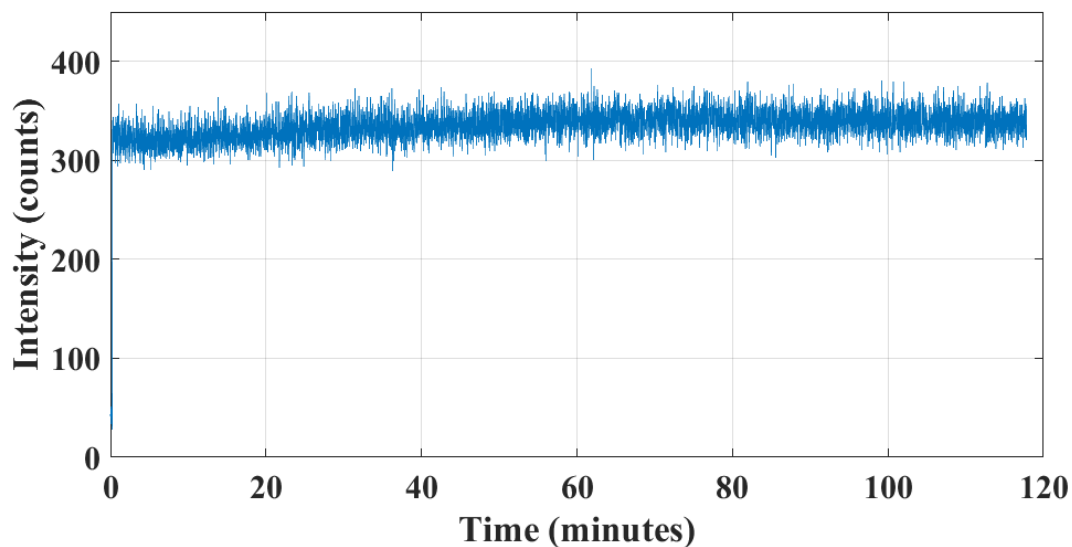


Figure 4-9 Temporal stability of 337 nm peak in plasma generated from clean dry air.

Temporal investigations showed the initial ramp up in intensity is effectively instantaneous (Figure 4-10), reaching near maximum intensity within seconds of ignition. The intensity then undergoes a gradual increase of 6.2 % in one hour, before reaching its maximum stable intensity.

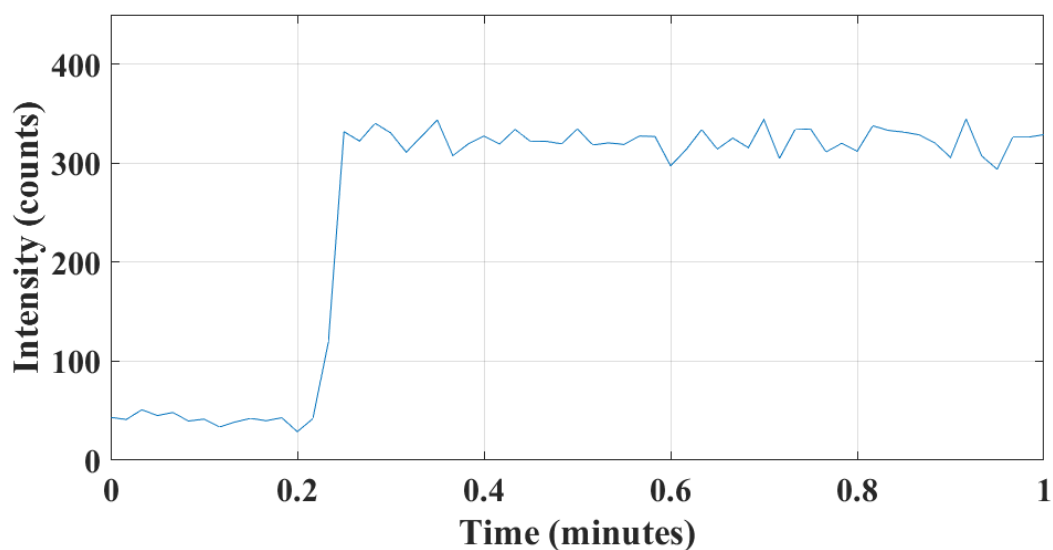


Figure 4-10 Detail of initial ramp up of air plasma, where the plasma was ignited at 0.2 minutes.

4.1.1.4.3 Spatial Maps

For these trials, the parameters were set to their maximum and minimum possible values. For the power, this was 0.9 A and 0.2A, which was the maximum output of the generator and the lowest output to sustain power, and for the gas 60 L/min which was the highest flow permitted by the mass flow controller, and 10 L/min which was the lowest flow that could sustain a plasma without overheating the torch.

When mapped in x and y, the plasma was shown to exist in 7 distinct regions, which correspond with the features seen in Figure 3-3 and Figure 3-9.

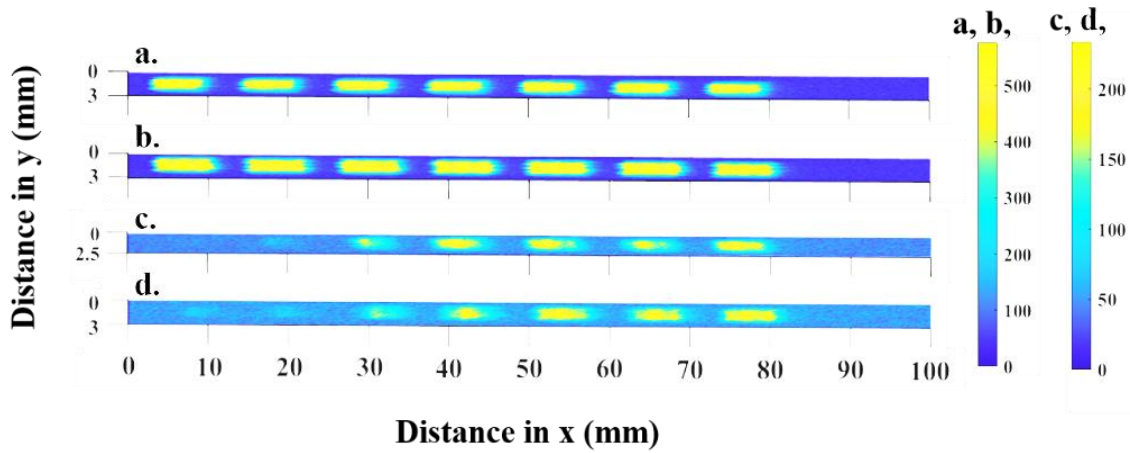


Figure 4-11 Spatial mapping of air plasma at a. 60 L/min 0.9 A, b. 10 L/min 0.9 A, c. 60 L/min 0.2 A, d. 10 L/min 0.2 A.

It is therefore likely that the features seen in the XCT images are indeed gas channels, resulting in uneven distribution of plasma across the torch opening. At the highest current of 0.9 A, there is no obvious difference between maximum gas flow (60 L/min) and minimum gas flow (10 L/min), suggesting ionisation is maximised at 10 L/min and gas flow in addition to this passes through the torch without undergoing ionisation or excitation. However, at the lowest current of 0.2 A, plasma generating regions 1 and 2 are significantly lower than regions 3 to 7. This suggests the gas flow within the torch and along the 7 gas channels observed in XCT images is not evenly distributed, and perhaps is faster across regions 1 and 2, allowing the gas less time in the electrode region to obtain enough energy to undergo excitation and ionisation.

Single passes in the y axis were then compared to further investigate the effects of current and gas flow. Figure 4-12 shows intensity of the 337 nm peak along the x axis where the gas flow was kept constant at 60 L/min and the generator current varied between 0.2 A and 0.9 A in increments of 0.1 A.

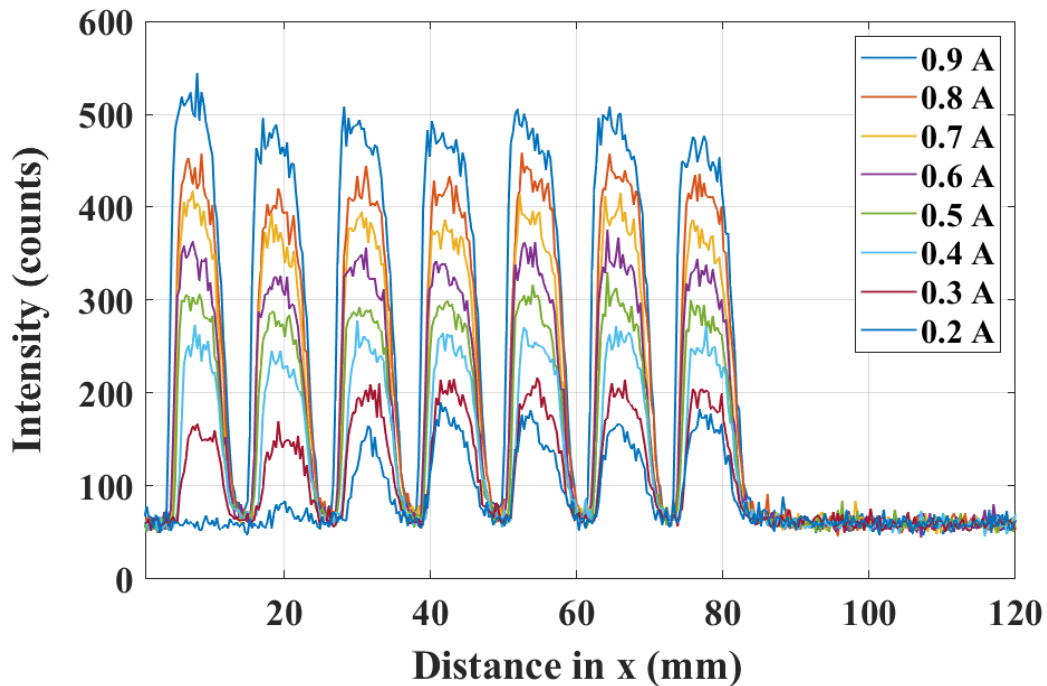


Figure 4-12 Intensities of air plasma at 60 L/min with varied generator current.

These investigations showed the intensity was highly dependent upon current from the generator, with a higher current resulting in higher intensity and thus higher energy in the plasma. This relationship appears linear for currents 0.9 A to 0.4 A, however at 0.3 A and 0.2 A regions 1 and 2 are significantly lower. This again is likely due to uneven distribution of gas flow within the torch resulting in lower energy transfer between the electrode system and gas as these regions. Consequently, there is less ionisation and excitation and in turn less plasma generation and its associated emissions at these regions.

To investigate the effect of gas flow, the current was set at 0.9 A and the gas flow varied between 10 L/min and 60 L/min in increments of 10 L/min. The results, shown in Figure 4-13, show that intensity is not dependent upon gas flow rate at these parameters. As noted previously, this suggests that ionisation is maximised at a flow rate lower than those measured, and gas flows over this do

not acquire enough energy in the electrode region of the torch to become excited or ionised. Also evident in Figure 4-13 are splitting of the 7 peaks into three sub peaks. This may be related to the arrays of presumed electrode microstructures seen in Figure 3-10. The absence of these features on other spectroscopy data could be due to changes in alignment of the collimating lens.

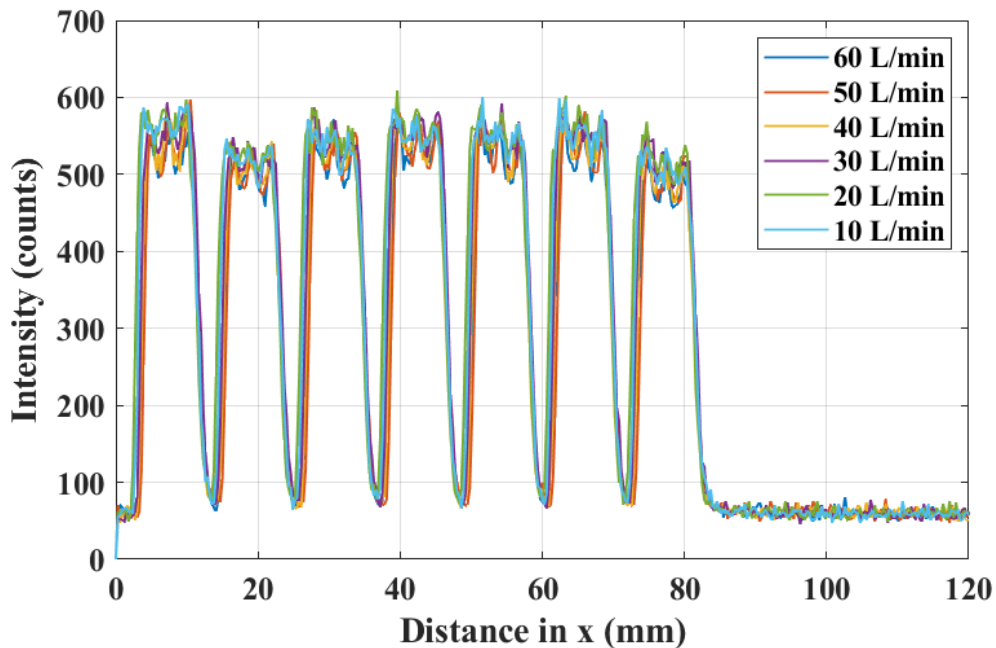


Figure 4-13 Intensities of air plasma at 0.9 A with varied gas flows.

4.1.1.5 Discussion

Characterisation techniques discussed in this chapter have greatly enhanced understanding of the torch's performance and the relationship between input parameters and plasma intensities. Perhaps of greatest implication is the uneven distribution of plasma due to the torch's internal structure, where 7 non-overlapping regions of plasma are generated, meaning processing of samples with the torch in its current design likely to need to be rastered.

Static spectra show that plasma produced from a supply of clean dry air is really just a lower intensity nitrogen plasma, and that oxygen molecules in the air, or any other component, do not undergo ionisation. The only peaks observed in this so-called air plasma can be attributed to nitrogen, yet at lower intensities than

observed in a pure nitrogen plasma with the same parameters. The nitrogen plasma exhibited peaks from both nitrogen and nitric oxide, showing the increased levels of ionisation of the feed gas.

The humid plasmas showed again how there is insufficient energy in the air plasma to ionise any component other than nitrogen, yet a humified nitrogen plasma results in nitrogen and nitric oxide as with the dry nitrogen plasma, but also evidence of hydroxyl radicals produced from water molecules within the feed gas, indicating a higher number of high energy electrons and therefore a higher degree of ionisation of the feed gas and a more efficient production of plasma.

Measurements of temporal stability have shown the torch reaches what is almost maximum intensity effectively instantaneously, which will save significant processing time and gas supply as there is no need for a warm up period before processing can begin. It also shows it can run for at least two hours without significant deviation from average intensity, which will allow a considerable number of samples, and thus surface area, to be processed without the need for downtime to allow the torch to cool.

Investigation of the impact upon intensity of gas flow and generator current has shown the gas flow to have no observable effect at the parameters measured, whereas generator current has significant impact, although this effect is not consistent across all plasma generating regions.

Together, knowledge gained will influence processing using this torch. Raster processing will be necessary to account for the spatial distribution of the plasma, and current from the generator will be kept at 0.9 A to maximise intensity. A gas flow rate of 40 L/min will be chosen to conserve gas supplies whilst also aiming to prevent any internal overheating in the torch.

OES data showed there to be no reactive species in the plasma and so the risk of damage from the mirrors through etching is negligible. Dry nitrogen plasma had the highest intensities and as such surface energy modification is likely to be most efficient with pure nitrogen as the feed gas.

5 Methodologies

The experiments conducted for this work can be broken down into individual packets that were combined and adapted according to the trial requirements.

The primary base methods were:

- Precleaning
- Plasma Processing
- Surface Energy Modification
- Soiling
- Reflectance
- Water washing
- Condensation Trials

Between these steps, characterisation was conducted to measure reflectance or water contact angle.

Throughout, the mirrors used were 3mm thick low iron backsilvered glass from AGC Glass Europe. The samples were etched with a unique sample number against which subsequent processing was logged, which allowed for known periods between processing. The mirrors were approximately 80 x 80 mm. Of all the mirror samples, one set of 6 was never subject to plasma processing so acted as the un-processed comparison, ensuring there were no residual effects of prior processing on the results.

During processing trials the mirrors were stored and transported in individual hard plastic cases, which protected them from strong air currents and contact with other items which could have altered their surface energy or soiling cover, thus affecting the data. During plasma processing itself, the samples were inside the chamber of the motion stage however had to have the surface exposed for the plasma treatment, and so were not protected from external effects such as air flow and redeposition or movement of sand across the surface. However this would also be the case for in-situ processing of mirrors in plants, and so was not considered to be a hindrance to the experiments. When samples were ageing between processing trials they were left uncovered on a laboratory table, which allowed for natural ageing of the surface by air currents and dust accumulation.

5.1 Pre-cleaning

At the beginning of each set of experiments, the mirror samples were subject to pre-cleaning procedure, to remove any soiling that may be adhered to the mirrors from previous experiments or dust that had settled out of the air.

The cleaning procedure consisted of a rinse in deionised water followed by rinses in acetone then IPA, with the wet surface lightly wiped with an optic wipe to remove stubborn surface soiling before being rinsed again with the solvents. The mirror was then dried by buffing with a low fibre transfer optic wipe.

The samples were used immediately after this pre-cleaning procedure to prevent any recontamination of the surface.

5.2 Plasma Processing

For all torch types, the torch was mounted inside an enclosure that was connected to an extraction system, to remove harmful gases such as ozone that are produced by the plasma. The enclosure was made of aluminium, with the transparent Perspex cover and outer enclosure protected with a UV blocking film, to protect the eyesight of the user.

During plasma processing, the samples were mounted on an Aerotech A3200 motion stage, the plasma torch was mounted above the stage onto a XR25C/M manual linear motion stage from Thorlabs, which allowed for precise adjustment of the processing height using a 150-801ME-H micrometer screw head. The height was set to 1 mm throughout as measured by allowing the lower edge of the torch to gently come into contact with the sample surface and then raising the torch by turning the micrometer screw by 2 full rotations, which equals 1 mm. In the case of the M-CCMDs, the dielectric opening of the torch was protected from impact by 1 mm high buffers at either end, therefore a z height of 1 mm can be considered to be 2 mm from the torch opening. Subsequent mentions of z height are from the lowest point on the torch, which is the buffer strips.

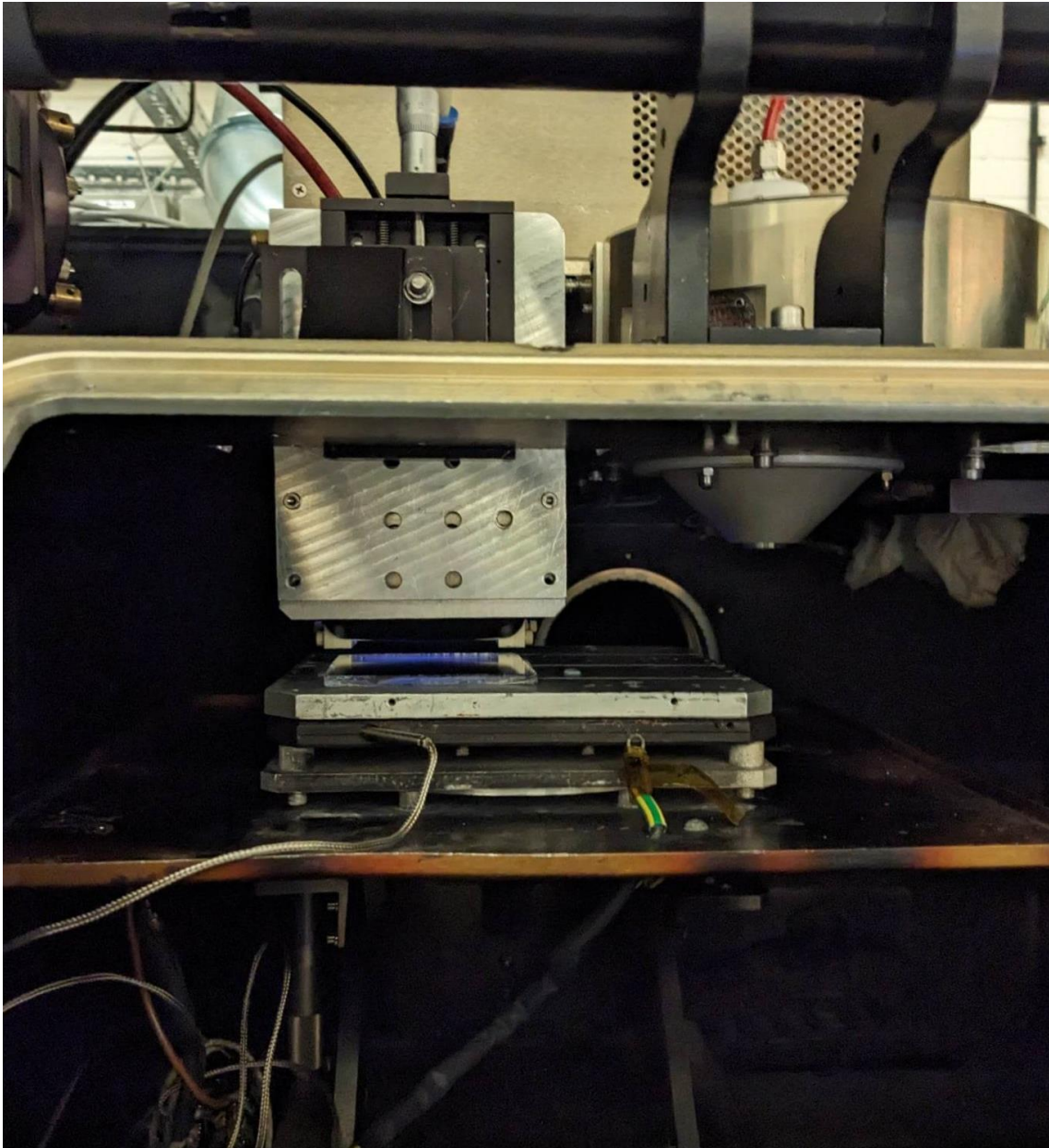


Figure 5-1 Photograph of the M-CCMD 3 torch during processing of a mirror.

Motion of the stage was programmed via custom software, with the linear speed being set in units of mm/min.

Care was taken such that the sample did not pass beneath the torch again after processing, either with the torch switched on or during its cooling period where unignited gas was flowed through the torch, so that the surface energy modification was not impacted beyond the initial plasma treatment.

5.3 Surface Energy Modification

Typically, surface processing effects would be determined using surface free energy (SFE) measurements, which is commonly calculated using the contact angles of liquid droplets deposited on the surface using an optical tensiometer. For this method, at least two different liquids of known surface tension must be used such that the surface energy can be calculated, with typical liquids being water, ethylene glycol and diiodomethane. A limitation of this method is that when testing a super-hydrophilic surface the liquid droplet spreads out considerably, often beyond the measurement window of the apparatus. Additionally, contact angles below 2° often cannot be reliably measured. For this reason, measurement of surface energy using liquid contact angles was not possible for this work, and instead the water contact angle (WCA) is used as an indication of surface energy. For the application of this work, wettability of the surface using water is an adequate measurement format.

Multiple methods of SFE calculation have been proposed, with common calculation methods being Young's, Fowke's and Owens, Wendt, Rabel and Kaelble (OWRK).

For Young's equation, a simple model of SFE, surface free energy γ_s is defined by the following:

$$\gamma_s = \gamma_{sl} + \gamma_l \cdot \cos\theta \quad (5-1)$$

Where γ_{sl} is the interfacial tension, γ_l is the surface tension, and θ is the contact angle of the liquid on the surface.

Fowke's expands on this equation to enable calculation of the interfacial tension into dispersive (D) and non-dispersive or polar (P) parts [192]:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2 \left(\sqrt{\gamma_s^D \cdot \gamma_l^D} + \sqrt{\gamma_s^P \cdot \gamma_l^P} \right) \quad (5-2)$$

When both the surface and the liquid are polar, such as in the case of water in contact with a plasma treated surface, the interfacial tension is low, meaning the water spreads more easily over the surface.

For measurement of water contact angle (WCA), a Theta Lite model optical tensiometer from Biolin Scientific was used, shown in Figure 5-2.



Figure 5-2 Stock photograph of a Theta Lite optical tensiometer of the same model used in this work [193].

The mirror sample is placed onto the stage which is raised such that the top surface is within the measurement window of the camera, as shown in Figure 5-3.

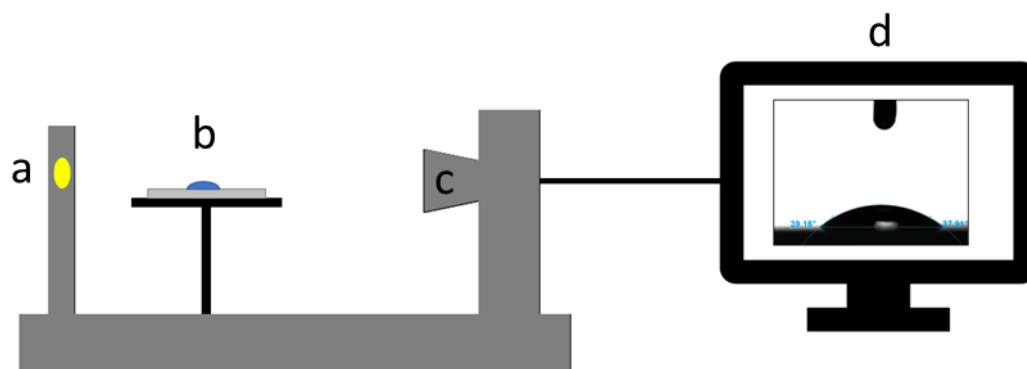


Figure 5-3 Optical Tensiometer setup showing components: a, light source; b, water droplet and mirror sample on stage; c, camera; d, computer and software analysis.

A 2 μL droplet of deionised water at 20°C is deposited onto the sample using a precision pipette immediately after which a measurement is captured using the Theta Lite optical tensiometer which employs a camera to take high resolution photographs of each droplet deposited on the surface. The images are then

analysed using specialist software OneAttension to measure the contact angle, as indicated in Figure 5-4.

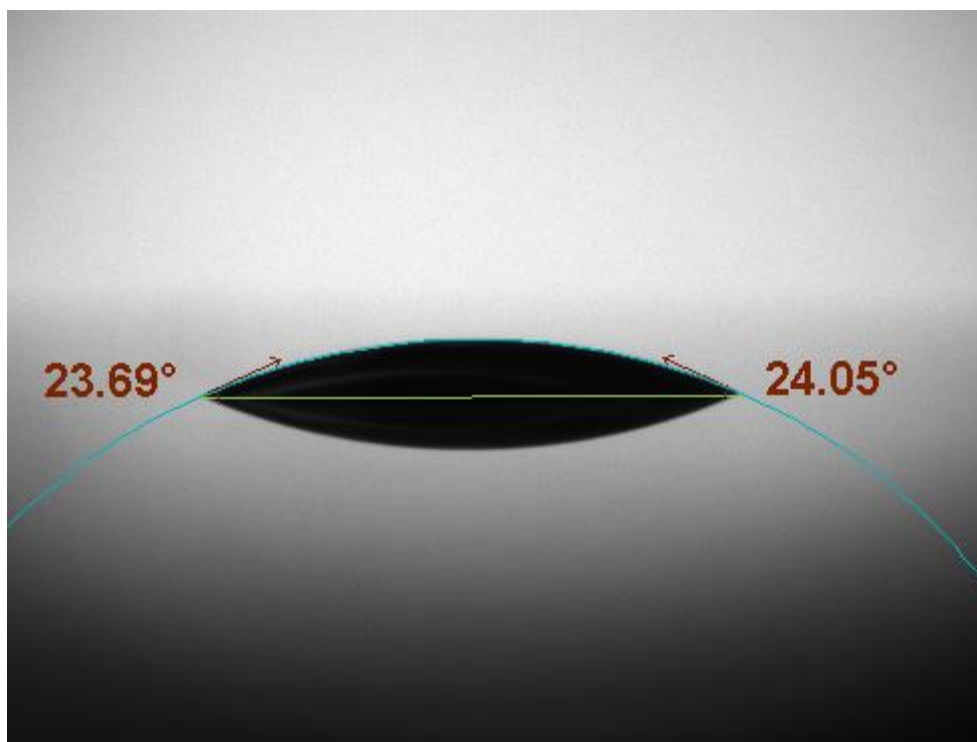


Figure 5-4 Screenshot of software analysis of a 2 μ L droplet of deionized water on a clean mirror surface prior to plasma processing.

As discussed, in order to measure surface energy, a minimum of two liquids are required with known polar and disperse parts, frequently these are deionized water on ethylene glycol due to their safety, availability and low cost, however in this work creation of superhydrophilic surfaces results in contact angles of less than 2° which could not be accurately measured with the equipment. This was due to two reasons, firstly that the droplet spread beyond the measurement zone, and also that such small angles were not identified and measured up by the measurement software (Figure 5-5).

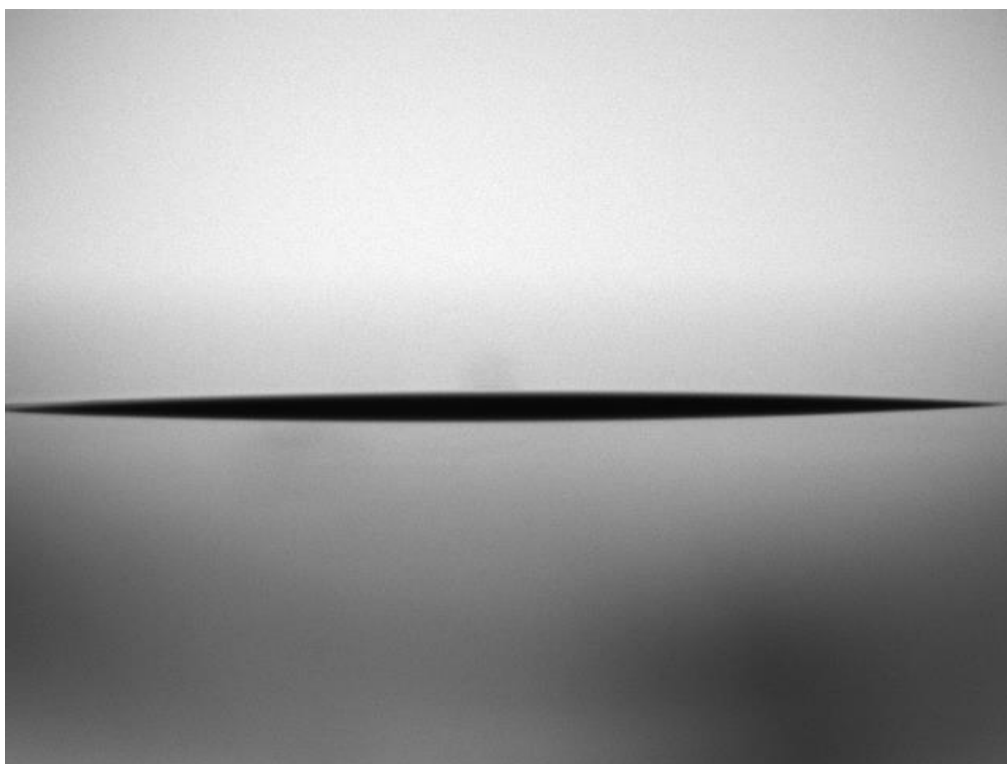


Figure 5-5 Example of a 2 μ L droplet of water on a plasma induced superhydrophilic surface, which was not possible to measure with the software.

The contact angle of ethylene glycol is lower than that of water on the hydrophilic surfaces, and as such it was not possible to calculate the surface energy of the processed samples as only one liquid (water) could be measured. For very small angles ($<2^\circ$) it was also not possible to measure the contact angle of the water droplets, and so where this is the case the angle is listed as exactly 2° . This approximation is acceptable for this work, as precise measurement of the surface energy is not undertaken, and is instead used as an indicator for the effect of the plasma processing on the surface, in which it is sufficient to consider the surface become super hydrophilic by the definition of $<5^\circ$.

5.4 Soiling

To artificially soil the samples, a soiling chamber was designed to allow for repeatable and representative soiling of samples in a safe manner.

The chamber consisted of a large plastic lidded enclosure into which two circular openings were created on one face and rubber sheeting affixed to allow the user's

arms into the chamber whilst minimising transfer of material from inside the soiling chamber to the outside. Another hole was drilled to allow for a connection with a vacuum cleaner with a HEPA (high efficiency particulate air) filter. These steps were necessary as the fine sand used during soiling poses a risk to human health [194].



Figure 5-6 Photograph of soiling chamber.

Within the chamber was a second box with a secure air-tight lid, inside which was a raised foam area where a double sided adhesive tape was applied such that the mirror samples could be held in place. The tape was removed and replaced as necessary as its adhesive qualities degraded.



Figure 5-7 Photograph of sample mounted inside inner soiling box.

The sand used was collected from Plataforma Solar de Almería (PSA) and sieved to $<125\ \mu\text{m}$. For each sample 0.4 mL of the sand was measured using a scoop and placed into the inner box of the soiling chamber and the lid, with mirror securely affixed, fastened.

The inner box was then tumbled by hand for 30 seconds as measured with a stop clock, after which it was placed lid down (with the mirror face-up) and the sand allowed to settle for a further 30 seconds. This method of soiling was adapted from a technique found in literature [195], and was found to result in the most repeatable and representative soiling of the mirror samples. Other trialled

methods such as depositing sand onto the mirror from a fine sieve held above the mirror, and producing airborne dust by directing compressed air to a pot of sand and allowing it to settle, resulted in inconsistent or poorly adhered soiling.

Once the sand had settled, the extraction vacuum was switched on and the box removed from the lid, such that any remaining airborne soiling was safely removed from the chamber. The mirror was then unaffixed from the lid, the rear face was gently wiped to remove excess soiling, and the mirror sample removed from the main chamber.

After each soiling run, the inner box was emptied of remaining soiling and a fresh quantity used for the following run. This was to ensure the particle size distribution of each soiling packet remained consistent, as the smaller particles adhered more often to the mirror than the larger particles [35], and therefore remaining soiling was of the larger particle size.

5.5 Reflectance

A common quantifier of cleanliness in CSP applications, a mirror's reflectance is a measurement of the proportion of light reflected from a surface compared to the intensity of the original light source. The reflectance of a mirror can be impacted by numerous factors, such as the purity and opacity of the glass used, the quality and integrity of the back-silver layer, or contaminants on the surface. Reflectometers, a type spectrophotometer, are equipment that can measure the reflectance of a surface, and portable versions are utilised in CSP plants for instantaneous measurement of mirror cleanliness.

A typical reflectometer will comprise primarily of a light source and a corresponding detector. The light source is typically one or more light emitting diodes (LEDs), which emits light that is reflected and in turn measured by the detector which can be a photodiode, a charged coupled device (CCD), or another light sensing device. The proportional difference between the light detected at the source and the light detected after reflectance from the surface gives the mirror's reflectance in reflectance units, often expressed as a percentage where 1 reflectance unit is 100%.

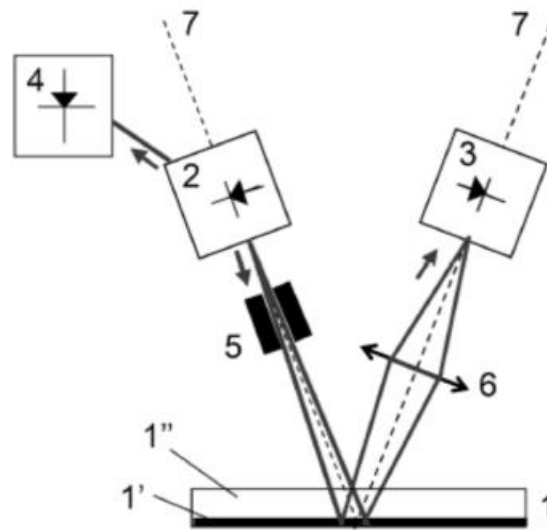


Figure 5-8 Schematic of detector apparatus for Condor SR-6.1 reflectometer showing components: 1, mirror; 1' reflecting surface; 1'', glass; 2, LED; 3, detector; 4, reference detector; 5, diaphragm; 6, lens; 7, optic edge [196].

The device used for reflectance measurements is a Condor SR-6.1 from Abengoa Solar New Technologies. It consists of 6 LEDs of wavelength 435, 525, 650, 780, 940, and 1050 nm each producing light with a beam spot size of 1 mm diameter at an incidence angle of 12° , from which specular reflectance is measured using one of six corresponding photodiodes at an acceptance angle of 204 mrad. It has an accuracy of ± 0.002 , a repeatability of ± 0.002 , and a resolution of ± 0.001 , all in reflectance units [197]. For all measurements only the 650 nm LED and its corresponding detector were used in line with measurement standardisation [198].

As the reflectometer has such a small spot size, and due to the inhomogenous nature of the soiling, a custom measurement rig was designed and constructed.

The rig, shown in Figure 5-9, consisted of an aluminium plate at the centre of which was a recessed area which held the mirror sample. For the work shown here, 9 measurement positions were chosen, as indicated in Figure 5-10. Each of the points was 30 mm apart, starting 10 mm from the edges of the mirror sample. The grid pattern of three rows of 3 points enabled measurements to be taken from the top, middle, and bottom of the sample, to investigate how the water

travels down the sample. This also enables more accurate measurements to be taken as multiple measurement locations allow averages to be calculated, which helps to overcome the inaccuracies caused by the aforementioned inhomogeneously distributed soiling. A single measurement would not be an accurate representation of the soiling or cleaning of the sample as a whole. Therefore, multiple points allow an average to be taken and therefore a more accurate measurement.

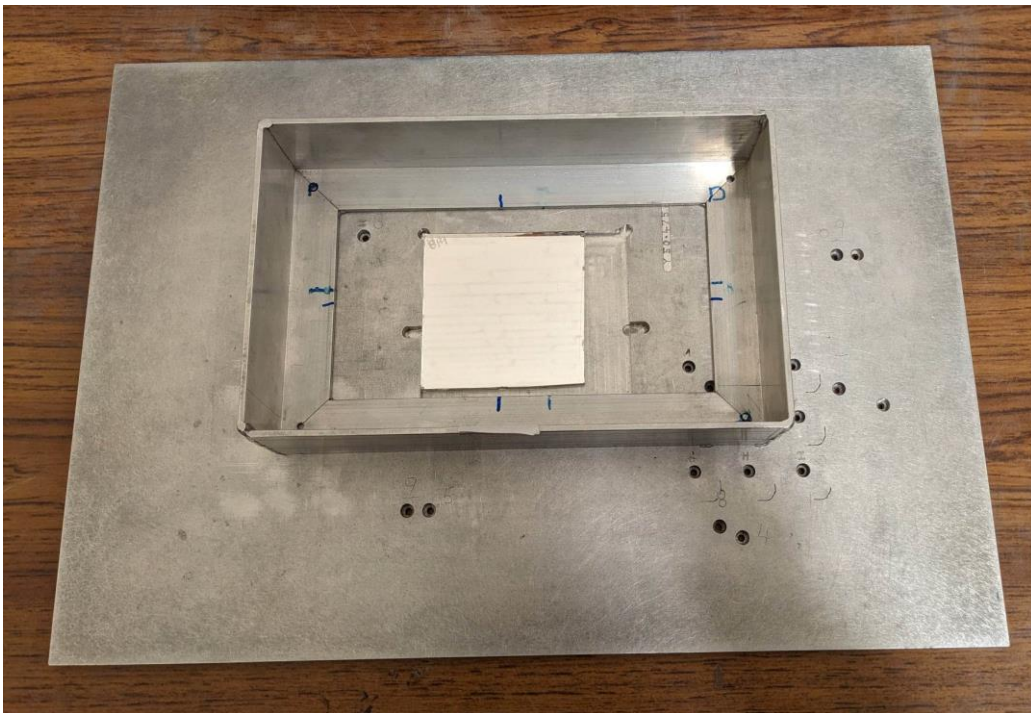


Figure 5-9 Measurement rig showing cradle in which the reflectometer sits above mirror placed in recess.

The reflectometer sat in an aluminium cradle which was fitted with holes at bottom of each corner, into which pegs were placed which slotted into corresponding holes drilled into the aluminium plate. This also ensured repeatable positioning of the reflectometer with regards to the sample, as even slight movement of the reflectometer could result in significant changes in measured reflectance. The rig allows before and after measurements of precise locations on the mirror.

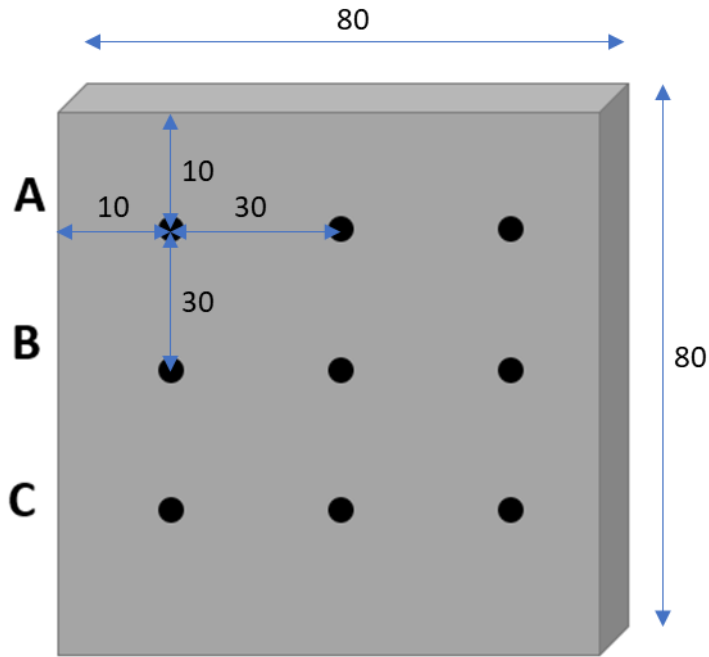


Figure 5-10 Diagram showing the locations of 9 reflectance measurement points on each sample, split into three rows. All dimensions are in millimeters.

5.6 Water Washing

To measure effect of washing efficiency a rig was constructed to enable repeatable and controllable washing of mirror samples.

The rig consisted of a frame constructed from aluminium profile with a water nozzle positioned on one end and the mirror samples mounted on a motion stage that passes through the produced water jet.

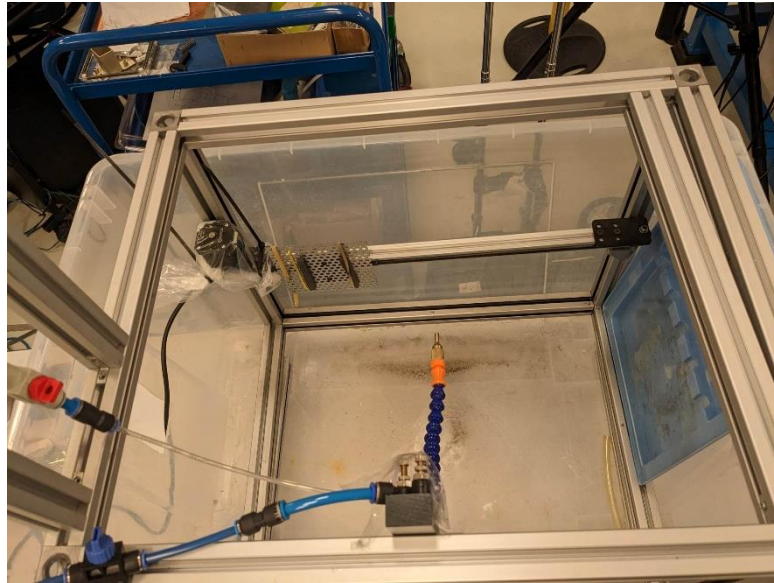


Figure 5-11 Photograph of the washing rig.



Figure 5-12 Detail of a mirror sample passing through the washing jet.

The motion stage was a belt driven linear actuator consisting of a NEMA17 stepper motor connected via a belt to a sample stage which was held onto a v-slot aluminium profile using four wheels. The sample holder consisted of a metal mesh onto which two strips of foam were adhered and elastic bungees threaded, allowing the samples to be held firmly onto the stage but also removed with ease.

Linear speed of the stage was controlled via an Arduino code uploaded to the uStepper S board, which instructed the motor to move the stage in a single linear motion through the water jet.

The speed was set in steps per second, from which linear speed, v , was calculated this using the equation

$$v = \omega r \quad (5-3)$$

Where ω is angular speed in radians/second and r is the radius of rotation in metres.

One step is equal to a rotation of 1.8° , equating to 200 steps per full rotation. The diameter of the rotating wheel including the belt was 23 mm resulting in a radius of 0.0115 m.

Thus the linear speed in m/s is

$$v = \frac{\text{steps per second}}{200} \times 2\pi \times 0.0115 \quad (5-4)$$

The maximum speed was 1100 steps/s, converting to a maximum linear speed of

$$v = \frac{1100}{200} \times 2\pi \times 0.0115 = 0.397 \text{ m/s} \quad (5-5)$$

This can be rearranged to calculate the rotational speed required in order to achieve a desired linear speed

$$\omega = \frac{v}{r} \quad (5-6)$$

$$\text{steps per second} = \frac{v \times 200}{2\pi \times 0.0115} \quad (5-7)$$

The water jet consisted of a nozzle that utilised the venturi effect to force water through a nozzle using only compressed air, as opposed to a pump driven system. For this, the nozzle was mounted on the upper strut of the rig, angled towards the path of the motion stage. At the top of the nozzle is a connector for compressed air and deionised water. The pressure of the compressed air was kept constant at 1.5 bar throughout, the flow of the air through the nozzle pulled with it deionised water from a container mounted on a stand on the top of the washing rig. The flow rate of the water was adjust via a screw valve and measured using a stop clock and a measuring cylinder.

The nozzle was set such that the jet produced passed across the top of the sample, indicated as Row A in Figure 5-13 and was identical through all procedures. This location was chosen such that the behaviour of the water (and the soiling with it) as it rolls down the sample can be observed and measured.

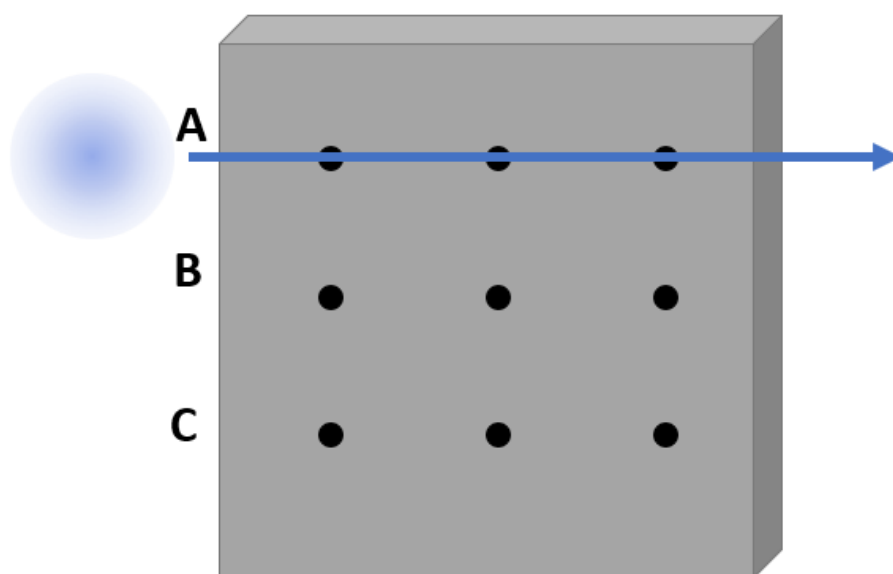


Figure 5-13 Diagram showing position of water jet across mirror sample relative to the 9 reflectance measurement points.

For washing trials, the samples were gently mounted onto the raised foam strips and held in place with the elastic bungees. The nozzle was then turned on by opening the air supply and water valves, and the water allowed to feed through and stabilise. The flow rate was checked by placing a measuring cylinder over

the nozzle and a stop clock used to time collection of 10 mL of water. This was conducted at the beginning of each trial set to ensure it was consistent.

The stage software was then coded with the correct speed and uploaded to the motor, resulting in a single pass of the stage and mounted sample through the spray area. The sample was left to rest in place for a few minutes before being gently removed from the mounting, so as to not disturb any beading left on the sample which could influence reflectance results.

5.7 Condensation Trials

To measure potential anti-soiling capability of plasma processed mirrors, the samples were first subject to the usual procedures as described above, before being subject to a condensation methodology.

For the “Self-cleaned” stage of the procedure, samples were placed in a condensation chamber, shown in Figure 5-14, which consisted of a chamber in which there were two ultrasonic humidifier devices fed by deionised water, and a cooled block that consisted of a copper topped aluminium block through which coolant flowed in channels, fed from a chiller unit set to 6°C.



Figure 5-14 Photograph of condensation chamber.

Temperature of the chamber and the block were measured via type K thermocouples and the humidity measured by a hygroscope. Humidity was kept at $70 \pm 10\%$ RH, as the humidity fluctuated such as when the chamber door was opened in order to take photographs. Temperature of the block was measured as 8°C and temperature of the chamber was 18°C . The angle of inclination of the block was 28° from horizontal which was the maximum permitted by the setup, seen in Figure 5-15. The samples were left undisturbed for 90 minutes, when the humidifiers and chiller were switched off and the sample left to dry fully on the inclined block.



Figure 5-15 Photograph of two mirror samples on the condensation block.

6 Surface Energy Modification

6.1 Theory

Plasma processing of the samples induces a hydrophilic surface primarily through the breaking of weak surface bonds which creates polar hydroxyl surface groups, as described previously in Chapter 2.15. This induced hydrophilicity of the surface has numerous effects on the behaviour of water. Most directly, a reduced water angle results in water spreading further over the surface and therefore a greater area of surface is covered by the water, discussed further in Chapter 5.3. This in turn has further influences on the behaviour of the water on the surface such as its drying behaviour, which will be discussed in this chapter.

6.2 Methodology

For Surface Energy Modification trials, mirrors were precleaned as in Chapter 5.1 then subject to plasma processing using one of the torches described in Chapter 3. Measurements taken were: WCA, using the goniometer; the time it takes for a droplet to dry, using a timer; and the size of the water droplet, measured using a digital calliper.

6.3 Sairem Microwave Trials

Initial processing of mirrors was carried out using the Sairem torch as described in Chapter 3.1. For this work, the power from the generator was changed between 50 and 200 W, in steps of 25 W. The standoff height was 10 mm and the mirror processed in a raster pattern with a step distance of 2 mm, at a speed of 30 m/min. Immediately after processing, the mirror sample was moved to the optical tensiometer and a 2 μ L droplet of deionised water deposited on the surface, the diameter of the droplet was measured using a digital calliper, from which the droplet area was calculated. The water contact angle was then measured using the software as described in Chapter 5.3.

Figure 6-1 shows the area covered by these droplets. It can be seen that a higher power from the generator results in a smaller contact angle, and therefore greater hydrophilicity of the mirror surface, causing the droplet to spread and cover a

greater area. This is true between 50 W and 175 W, however at 200 W the effect is slightly less than that at 175 W. This is in agreement with previous processing of samples using this torch and is likely due to reduced plasma stability at these higher powers [199].

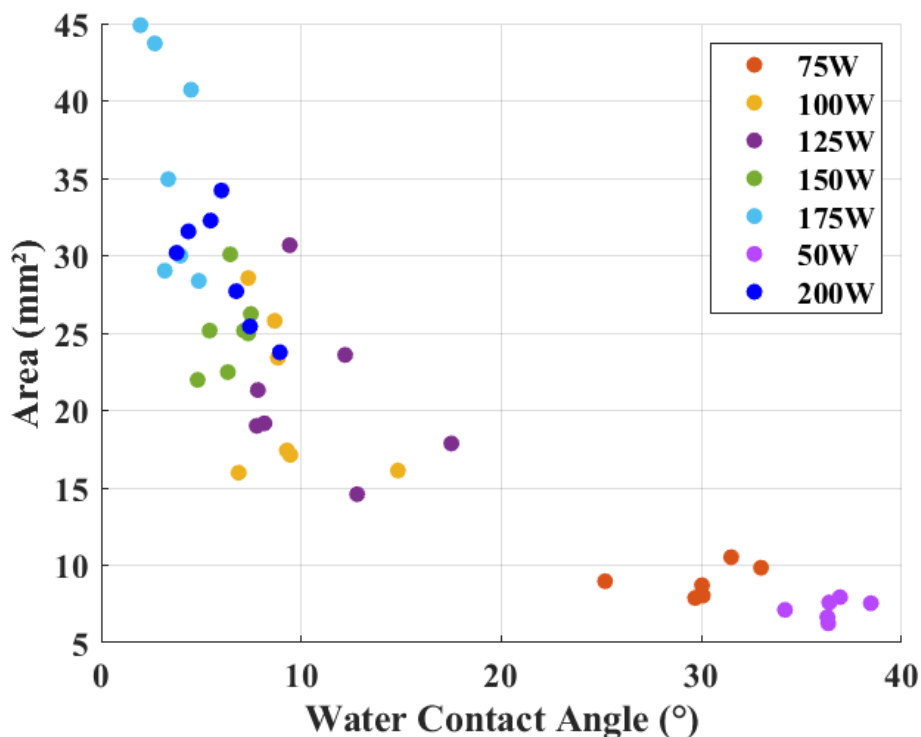


Figure 6-1 Graph showing the area covered by a 2 μ L droplet of water with relation to its Water Contact Angle.

The drying of the droplets was also investigated. Separately to the area trials, 2 μ L water droplets were deposited onto the surface after processing at the previous parameters and the time to dry was calculated from the moment the droplet is deposited onto the mirror, to the complete evaporation of the droplet as determined visually. Due to the timing constraints, it was not possible to measure the water contact angle for these trials, and so instead they have been grouped on Figure 6-2 to the average contact angle for that power.

Trials showed that the higher power of the plasma, and therefore the smaller contact angle and greater area, resulted in a faster drying time.

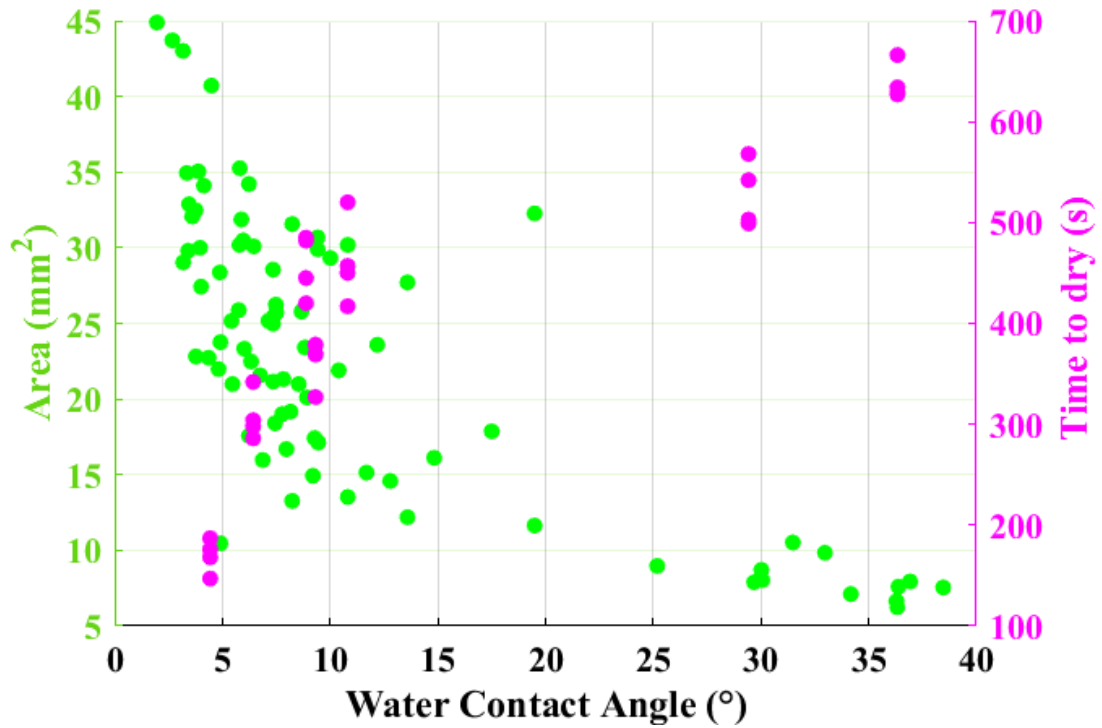


Figure 6-2 A graph showing how the water contact angle of a water droplet influences its area and also the time it takes to dry.

The reduced evaporation time seen is due to the increased area of the droplet as molecules of water evaporate from the interface between the water and the air, which is larger with respect to the volume in the case of low contact angle droplets [200].

The rate of evaporation of a sessile droplet on a solid surface is given by

$$\text{Rate of evaporation} = \frac{dm}{dt} = -\rho \frac{dV}{dt} \quad (6-1)$$

Where m is the mass of the droplet, t is the time, ρ is the density of the liquid, and V is the volume of the droplet, which is further defined as

$$V = \pi r_b^3 (2 - 3\cos\theta + \cos^3\theta) / (3\sin^3\theta) \quad (6-2)$$

Where θ is the contact angle between the water and the solid surface and r_b is the radius of the droplet.

As the water evaporates at a constant rate from the surface, the height of the droplet lowers, and thus the contact angle also decreases. During this r_b initially remains constant before receding rapidly in the final stages of evaporation [201].

Therefore, due to the nature of evaporation from the surface area, a greater radius and smaller contact angle therefore results in a higher rate of evaporation and faster drying time. Or more simply, the more hydrophilic a surface is the faster water will evaporate from it.

This may be advantageous in solar soiling applications as soiling is more likely to adhere to a wet surface, for example where water in the air condenses onto the cool mirror surface overnight, which significantly increases the rate of soiling through capillary forces and increases likelihood of caking and cementation, as well as reducing the rebound of particles which would otherwise bounce off the mirror surface in dry conditions [38]. Therefore, more rapid evaporation of water on the mirrors after cleaning will reduce the rate and severity of soiling immediately after cleaning.

A wet surface decreases likelihood of particle rebound, meaning more of the particles that reach the surface will remain on it, rather than bouncing off. Additionally, soiling that is incorporated into surface water that subsequently evaporates then undergoes caking and cementation, leading to soiling that is more strongly adhered to the surface and therefore more difficult to remove during washing. Therefore minimising the amount of time that there is water present on the mirror surface would be beneficial to soiling reduction and more efficient washing.

However, condensation can also form more readily on hydrophilic surfaces than hydrophobic, which may negate this effect if there is a higher level of condensation on plasma processed mirrors. In CSP plants water typically condenses onto the cold mirrors at night [53]. In laboratory conditions, condensation has been found to form more on clean hydrophilic surfaces [202]. In both cases, the process of condensation begins at surface imperfections, either on the surface itself or where there is contamination. Therefore, formation of dew on a surface is complicated in the presence of soiling.

Condensation on a mirror is detrimental where it forms and evaporates on the surface, leaving with it the condensation; however, if the mass of the water in the formed droplets is sufficient it will roll down the surface, taking with it soiling in the same manner as with water washing [203]. Therefore, where condensation is formed it may be beneficial for a hydrophilic surface to increase the quantity of water condensed upon it, to facilitate natural cleaning using the water held in the ambient atmosphere. This is discussed in more detail in Chapter 10.

6.4 M-CCMD Trials

Similar trials were conducted with the M-CCMD torches.

For these trials, the procedures were identical in that the torch was mounted in the enclosure above the sample, which moved beneath it. Again the WCA was determined by depositing a 2 μ L drop of deionised water onto the glass, its diameter measured with a digital calliper and the WCA measured using the optical tensiometer. The power was kept constant, controlled via the generator output current at 0.3 A as this was its maximum stable output, and gas flow also constant at 40 L/min as this was shown to incur a measurable effect on the surface and also allowed sufficient cooling of the torch device without the requirement to utilise the additional cooling circuit. The speed of processing a single pass controlled between 50 mm/min and 4 m/min. As shown in Figure 6-3, the effect is the same as with the Sairem torch, a smaller contact angle results in greater spreading of the droplet and consequently a larger area covered.

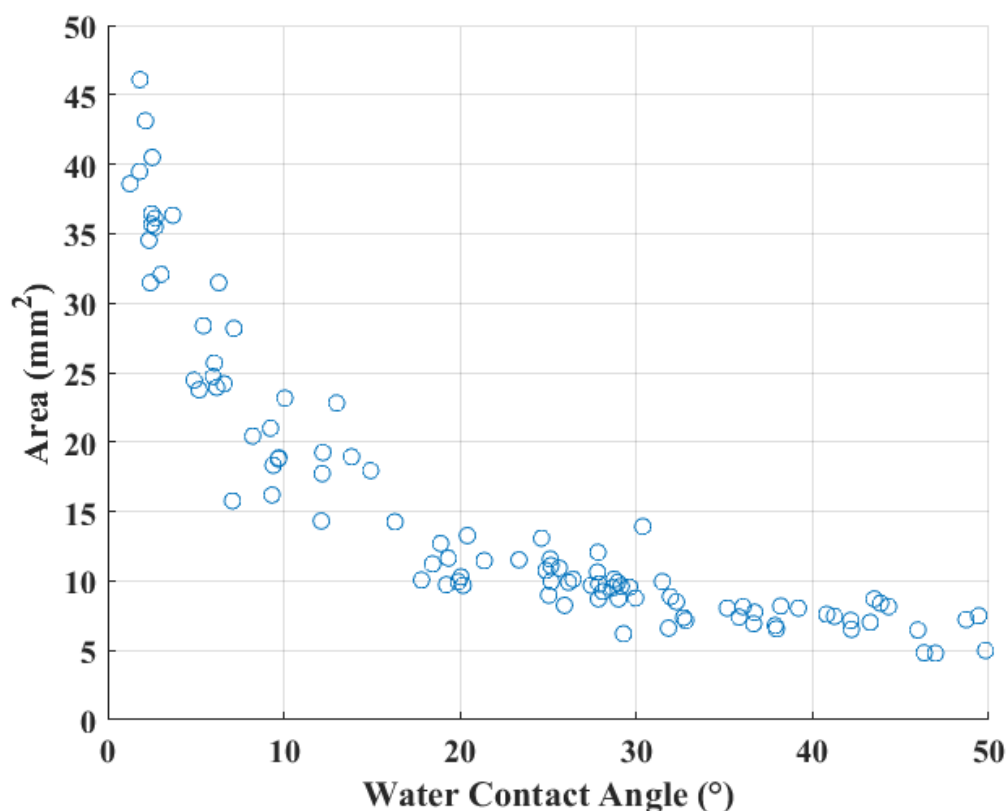


Figure 6-3 Graph of the area of a 2 μ L droplet of water and its contact angle, after processing using the M-CCMD 3.

When plotted against the processing speed as in Figure 6-4, it can be seen a slower speed results in a lower WCA and a more hydrophilic surface.

This is due to the plasma having a greater time to interact with the surface during the slower speeds, and thus more of the surface bonds are broken to produce the polar surface groups, resulting in a higher hydrophilicity and a lower WCA.

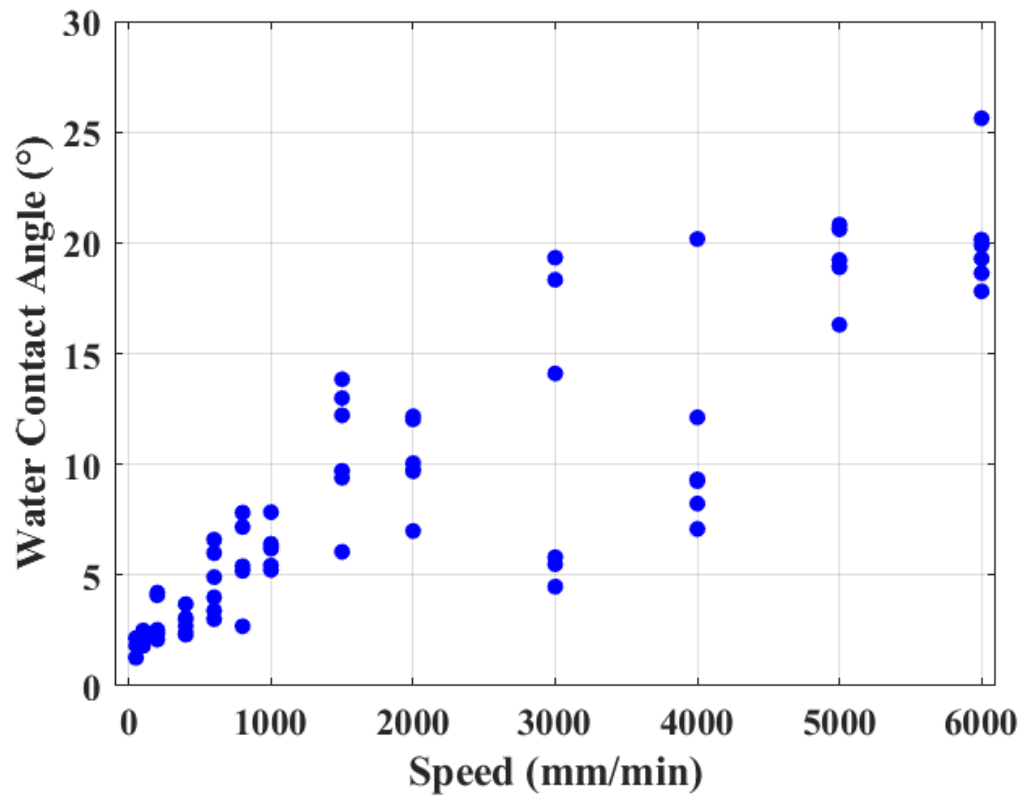


Figure 6-4 Graph showing the water contact angle achieved after plasma processing at different speeds.

This effect is not permanent and is subject to an ageing effect, where the created surface polar groups gradually recombine with the surface reforming the weak bonds that were broken by the plasma processing.

To measure this, samples were processed at the same speed of 50 mm/min and the WCA measured daily.

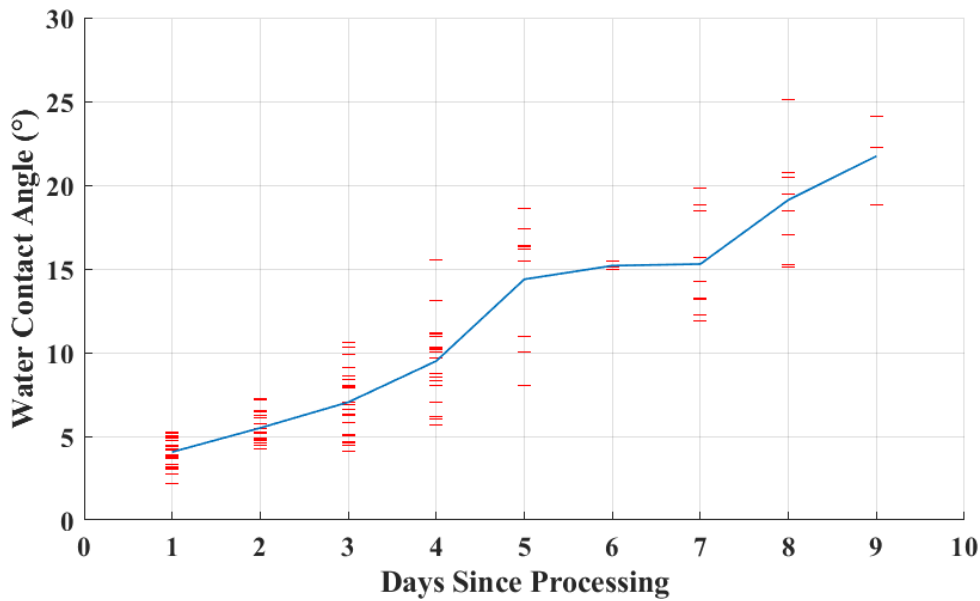


Figure 6-5 Graph showing the daily ageing of the surface after plasma processing.

As shown in Figure 6-5, not only does the average WCA of the surface increases every day over the 8 day measurement period, the range of values increases too. This is due to the sometimes random nature of the ageing process, where particles of dust or debris may fall onto the surface, as seen in Figure 6-6, in which particles of soiling from the laboratory are seen on the surface. Whilst these particles fall evenly on the surface on a macroscopic level, on the level of the surface bonds these particles of dust can cause significant local variations in surface energy as they knock into and effectively flatten or cap off the polar surface groups. Even if this surface soiling is then removed, the flattening of the surface group remains.

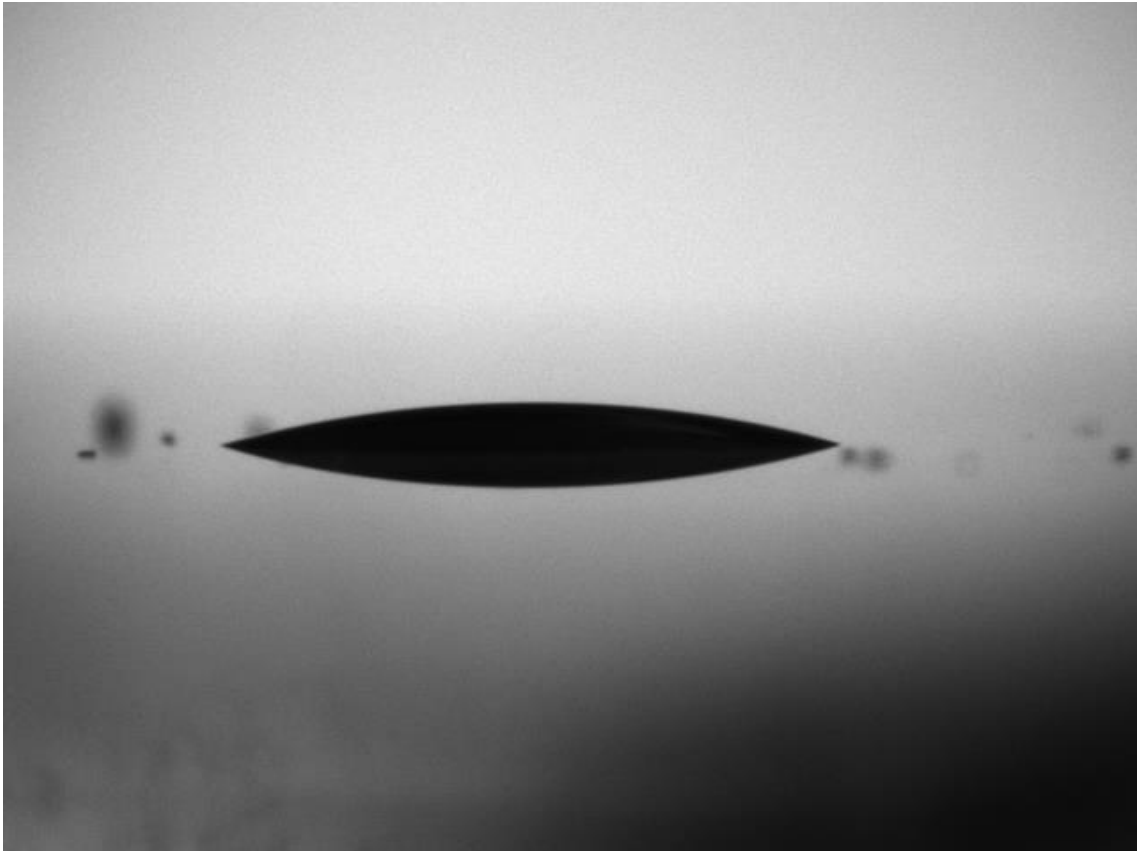


Figure 6-6 Photograph of a water droplet on a mirror surface showing contamination.

One sample as allowed to age further, for 18 days, the WCA of which is shown in Figure 6-7 and displays a logarithmic increase in WCA over the 18 days, where the hydrophilic effect decays rapidly over the first week before levelling to approximately 25° at the end of the measurement period.

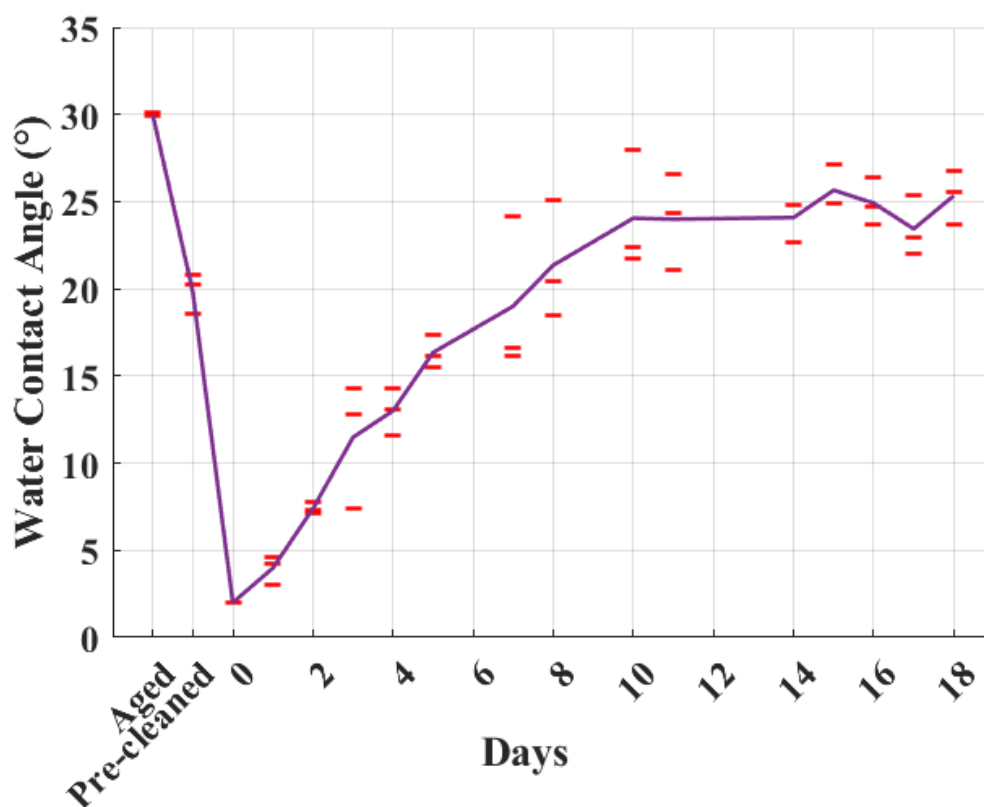


Figure 6-7 Graph showing ageing of a sample for 18 days after plasma processing.

The influence of the starting state of the surface before plasma treatment was also investigated, to determine whether the samples needed to be left to adequately age between processing. For this, the mirror samples used for the ageing trials were reprocessed with the same plasma parameters and the WCA measured.

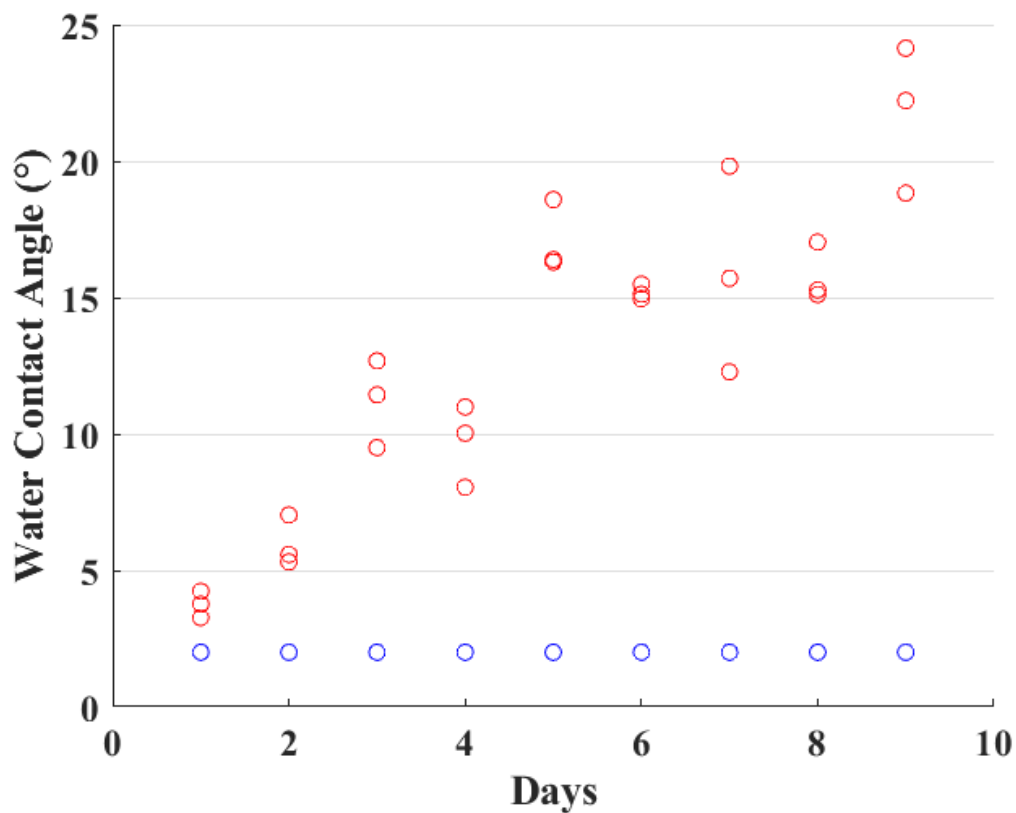


Figure 6-8 Graph showing the water contact angle before (red) and after (blue) reprocessing samples.

In every case, the WCA returned to below 2°, as in the WCA was below what could be measured accurately by the goniometer, seen in Figure 6-8. Therefore, it was not necessary in subsequent processing to allow the samples to age between trials.

7 Plasma Only Cleaning

A proposed solution with a potential 100% reduction in water use would be to use the plasma to remove the soiling from the mirrors without any additional washing.

Plasma cleaning is a well established tool in many industries however is generally employed to remove organic contamination from surfaces, removal of soiling of the type typically found in CSP applications has not been studied nor employed in industrial use.

7.1 Theory

In order to remove soiling the plasma can target either the soiling particles themselves, their adhesion forces to the mirror surface, or a combination of the two.

Targeting the particles generally involves addition of a chemically reactive species that reacts with the soiling, or generation of a particular radiation whose wavelength targets specific bonds within the particles. This approach, to fragment the particles to enable them to lift from the surface, poses a number of challenges with this application. Firstly, that CSP mirror soiling is of many different types of particles, of different sizes and compositions, therefore it would not be beneficial to tailor the plasma to target a particular bond within a particular molecule as it would affect only a proportion of the soiling, leaving the rest of the contamination behind. Additionally, in order to have sufficient energy or reactive species to target soiling, the plasma would also risk damaging the mirror surface itself, which chemically is not dissimilar to the soiling. As discussed in Chapter 2.5.1, soiling is comprised of multiple varieties of particle including mineral, organic, and others, however the most prolific are the mineral dusts particularly SiO_2 in its natural crystalline form of quartz. The primary component of solar glass, and most glass for other use, is also SiO_2 , which for example constitutes 69 – 74% of the solar grade glass offered by supplier AGC Solar Europe [204], indeed sand is the raw material for the production of glass, and whilst there are changes in the larger

structure during the glass forming process, the structure of the silica on a molecular and local level remains largely unchanged [205], and thus any process that would target the specific bonds of quartz form SiO_2 soiling are also likely to affect the structure of the silica in the glass, which could lead to degradation and even failure of the mirror, and so must be avoided [206].

Using plasma to overcome the adhesion bonds between the mirror and the soiling shows more promise, although whilst a plasma of sufficient energy could overcome most soiling bonds easily, the risk of thermal shock or damage to the glass is high. Consequently, only non-thermal plasma sources have been investigated in this work as this significantly reduces the risk of thermal damage to the mirrors.

As discussed previously, soiling bonds to the surface via three forces: capillary, Van der Waals, and electrostatic. Capillary forces occur only in levels of high humidity and are therefore not considered significant in dry soiling.

Electrostatic forces exist where there is charge in the particle that is attracted to charge on the mirror surface. Plasma, whilst holding an overall neutral charge, is comprised of charged particles. There are heavier positively charged ions, which in the non-thermal plasmas investigated have relatively low energy, and negatively charged electrons, which have higher energy and greater abundance. It is therefore possible that charge in the plasma can overcome electrostatic adhesion forces.

Van der Waals are in most circumstances the most significant adhesion force in soiling, therefore targeting of these bonds would result in the greatest cleaning ability of the plasma. These forces fall into three categories depending on the dipoles of the particles and surface: Keesom, dipole-dipole; Debye, induced dipole – dipole; and London, induced dipole – induced dipole.

7.2 Methodology

For plasma only cleaning, samples were pre-cleaned and soiled as described in Chapter 5, they were then secured onto the motion stage in the plasma chamber and subject to plasma processing at parameters of 0.3 A, 40 L/min, N_2 , 50

mm/min speed at a height of 1 mm, as these parameters were demonstrated in previous investigations such as the surface energy modification trials discussed in Chapter 6.4 to have a measurable effect on the surface as well as generating a stable plasma necessary for repeatable and homogenous processing. Hereon in these parameters are defined as “standard parameters”. Cleanliness was measured as reflectance at each stage, as shown in Figure 7-1.

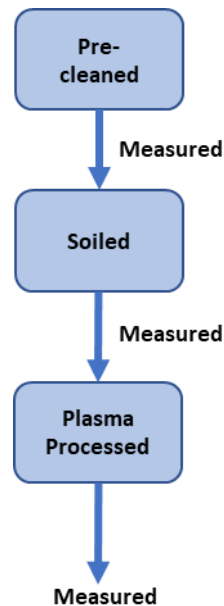


Figure 7-1 Chart showing plasma only cleaning methodology steps.

7.3 Results

Plasma only cleaning caused an increase in reflectance, indicating a removal of some of the surface soiling, however this was not sufficient to render the mirrors adequately clean for CSP application, which considers mirrors of above 90% specular reflectance to be clean, whereas the trials here achieved a maximum average reflectance of only 86.5%.

The average reflectance of the pre-cleaned samples was 94.8%, which fell to 82.0% after the soiling procedure. As shown in Figure 7-2, after plasma processing the average reflectance raised to only 86.5%, an increase of 4.5%. The range of the plasma processed measurements was also large, with a standard deviation of 4.8%, a slight decrease from the 5.1% for the soiled

samples, however still significantly greater than the 0.1% value for the pre-cleaned samples.

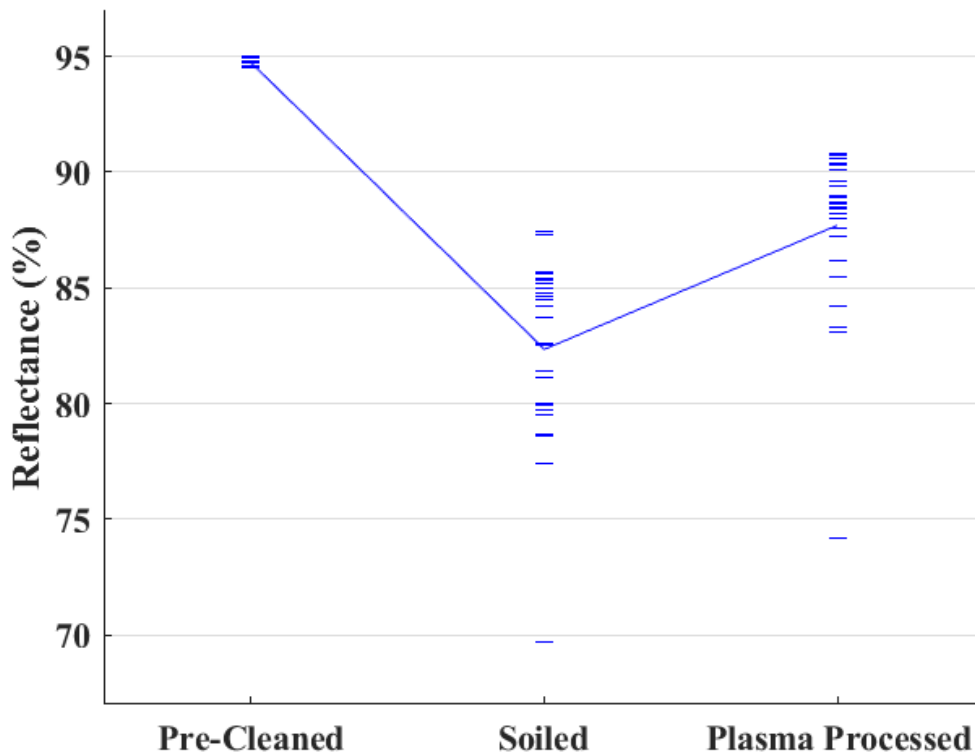


Figure 7-2 Reflectance of mirror samples subject only to plasma cleaning.

The most probable cause of the soiling removal for this process is physical bombardment of the ions against the soiling particles, dislodging them from the surface before blowing them away as the plasma returns to a gaseous state. The plasma is low temperature and spectroscopy described in chapter 4.1 has shown there are no significant populations of reactive species, therefore chemical interaction with the soiling or the adhesive bonds is unlikely.

It may be possible to enhance the effect of plasma only cleaning by changing the plasma parameters, for example using a higher power plasma or by incorporating reactive species into the plasma, either in the feed gas or downstream of plasma generation, however doing so would risk damage to the mirror surface. Glass, being comprised mainly of SiO_2 , is chemically similar to many of the most commonly seen constituents of soiling as discussed in chapter 2.5.1, and

therefore targeting the bonds of these molecules is likely to also affect the bonding of the mirror.

A higher power and therefore higher temperature plasma may also remove a greater degree of soiling, however again the risk of damage to the mirrors through melting or thermal shock also increases with this approach.

It was therefore decided that plasma-only cleaning was not feasible, and consequently another approach was taken where plasma was used in conjunction with more conventional cleaning methods in a hybrid system.

8 Hybrid Cleaning

As discussed in chapter 7, plasma only cleaning is not a feasible solution to soiling removal, and as such a hybrid approach has been investigated, combining plasma processing with more conventional water-based cleaning methods.

8.1 Theory

As discussed in literature review section 2.15 and demonstrated in experimental chapter section 6, plasma has successfully modified the surface energy of glass to produce a hydrophilic and superhydrophilic surface. This results in a significant change in behaviour of water on plasma processed glass versus those unprocessed. Therefore, it follows that water used during washing of mirrors treated with plasma will also behave differently, potentially resulting in a greater cleaning effect, which could reduce the water required to reach adequate cleanliness. This hypothesis is supported by literature, for example in the textile industry where literature which discusses how plasma treatment of textiles resulted in more efficient use of water-based dyes as a result of the induced hydrophilicity. A review of such techniques by Haji et al. discusses multiple studies where plasma processing of both natural and synthetic textiles resulted in improved dyability of the fibres, which necessitates less dye, and therefore water, being required to colour the fabrics to the same depth as with non-plasma processed textiles [207]. A similar review by Zille et al. described how plasma treatment could be used to replace conventional wet-chemical pre-treatment, meaning the use of water during pre-treatment could be completely eliminated, saving considerable quantities of water [208].

Plasma has also been studied for use in agriculture, discussed in a review by Ranieri et al., where seeds exposed to a DBD plasma treatment showed increased water uptake due to the plasma induced hydrophilic surface, meaning less water was required both to induce germination and to sustain them during growth, as the water adheres to the seeds for longer to be absorbed and incorporated, rather than running over and off the seed being lost [209].

8.2 Methodology

For hybrid cleaning trials, the samples were subject to the same procedures of pre-cleaning and soiling as described in Chapter 5. Half of the samples were then subject to plasma processing at previously defined standard parameters. They were then immediately washed as per Chapter 5.6, with the parameters varied being the flow rate of water from the spray nozzle, listed in Table 8-1 and grouped into three classifications of Mist, Spray, and Jet washing in order of increasing flow, and the washing speed of between 0.25 m/min and 20 m/min depending on the trial group.

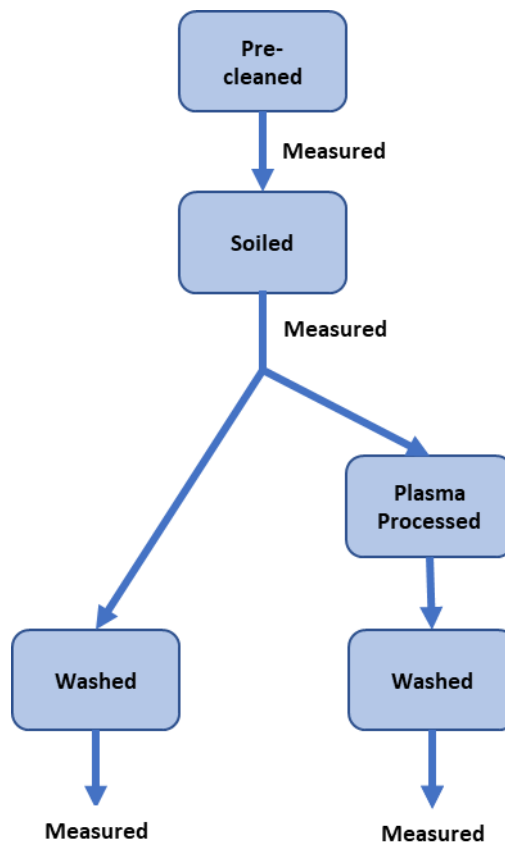


Figure 8-1 Chart showing hybrid washing methodology steps.

Table 8-1 Hybrid washing trial water flow parameter grouping.

Trial group	Water Flow (L/min)
Mist	0.01
Spray	0.02
Jet	0.06

Cleanliness was measured between each step as reflectance according to Chapter 5.5 and shown in Figure 8-1. The 9 measurement points were split into three rows, indicated as row A, row B, and row C, where the spray of water passed across row A, as shown in Figure 8-2.

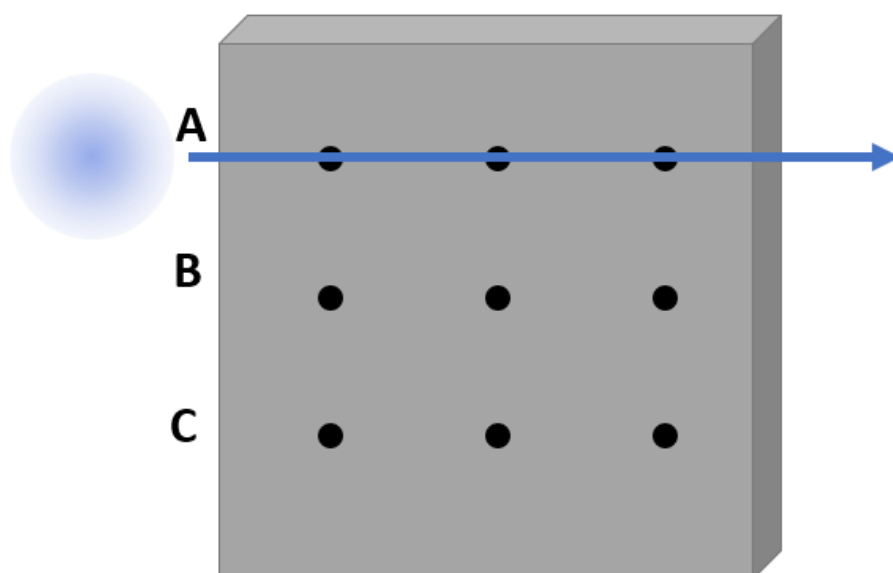


Figure 8-2 Diagram showing position of water jet and measurement points.

This work was split into three main sections according to the nozzle flow: mist trials, spray trials, and jet trials, with the water flow rate increasing for each set. Flow rate was calculated by measuring the water collected in a measuring cylinder placed over the nozzle opening over a set period. The flow rate defined here thus includes only the water flow through the nozzle and does not include the accompanying air flow, which was kept constant throughout as well as the line pressure, kept at 1.5 bar throughout.

Mist spraying was the lowest flow of 0.01 L/min, and produced a thick mist from the nozzle without a well-defined footprint. For spray trials, the flow was doubled to 0.02 L/min, which produced a spray from the nozzle. For the jet trials, the flow was increased to the maximum repeatable flow setting of 0.06 L/min, producing a jet which was surrounded by a further thick mist.

For the washing trials, the equivalent water consumption rate per m² was calculated, such that the work could better be compared to real world cleaning applications.

An example of the calculation is as follows:

Considering the jet trials where the water flow rate was 0.06 L/min, and a washing speed of 2.5 m/min.

The samples are approximately 80 mm x 80 mm, an area of 6,400 mm², which is 1/156.25 of 1 m². Assuming a width of exactly 80 mm (here our distance, x , at a speed (v) of 2.5 m/min, or 41.7 mm/second

$$t = \frac{x}{v} = \frac{80}{41.7} = 1.9 \text{ s} \quad (8-1)$$

the sample takes 1.9 seconds to pass through the jet.

0.06 L/min is equivalent to 0.001 L/second, therefore the water consumption rate is

$$1.9 \times 0.001 = 0.0019 \text{ L/sample} \quad (8-2)$$

Scaling up to 1 m²

$$0.0019 \times 156.25 = 0.3 \text{ L/m}^2 \quad (8-3)$$

8.3 Mist Trials

For misting trials, the flow rate from the nozzle was set at 0.01 L/min which resulted in a mist spray onto the sample.

At these parameters, the water consumption per sample is as below:

Table 8-2 Water Consumption Rate of mist washing trials.

Speed (m/min)	Water consumption (L/m ²)
2.5	0.05
5	0.025
10	0.0125
15	0.008333
20	0.00625

Behaviour of the water as it landed onto the sample showed significant visual difference between plasma processed and un-processed samples, as shown in Figure 8-3. For all parameters, the plasma processed samples showed much greater downwards movement of the water as well as a more homogenous distribution of water at the top row.

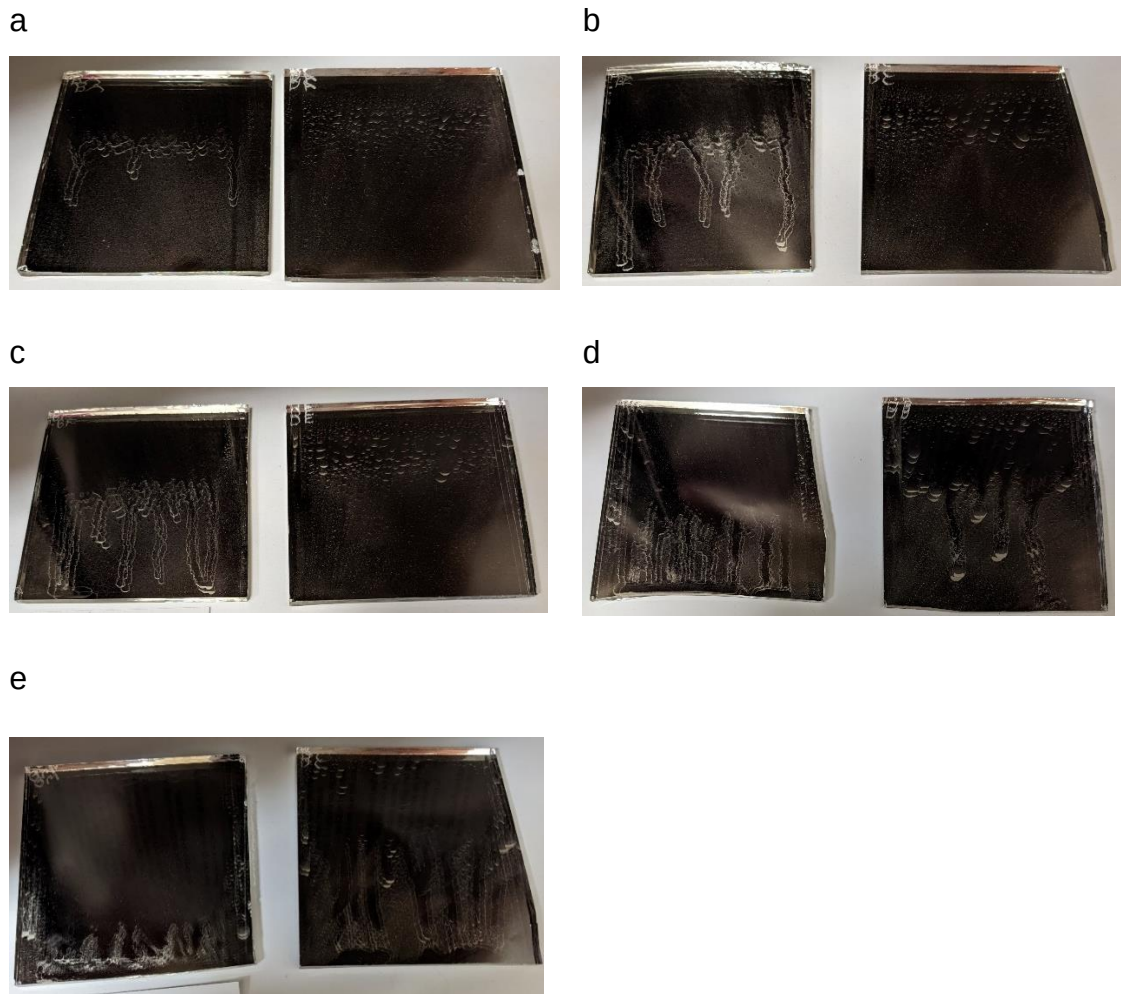


Figure 8-3 Photographs of one set of samples subject to the same washing procedure after plasma processing (left) or without plasma processing (right) at washing speeds of a = 20 m/min, b = 15 m/min, c = 10 m/min, d = 5 m/min, e = 2.5 m/min.

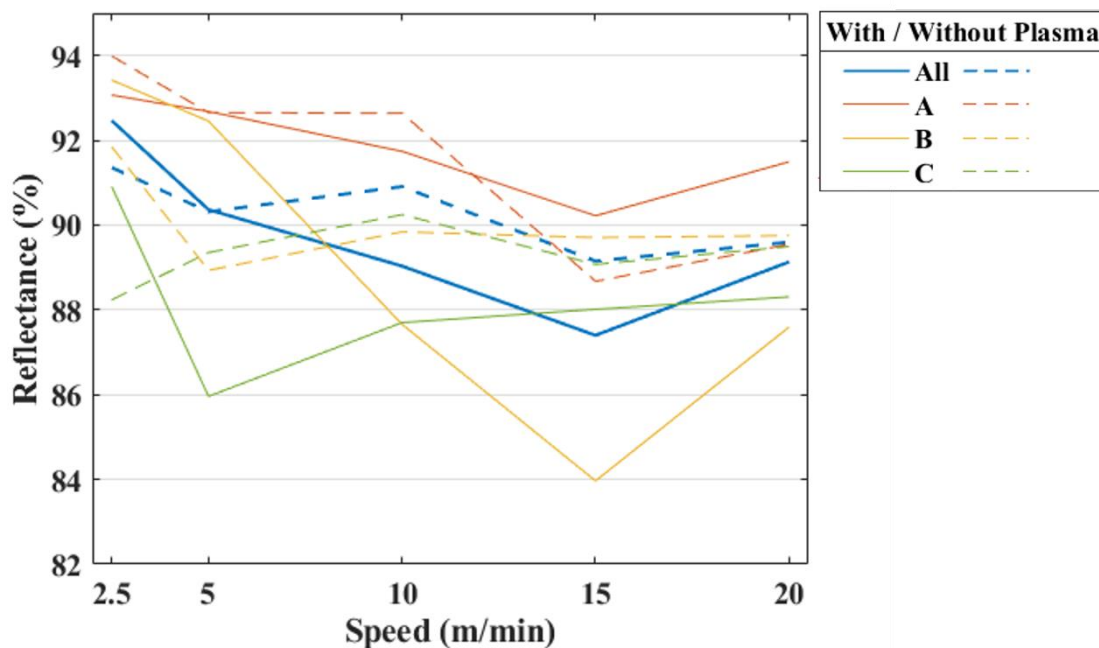


Figure 8-4 Average reflectance values for the samples in mist trials.

The average values of reflectance across both the whole sample and per row is displayed in Figure 8-4 and shows that slower speeds result in higher reflectance values, as more water falls onto the mirror during each pass, which increases the incidence of the water reaching adequate mass to roll down the mirror and drag with it soiling. There appears to be no benefit of plasma processing prior to washing in terms of cleaning efficiency, however the inhomogeneous and random nature of both soiling and bead formation means the average of all values does not necessarily convey the data accurately, as for example an area of particularly high soiling can significantly bring down the average. To overcome this, the individual measurement points are also plotted, as in Figure 8-5 and Figure 8-6, which better shows the distribution of the data.

For un-processed samples, the water formed beads on the surface which depending on mass either dried in place or rolled down the surface of the mirror, taking with it most soiling. As seen in Figure 8-5, this resulted in higher reflectance at row A as the soiling was lifted and either carried down the mirror or concentrated into the bead location and redeposited in a more concentrated fashion upon evaporation of the bead. Slower speeds allowed for a greater

quantity of water to be deposited onto the mirror and therefore more of the beads had the required mass to travel down the mirror, both increasing the washing effect at row A and increasing the likeliness of the lower rows B and C showing increased reflectance as the bead pulls soiling with it.

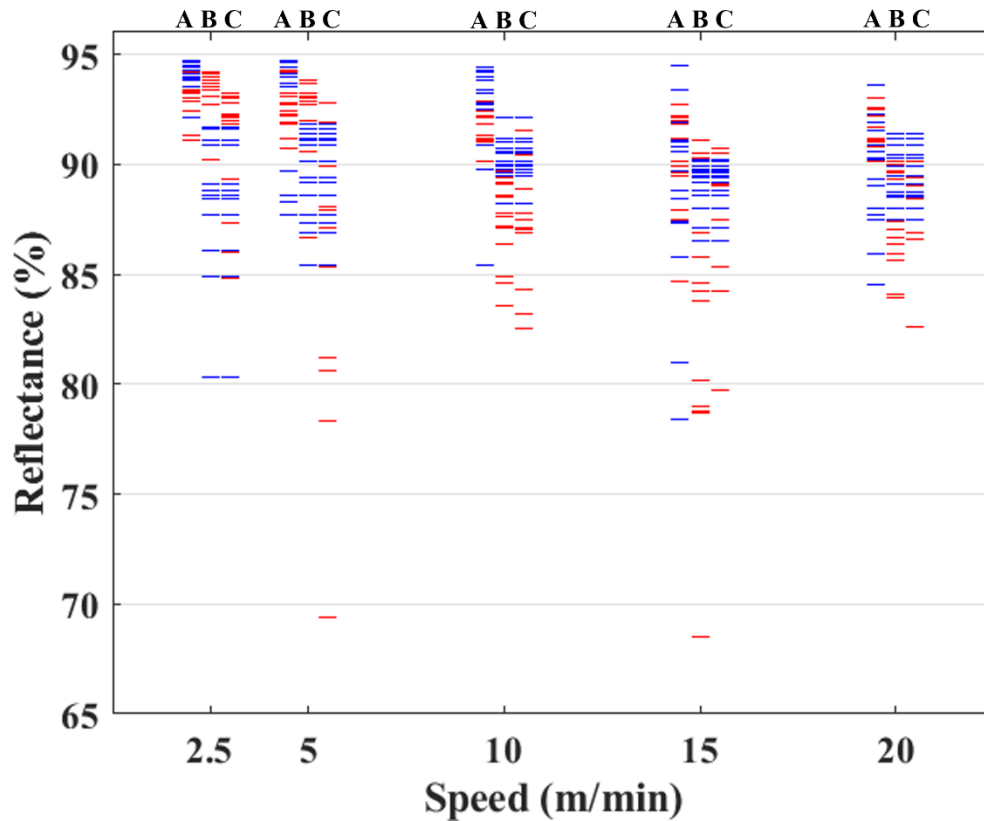


Figure 8-5 Reflectance values of samples with (red) and without (blue) plasma processing prior to water washing.

In some instances however there is a decrease in reflectance, as seen in Figure 8-6, caused by soiling being pulled from its more homogenous distribution to concentrated circles where the beads form and then evaporate, either in place or at a distance down the mirror sample and redeposited from row A to rows B or C. Therefore, it can be considered that although there is an overall increase in reflectance there is also significant redistribution of soiling that remains on the sample. This is especially the case at faster speeds where the majority of beading does not travel the full distance of the mirror and therefore does not truly remove soiling but instead simply lifts then redeposits the soiling further down the mirror.

Often, redeposition is higher in plasma processed samples, this is due to the higher number of tracks formed on these samples, as shown in Figure 8-7 which shows higher rate movement of soiling down the mirror.

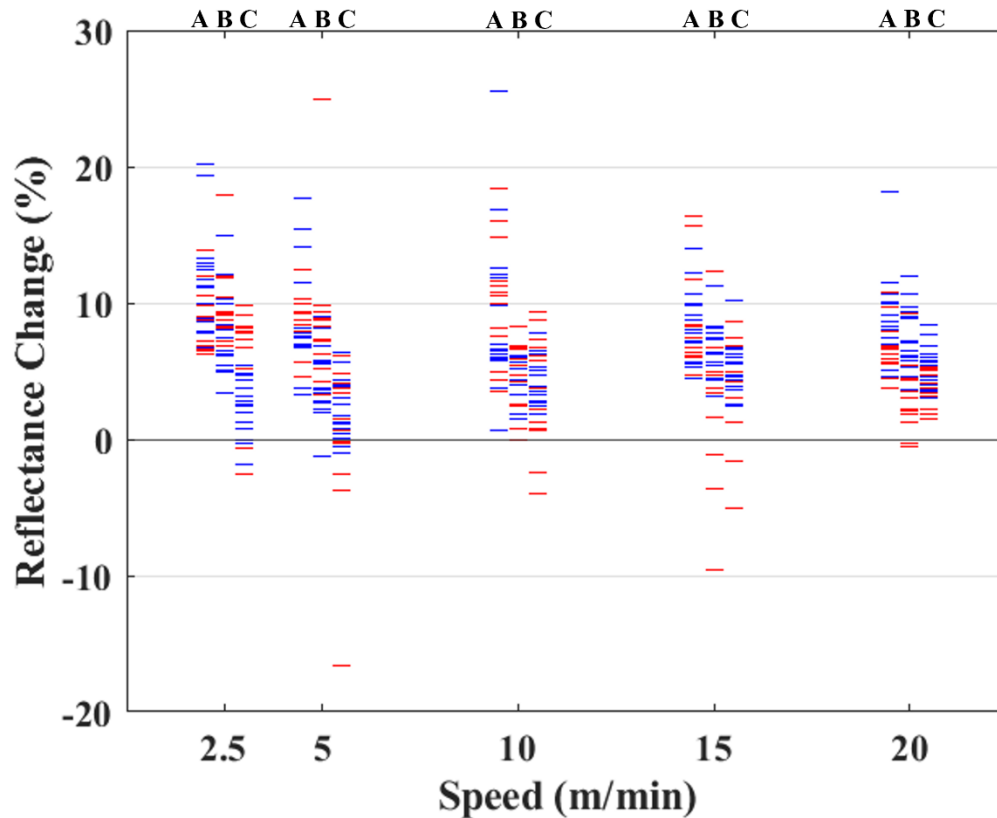


Figure 8-6 Change in reflectance of samples with (red) and without (blue) plasma processing prior to water washing.

For plasma processed samples the water does not bead up, rather it forms a thin layer on the sample which initially falls down the mirror in a more evenly distributed manner than the bead tracks on the un-processed samples, eventually forming into tracks similar to the beading on the un-processed samples, likely due to its path being diverted by soiling particles for which there is not enough force to pick up into the travelling water. Redeposition, resulting in negative changes in reflectance, was seen more frequently with plasma treated samples, in part due to the increased rate of evaporation of the water from the mirror surface. Resulting in the water and soiling carried with it not falling off the mirror.

Assuming the same mass of water is deposited onto the samples, on plasma processed samples this mass is evenly distributed across the processed area, resulting in a consistent but lower force pulling on the soiling particles, and therefore smaller particles that require more force to remove are not removed, particularly in row A where plasma processed samples often showed lower reflectance values than on unprocessed samples, as seen in Table 8-3.

Table 8-3 Average reflectance (%) of samples with and without plasma processing prior to mist washing. Cells shaded in green indicate areas considered “clean” by the criterion of above 90% reflectance.

	With plasma				Without plasma			
Speed (m/min)	A	B	C	All	A	B	C	All
2.5	93.1	93.4	90.9	92.5	94.0	91.8	88.2	91.4
5	92.7	92.5	86.0	90.4	92.7	88.9	89.4	90.3
10	91.7	87.7	87.7	89.0	92.6	89.8	90.2	90.9
15	90.2	84.0	88.0	87.4	88.7	89.7	89.1	89.2
20	91.5	87.6	88.3	89.1	89.5	89.8	89.5	89.6

On the un-processed samples, the mass is distributed unevenly in beads of varying size, and so the soiling is either subjected to no downwards force in areas with no beading, or relatively large downward force, in the vertical path of the bead, enabling those areas to be cleaned more effectively.

This beading and generation of tracks was also measured, for this the number of tracks, where the bead makes downward travel across the surface, was measured as started tracks, which do not reach the sample edge, and completed tracks, where the bead reaches the end of the sample. An example of this measurement is shown in Figure 8-7 which also shows the measured width of the washing area, discussed further with Figure 8-9.

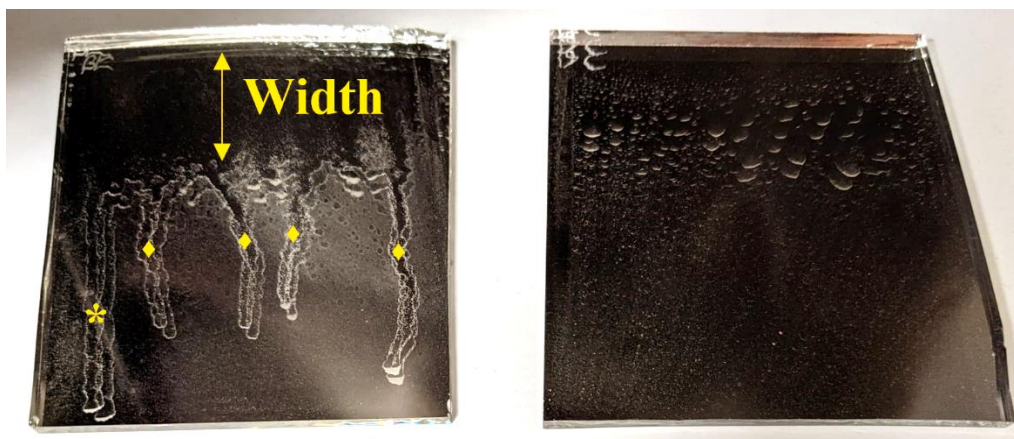


Figure 8-7 Image of samples processed at 15 m/min washing speed, showing measurement of washed area width, tracks (♦) and completed tracks (*), the non plasma processed sample on the right has no width and no tracks.

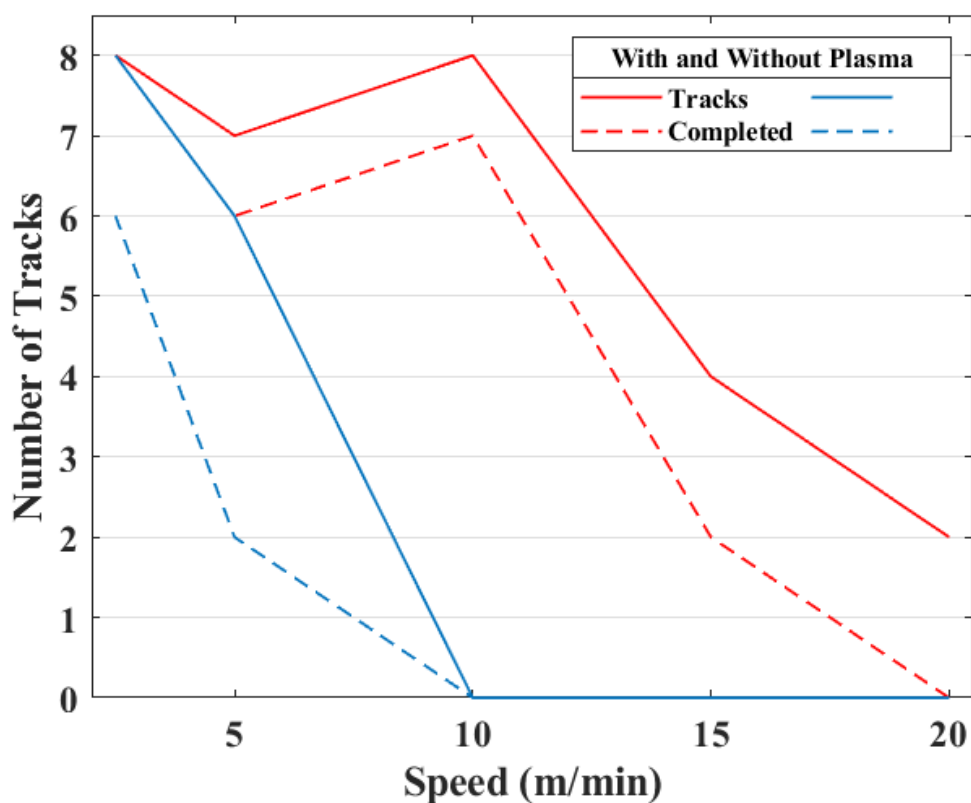


Figure 8-8 Average number of tracks on samples with (red) and without (blue) plasma processing.

It can be seen on Figure 8-8 that plasma processed samples have a higher number of tracks on at every speed, and also a greater number of those tracks are completed, indicating that more soiling is being removed as the water is

reaching the end of the sample and therefore will have minimal redeposition. For non-plasma processed samples, above speeds of 10 m/min there are no tracks formed at all, as the water that lands on the sample beads up and dries in place, resulting only in local redeposition of the soiling.

Another impact of the plasma processing on the samples is the width of the wetted region, not including tracks, which was measured at three points across each sample with a digital calliper and averaged.

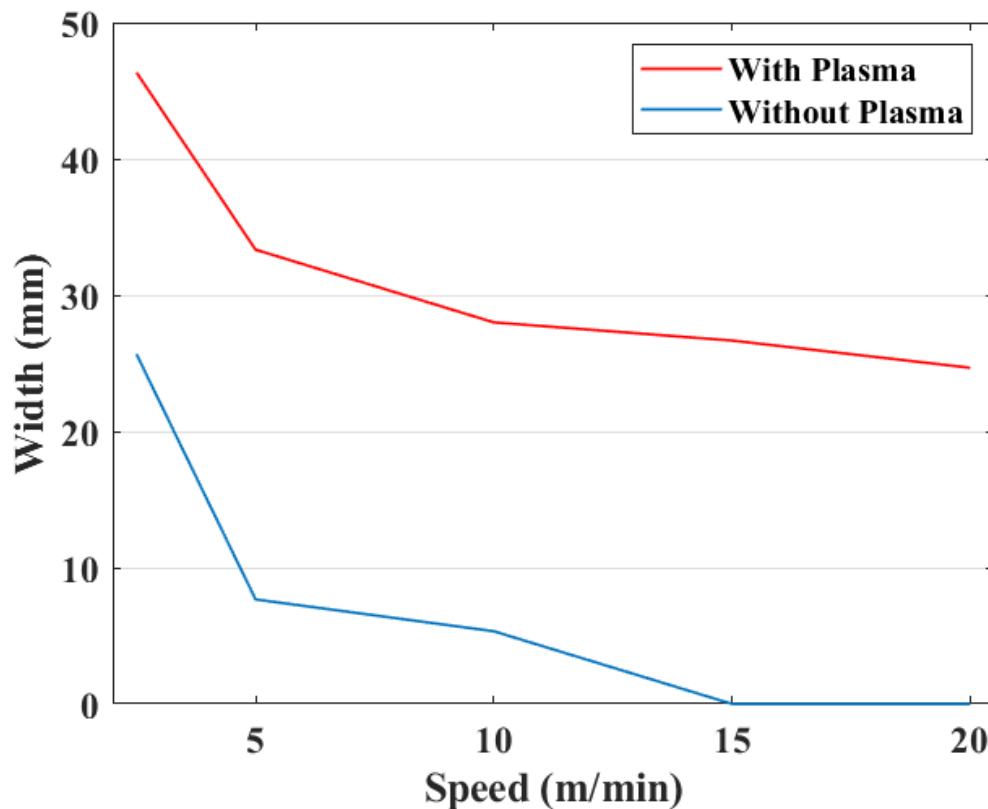


Figure 8-9 Width of mist washed area on samples with and without plasma processing.

This parameter again showed the benefit of plasma processing prior to water washing, where the width of the washed area was greater at every speed as shown on Figure 8-9, indicating better cleaning. Again, here there is on average no width measured at speeds of 15 m/min and 20 m/min for non-plasma processed samples, as there is no measurable movement of the water and therefore soiling on the mirror sample.

As cleaning was not satisfactory at these parameters, the water nozzle was increased and the trials repeated in a new set named Spray Trials.

8.4 Spray Trials

For spray washing trials, soiling and plasma processing were carried out as in the mist washing trials. The washing rig remained the same except for the flow rate of the nozzle which was increased to 0.02 L/min. The resultant water consumption rates are:

Table 8-4 Water consumption rates of spray washing trials.

Speed (m/min)	Water Consumption (L/m ²)
2.5	0.1
5	0.05
10	0.025
15	0.016667
20	0.0125

Spray washing exhibited similar behaviour to mist washing trials, as is apparent in Figure 8-10 but resulted in higher overall cleanliness.

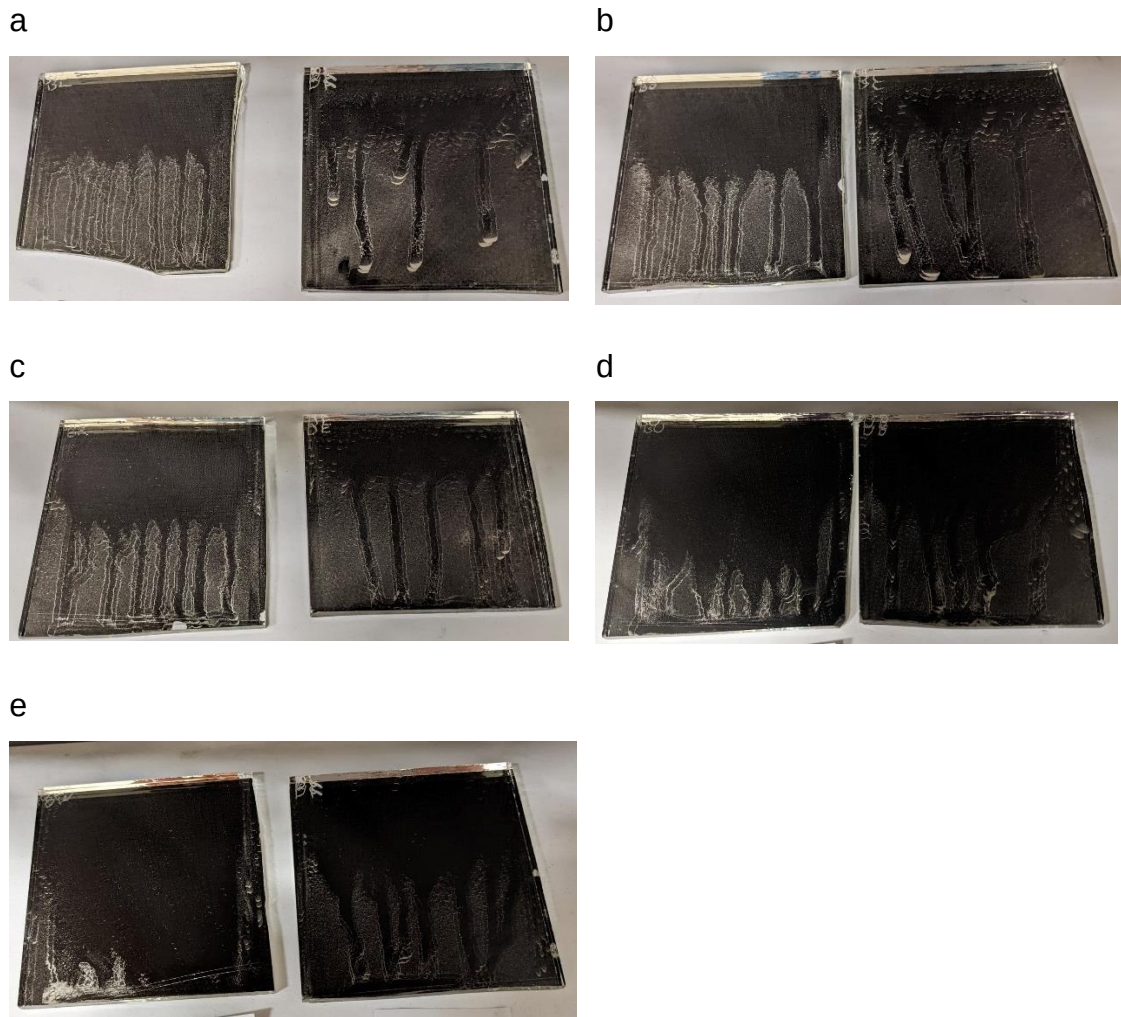


Figure 8-10 Photographs of one set of samples subject to the spray washing procedure after plasma processing (left) or without plasma processing (right) at washing speeds of a = 20 m/min, b = 15 m/min, c = 10 m/min, d = 5 m/min, e = 2.5 m/min.

Row A again showed the highest reflectance, seen in Table **8-5**, with plasma processed samples showing slightly lower values of reflectance, where the water and soiling behaved in a similar manner to in mist trials with soiling in the first row lifted by the water but not necessarily carried down and off the sample.

Table 8-5 Average reflectance (%) of samples with and without plasma processing prior to spray washing. Cells shaded in green indicate areas considered “clean” by the criterion of above 90% reflectance.

	With plasma				Without plasma			
Speed (m/min)	A	B	C	All	A	B	C	All
2.5	93.1	93.4	90.9	92.5	94.0	91.8	88.2	91.4
5	92.7	92.5	86.0	90.4	92.7	88.9	89.4	90.3
10	91.7	87.7	87.7	89.0	92.6	89.8	90.2	90.9
15	90.2	84.0	88.0	87.4	88.7	89.7	89.1	89.2
20	91.5	87.6	88.3	89.1	89.5	89.8	89.5	89.6

Washing at row A was consistently high across the speeds, as seen in Figure 8-11, and was higher with non-processed samples than with plasma processed samples.

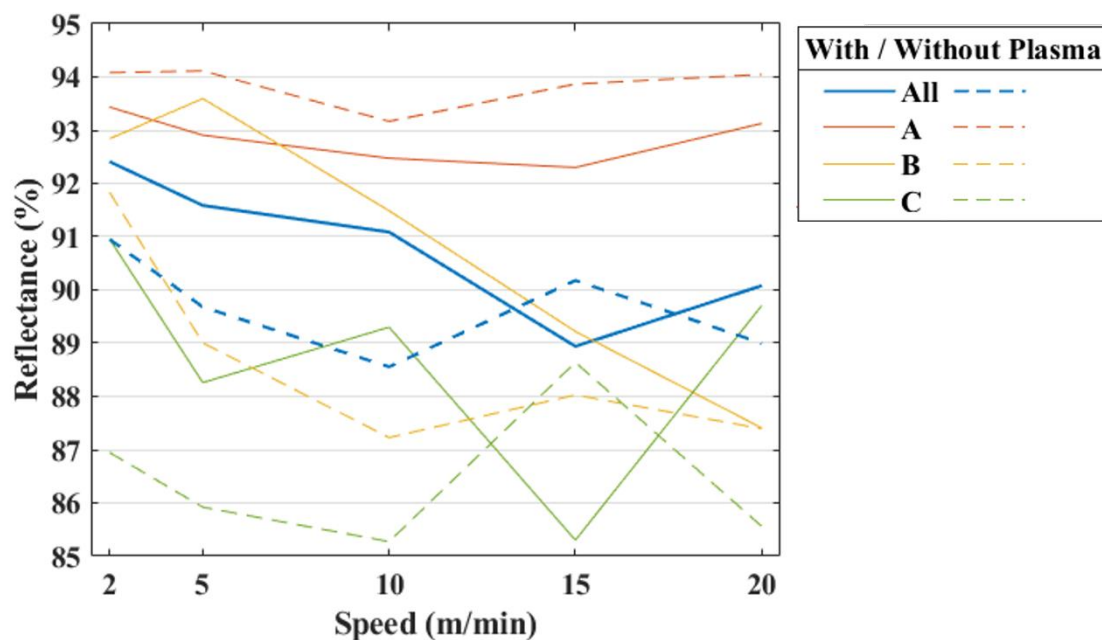


Figure 8-11 Average reflectance of samples with and without plasma processing.

At row B washing was more effective at slower speeds as more of the water directed at row A travels down the sample and washes beneath it in row B. This washing effect is greater for plasma processed samples than non-processed samples as the water travels down the sample in a more homogenous manner and therefore there gives rise to more consistent and higher soiling removal.

At row C washing was more erratic in nature, with significant range in values, this is due to the random nature of tracks created and the deposition of soiling within these tracks. If a track is formed within the area of a measurement point then reflectance can either be high, where soiling has been dragged down the sample, or low, where soiling has redeposited within or at the edge of the track.

It is for this reason that the reflectance of row C at 15 m/min does not fit the general trend of the data.

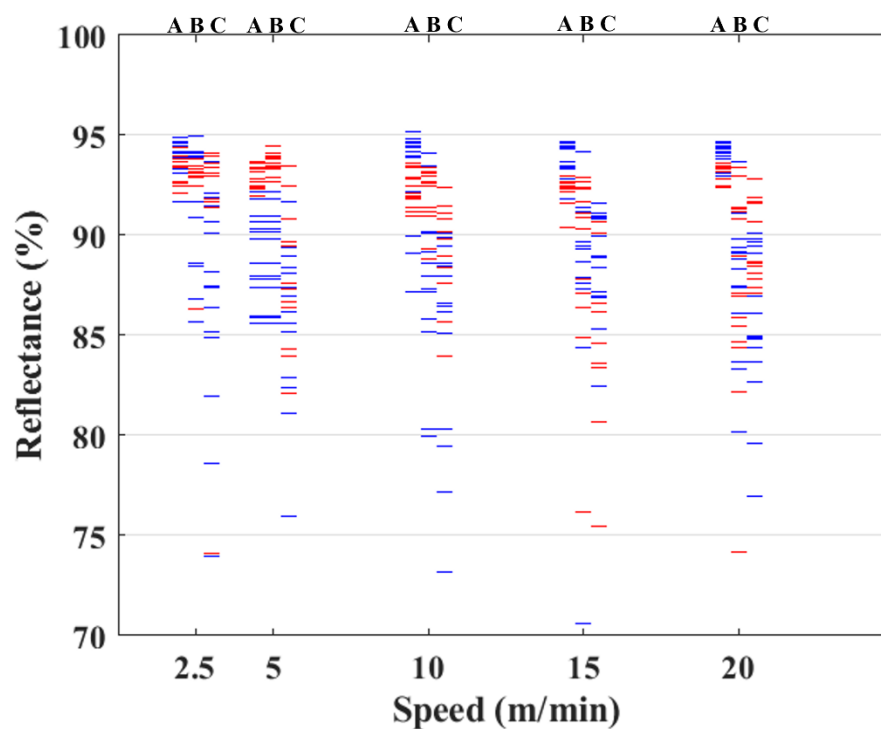


Figure 8-12 Reflectance values of samples with (red) and without (blue) plasma processing prior to spray washing.

It can be seen in Figure 8-12 that the unprocessed samples have significantly higher range in values, and many more datapoints with very low values of

reflectance. This occurs as the water is redeposited onto the samples due to incomplete tracks.

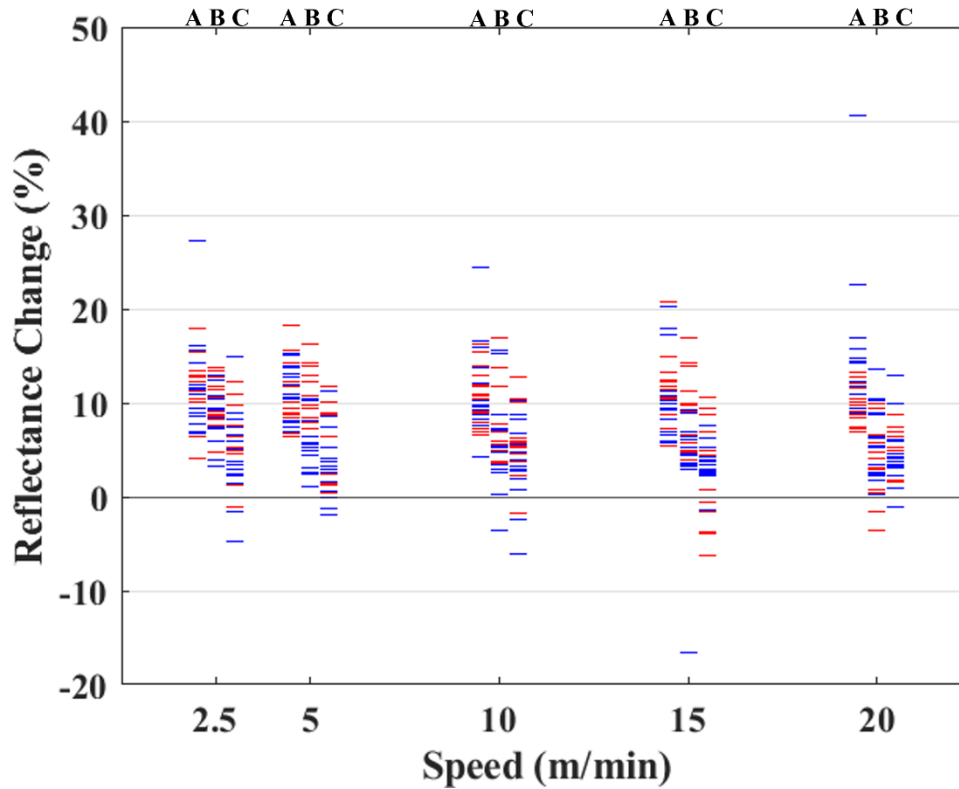


Figure 8-13 Change in reflectance of mirror samples with(red) and without (blue) prior plasma processing.

There is still some redeposition of soiling in rows B and C as seen in Figure 8-13, more so in non-plasma processed samples, due to the lower chance of tracks being completed, as seen in Figure 8-14 which shows that on the plasma processed samples, at speeds of 2.5 m/min to 15 m/min all tracks started are completed whereas on the non-plasma processed samples on average none of the tracks are completed at any speed.

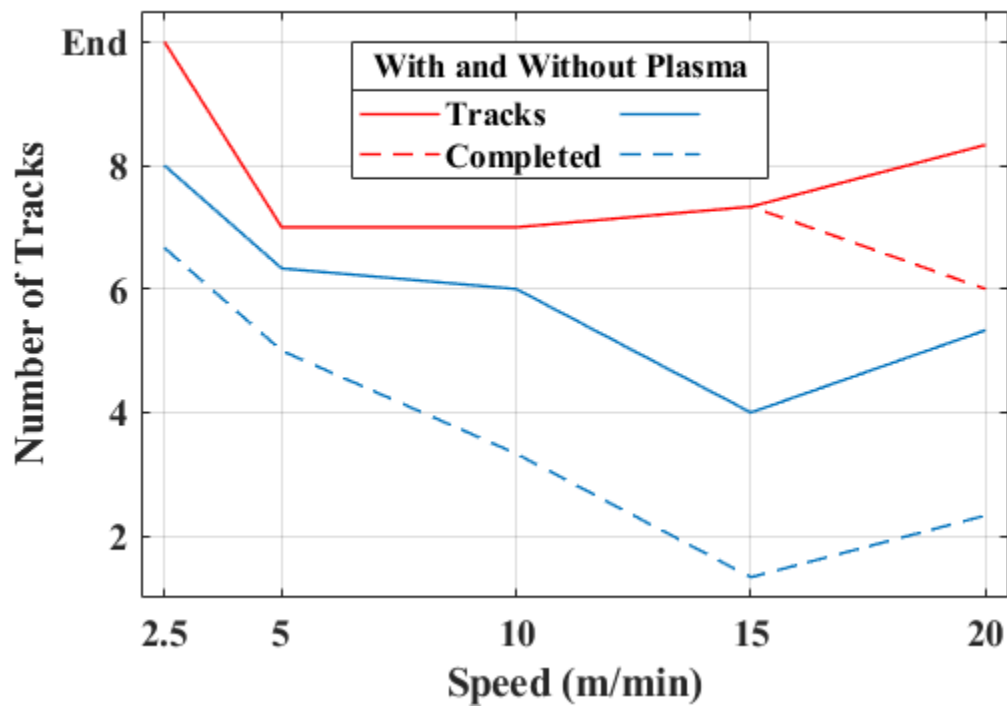


Figure 8-14 Number of started and completed tracks on washed mirror samples.

On this figure, “End” on the y axis indicates the washing area was the whole width of the sample, therefore there were no individual tracks to measure. This is also reflected in Figure 8-15, which shows at a washing speed of 2.5 m/min the average washed area of the plasma processed samples was 80 mm, which is the total length of the sample.

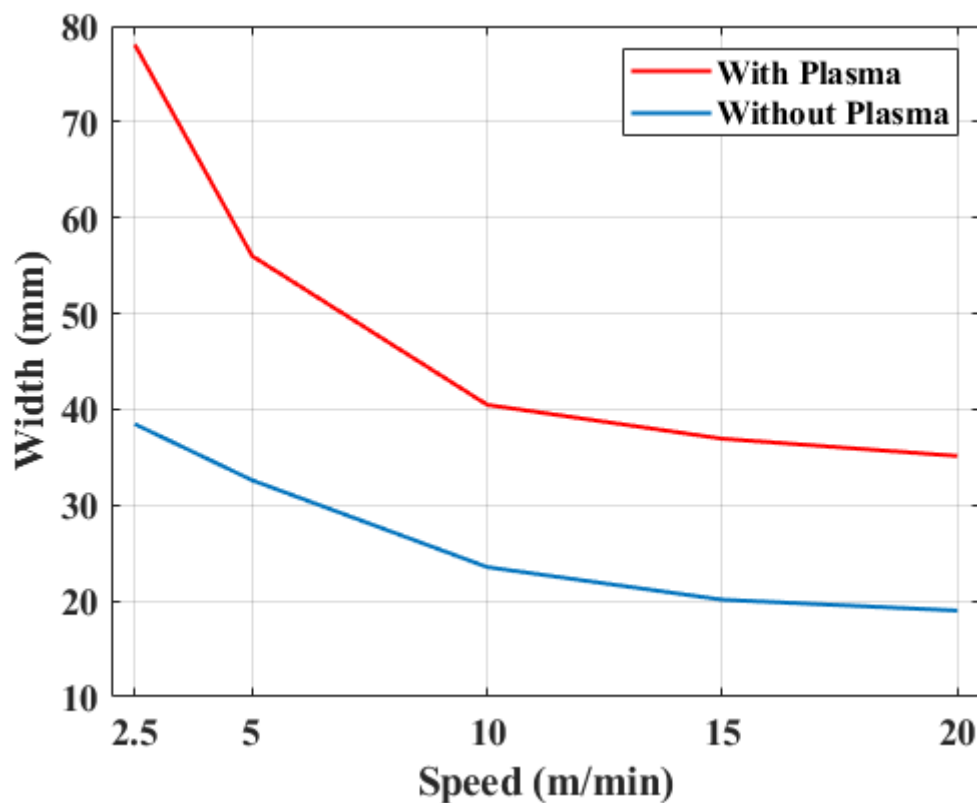


Figure 8-15 Width of spray washed area on samples with and without plasma processing.

Even where the width of the washed area was the entire length of the sample, the sample was not considered adequately cleaned as some soiling remained, even in fully wetted areas. This is evidenced as the average clean (pre-soiled) reflectance values of the 2.5 m/min set was 94.7%, whereas the average reflectance value after water washing was only 92.5% for the whole mirror area, which was 93.1% at row A, 93.4% at row B, at 90.9% for row C.

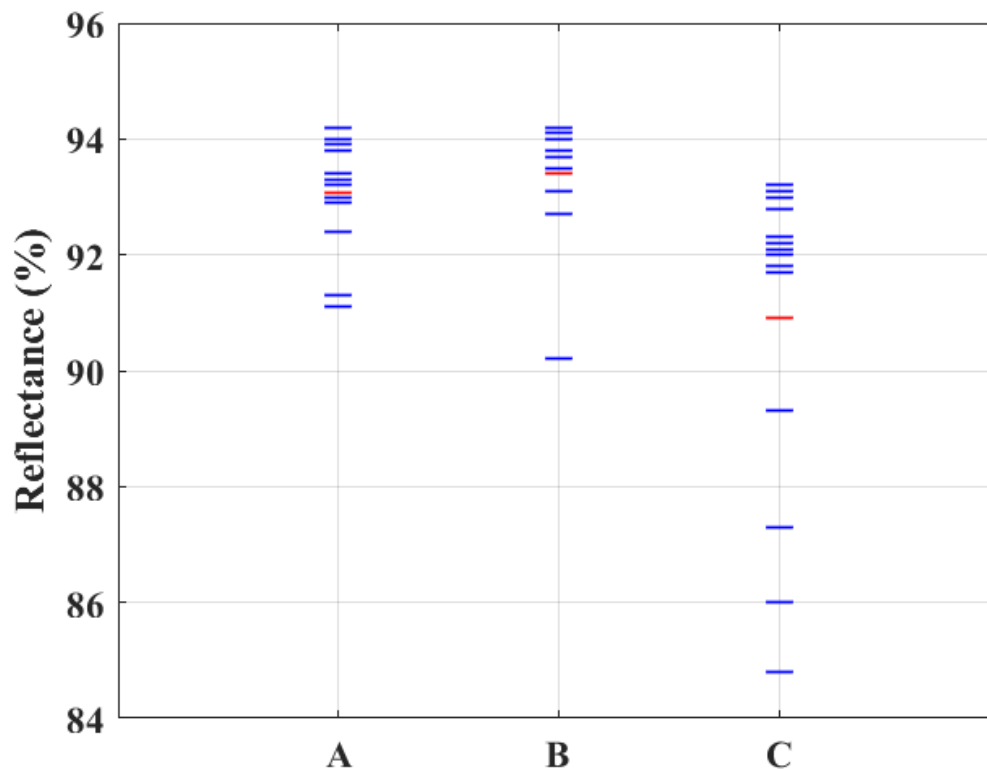


Figure 8-16 Reflectance values of rows A, B, and C (blue) and the average value for each (red) for the 2.5 m/min washing speed spray trial set.

These values meet the threshold for greater than 90% reflectance considered clean in CSP plants however is lower than the true clean, unsoiled value. Additionally, individual points on the mirrors can be below this threshold, as shown in Figure 8-16. Therefore, for the final set of trials the water flow rate was again increased, and the trials repeated.

8.5 Jet Trials

For the third set of washing trials the flow from the nozzle was increased to 0.06 L/min, which was the maximum consistent and controllable value possible.

At this flow rate, the water consumption rates are as below:

Table 8-6 Table showing equivalent water consumption rates of jet washing trials.

Speed (m/min)	Water Consumption (L/m ²)
2.5	0.3
5	0.15
10	0.075
15	0.05
20	0.0375

The washing performance of jet trials were significantly better, as seen in Figure 8-17, which shows multiple tracks for both plasma processed and unprocessed samples, as well as larger washing area width for all, especially the plasma processed samples. Reflectance values were also higher, as shown in Table 8-7.

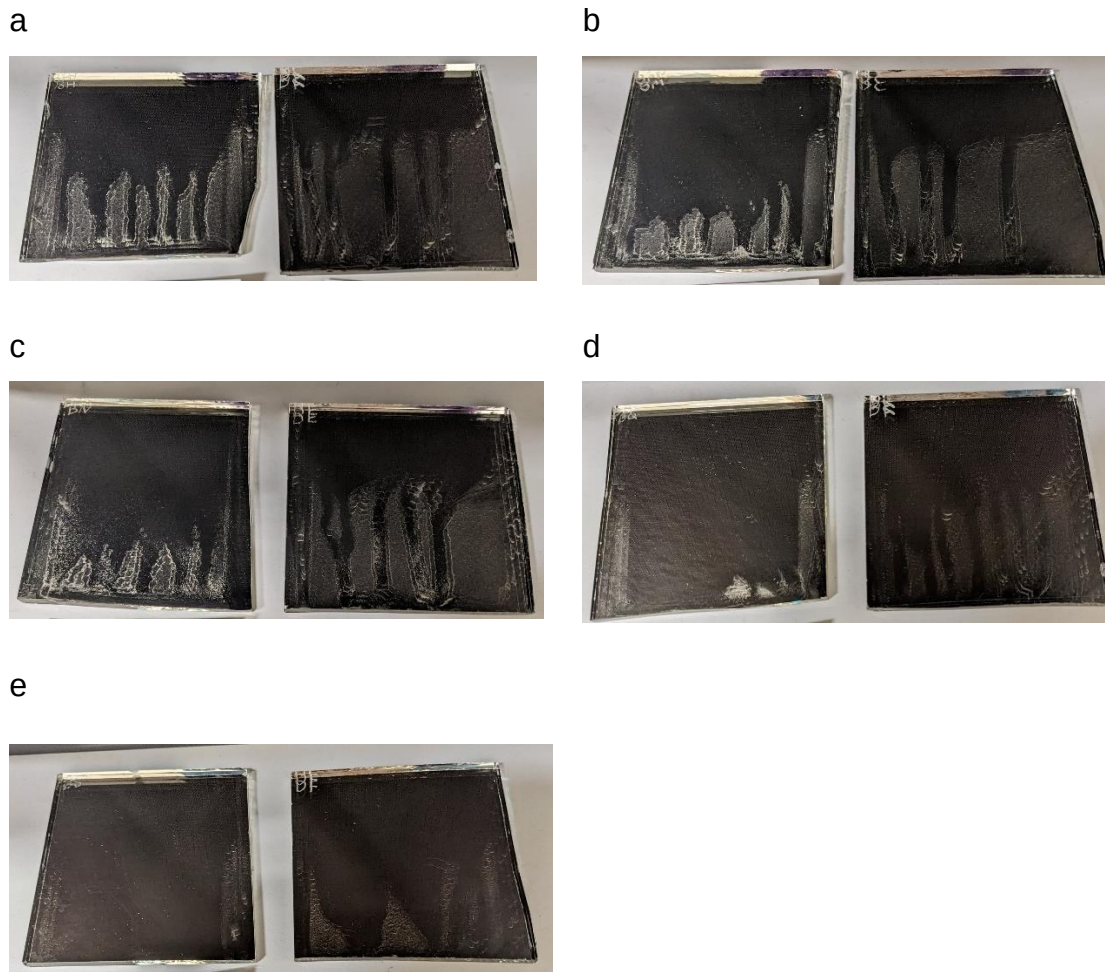


Figure 8-17 Photographs of one set of samples subject to the jet washing procedure after plasma processing (left) or without plasma processing (right) at washing speeds of a = 20 m/min, b = 15 m/min, c = 10 m/min, d = 5 m/min, e = 2.5 m/min.

As seen in Figure 8-18, behaviour was much the same as seen in both mist and spray trials, with higher values of reflectance at all rows but particularly in row A, where the water jet first makes contact with the sample.

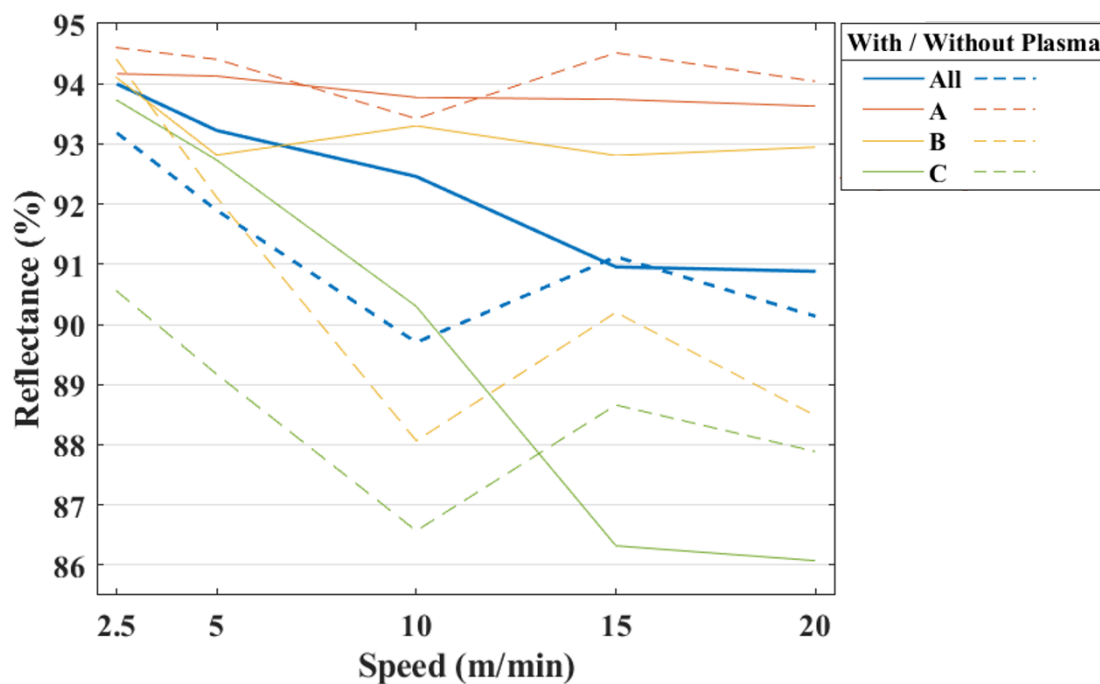


Figure 8-18 Average reflectance of samples with and without plasma processing.

Here row B also has significantly higher and more consistent cleaning when subject to prior plasma processing, shown also in Table 8-7.

Table 8-7 Average reflectance (%) of samples with and without plasma processing prior to jet washing. Cells shaded in green indicate areas considered “clean” by the criterion of above 90% reflectance.

	With plasma				Without plasma			
Speed (m/min)	A	B	C	All	A	B	C	All
2.5	93.4	92.8	91.0	92.4	94.1	91.8	86.9	91.0
5	92.9	93.6	88.3	91.6	94.1	89.0	85.9	89.7
10	92.5	91.5	89.3	91.1	93.2	87.2	85.3	88.6
15	92.3	89.2	85.3	88.9	93.9	88.0	88.6	90.2
20	93.1	87.4	89.7	90.1	94.0	87.4	85.6	89.0

It can be seen in Figure 8-19, as with the previous trials, plasma processing has greater effect in improving washing in rows B and C, especially at higher speeds with lower water consumptions.

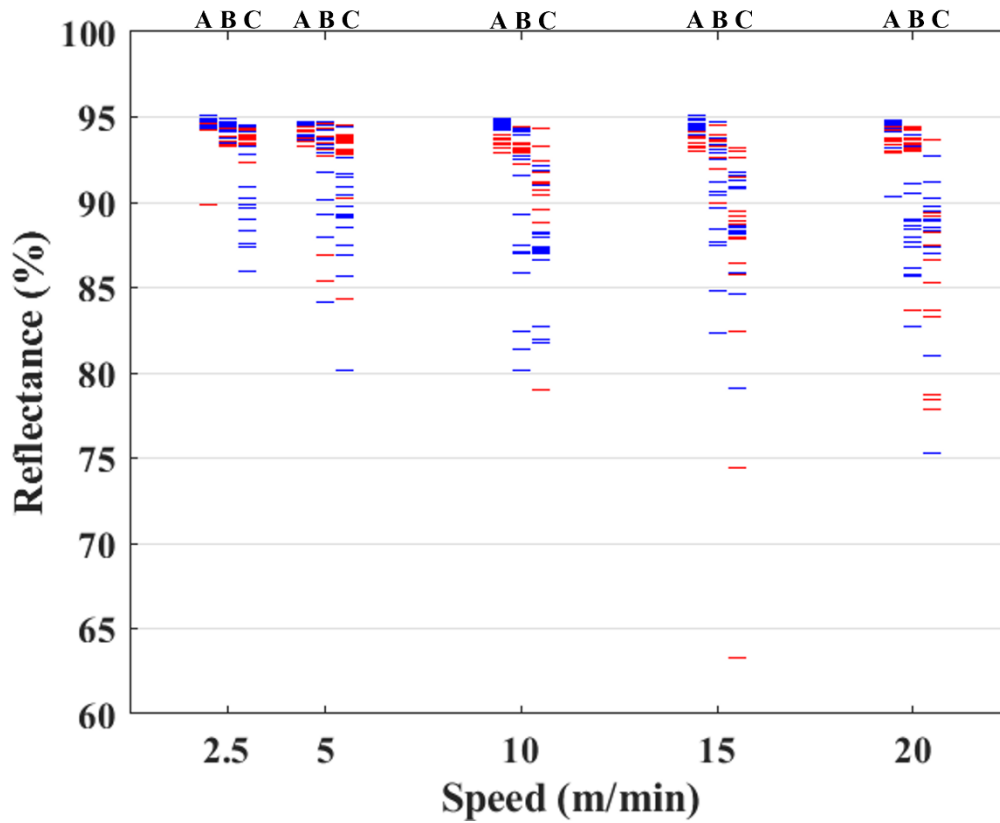


Figure 8-19 Reflectance values of samples with (red) and without (blue) plasma processing prior to jet washing.

There was still some redeposition of the soiling, as seen in Figure 8-20 , however considerably less than with the mist and spray trials.

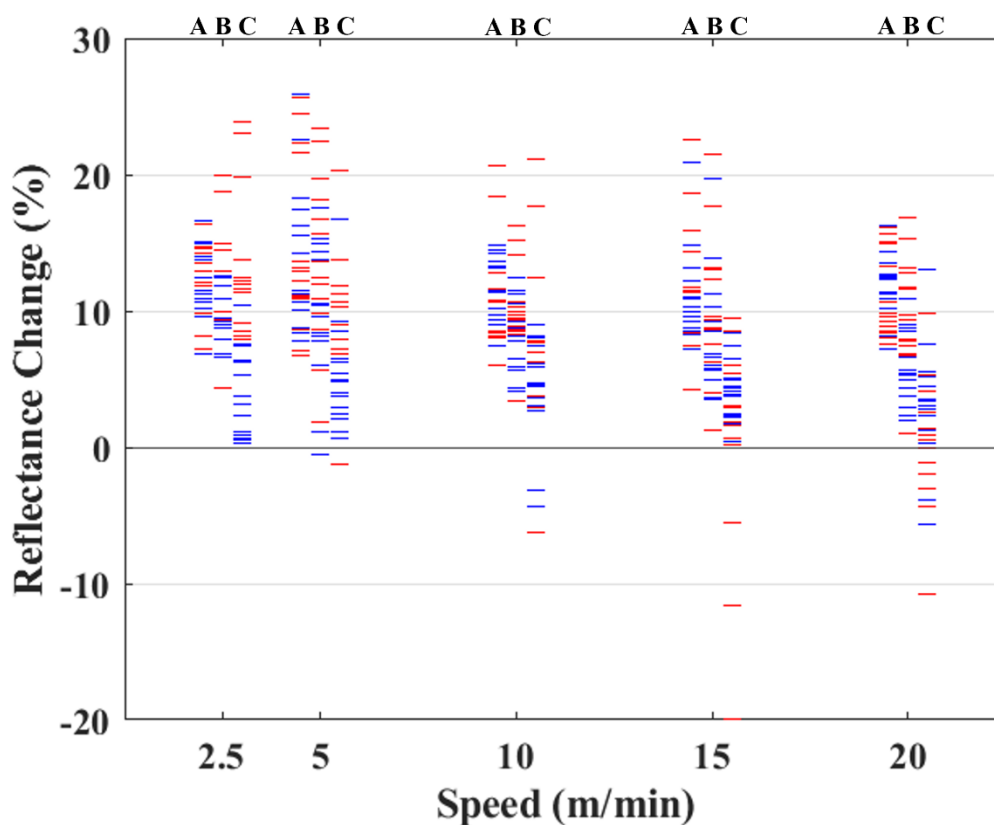


Figure 8-20 Change in reflectance of mirror samples with (red) and without (blue) prior plasma processing.

As before, this is due to the water that falls initially onto row A being more likely to roll down onto the lower rows, resulting in a higher incidence of soiling removal with these tracks and washing width areas shown in Figure 8-21 and Figure 8-22.

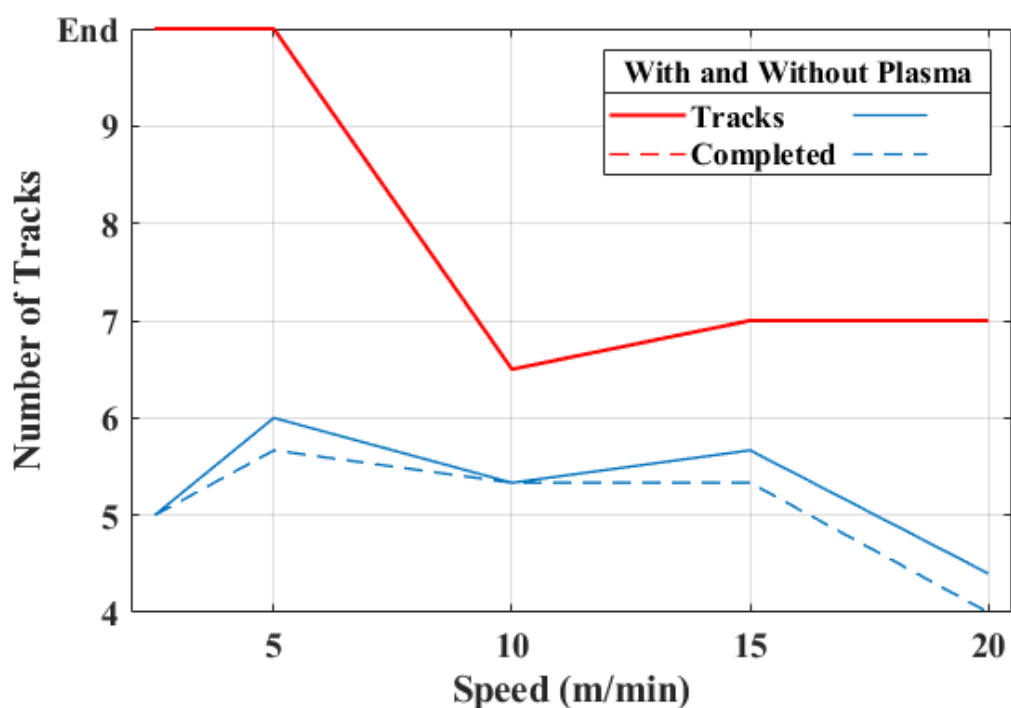


Figure 8-21 Number of started and completed tracks on jet washed mirror samples.

For jet wash trials, not only did the plasma processed samples have a greater number of tracks formed, but all of the tracks started were completed, and as such the completed plot line is not visible on Figure 8-21. Non-plasma processed samples had a higher number of tracks than in previous trials, but still there were uncompleted tracks, which results in redeposition of soiling further down the sample, rather than removal of the soiling from the mirror.

The width of the washed area was again higher for plasma processed than non-processed samples, with the entire sample washed at speeds of 2.5 m/min and 5 m/min.

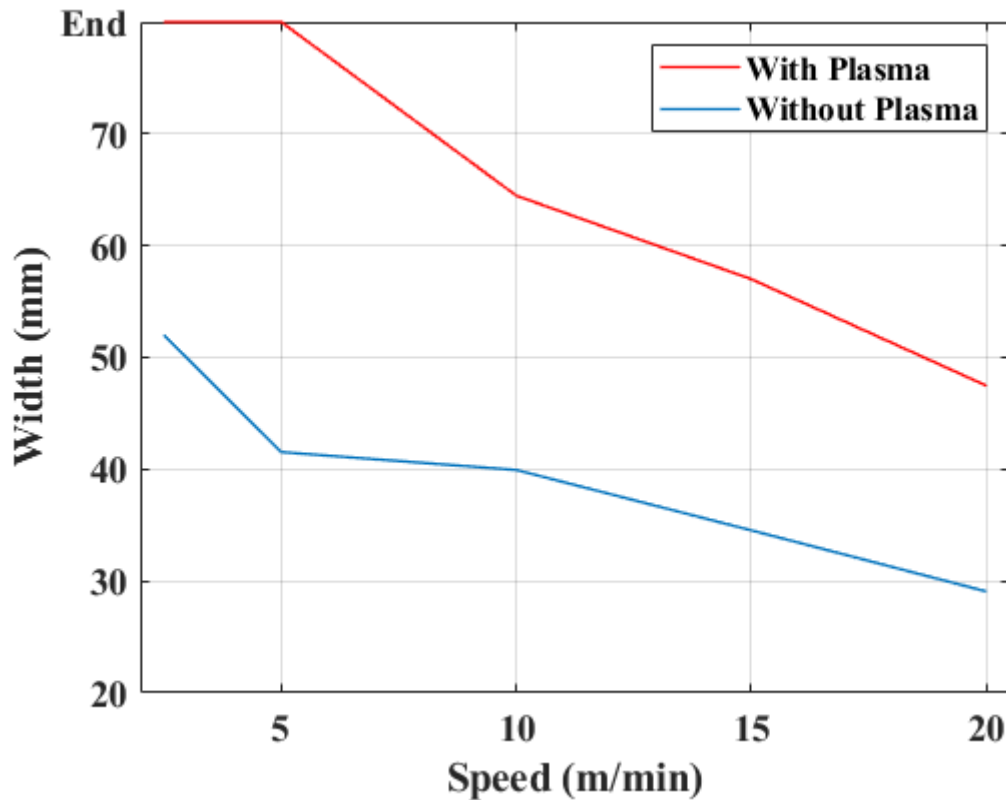


Figure 8-22 Width of jet washed area on samples with and without plasma processing.

Jet washing was still not adequate at the parameters investigated as the reflectance values were still frequently below the 90% clean threshold, seen in Figure 8-19, however the flow rate from the nozzle could not be increased, and so for the final section of washing trials the water flow rate was kept the same as in jet trials and the speed gradually lowered until complete cleaning was achieved.

8.6 Complete Cleaning Trials

For the final set of trials, the water flow rate was kept at 0.06 L/min as in the jet trials, and the speed of the washing rig gradually lowered from 2.5 m/min in increments of 0.5 m/min until every sample washed from each batch was completely clean. The plasma parameters were as in all washing trials.

At these speeds, the water consumption rate is as in Table 8-8.

Table 8-8 Water consumption rates for complete cleaning trials.

Speed (m/min)	Water Consumption (L/m ²)
0.25	3
0.5	1.5
1	0.75
1.5	0.5
2	0.375
2.5	0.3

Completely clean was defined as when the entire sample was washed (i.e. width = 80 mm) and reflectance was above 93%. This was further split into three categories:

- Criteria A: when every measurement point was above 93%
- Criteria B: when the average across each row was above 93%
- Criteria C: when the average across the whole sample was above 93%.

For plasma processed samples criteria A, the most strict, was met when the speed was 2 m/min, as shown in Figure 8-23.

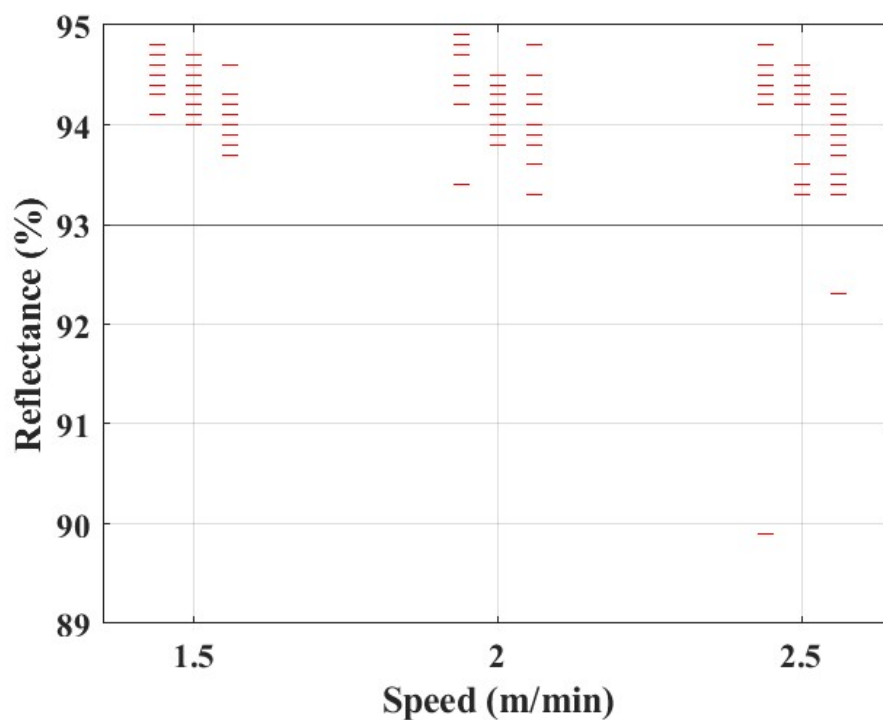


Figure 8-23 Reflectance values of plasma processed samples in complete cleaning trials.

For the samples not subject to plasma prior to water washing, Criteria A was still not met at 0.5 m/min, therefore a slower speed of 0.25 m/min was also investigated, at which point Criteria A was met, as seen in Figure 8-24.

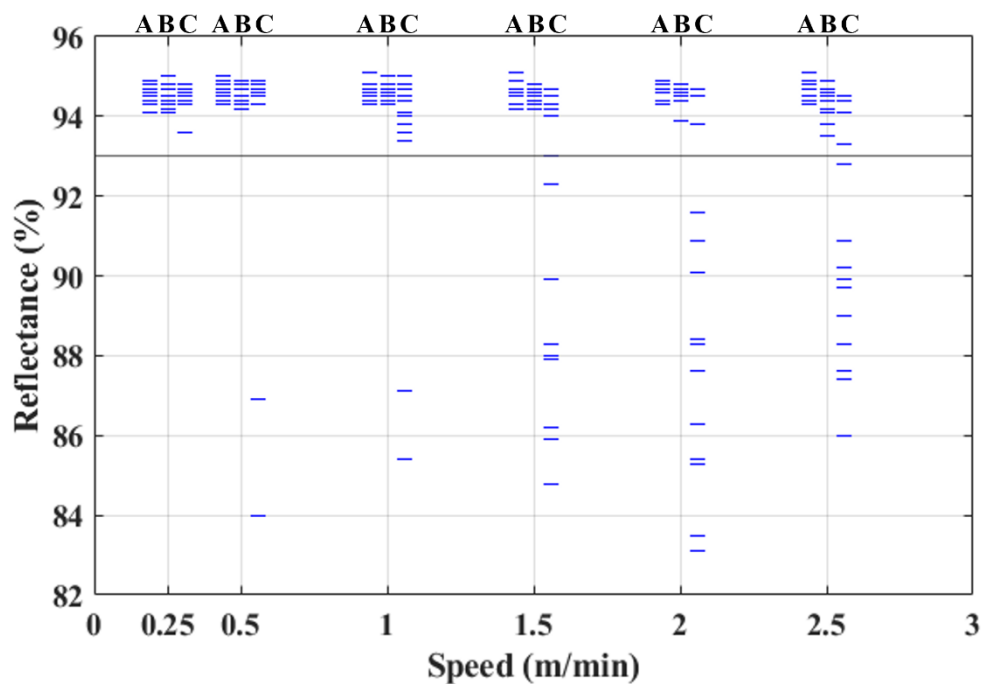


Figure 8-24 Reflectance values of non-plasma processed samples in complete cleaning trials.

As can be seen from both figures, samples can be mostly clean however a few data points can be well below the 93% threshold, due again to the random nature of both soiling and track formation location. It is for this reason that the average values were considered for Criteria B and C, which is displayed in Table 8-9. Here, cells shaded in green are considered clean at the threshold of above 90% as before, and cells shaded in blue are above the new threshold of 93%. It can be seen that Row C is often below the 93% threshold however only in one case is below 90%. As previously described, Row C has lower reflectance values due to redeposition of soiling from the above rows A and B. This occurs less often with plasma processed samples, as the water rolls down the surface in a more evenly distributed sheet, therefore redeposition is distributed over a large area, not localised in areas of relatively higher soiling as on the samples not subject to prior plasma processing. Row A is above the 93% threshold for all speeds on both plasma processed and unprocessed samples as this is where the jet first strikes the mirror, having the maximum cleaning effect, and Row B is above the 93% threshold in all but the fastest of the speeds investigated for plasma processed samples, 5 m/min.

Table 8-9 Average reflectance (%) of samples with and without plasma processing prior to complete washing. Cells shaded in green and blue indicate average reflectance values of higher than 90% and 93% respectively.

	With plasma				Without plasma			
Speed (m/min)	Row A	Row B	Row C	All	Row A	Row B	Row C	All
0.25					94.6	94.6	94.5	94.6
0.5					94.6	94.5	93.4	94.2
1					94.6	94.6	92.7	93.9
1.5	94.6	94.3	94.0	94.0	94.6	94.5	90.8	93.3
2	94.5	94.3	94.0	94.3	94.7	94.6	89.2	92.8
2.5	94.2	94.1	93.7	94.3	94.6	94.4	90.6	93.2
5	94.1	92.8	92.7	93.2				

The speed at which Criteria A, B, and C were met for plasma processed and non-plasma processed samples is listed in Table 8-10 and shows that for every criteria, the plasma processed samples were fully cleaned at a faster speed than for the non-plasma processed samples. The difference in speed required for washing is greatest for Criteria A, where plasma processed samples met the criteria 8 times faster than non-plasma processed samples, at 2 m/min and 0.25 m/min respectively.

Table 8-10 Speed and water consumption of washing to meet cleanliness criteria.

	Criteria A		Criteria B		Criteria C	
	Speed (m/min)	Water Consumption (L/m ²)	Speed (m/min)	Water Consumption (L/m ²)	Speed (m/min)	Water Consumption (L/m ²)
Plasma	2	0.375	2.5	0.3	5	0.15
No Plasma	0.25	3	0.5	1.5	2	0.375

When plotted against the equivalent water consumption per m² rather than speed, as in Figure 8-25, it can be seen that for all samples a higher water consumption results in a higher cleanliness. For plasma processed samples, adequate cleanliness of greater than 93% was achieved at water consumption rates much lower than on non-plasma processed samples, demonstrating that the water is used much more effectively and efficiently.

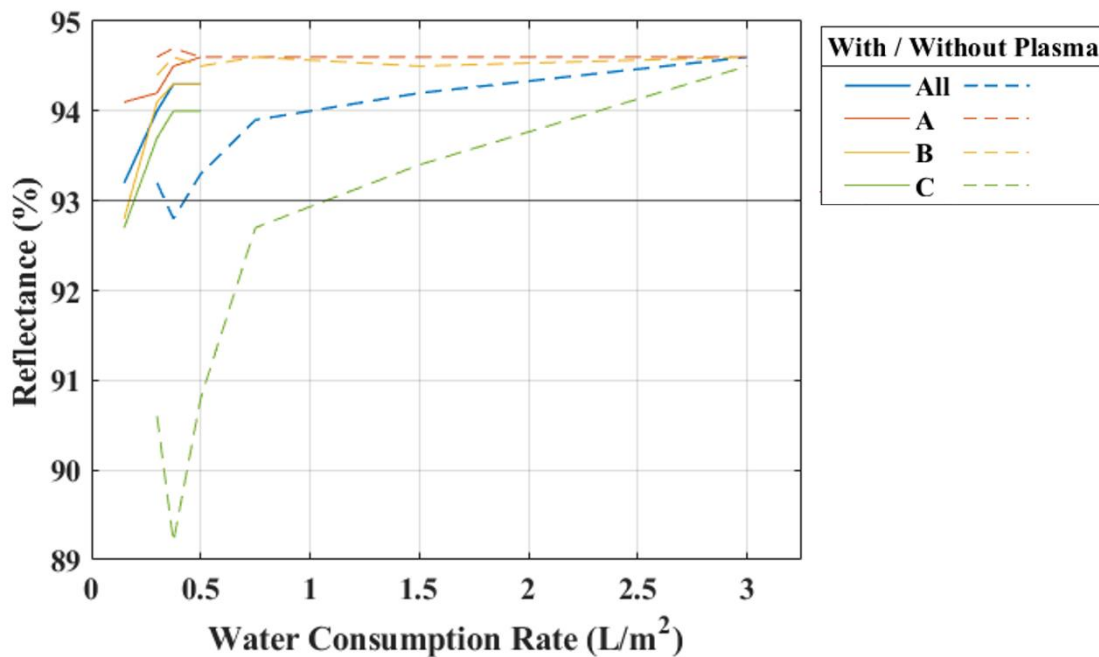


Figure 8-25 Average reflectance of samples in complete cleaning trials against the equivalent Water Consumption Rate.

Considering criteria A, which has the strictest definition of cleanliness, plasma processed samples achieve full cleanliness with 8 times less water than non-plasma processed samples, a saving of 87.5%. For Criteria B, they use 5 times less water or a saving of 80%, and for Criteria C the plasma processed samples use 2.5 less than on non-processed samples, a saving of 60%.

9 Anti-Soiling

It is important that any saving in water used during mirror washing is not negated by a subsequent increase in the rate of soiling from the plasma processing of the mirror surface, which would require shorter durations between washing and therefore a higher total water consumption due to increased washing frequency. The effects of a higher surface energy induced by plasma processing on soiling adhesion has not been previously investigated, therefore it is not known if the soiling will increase.

Conversely, there is the potential for a reduction in soiling adhesion as a result of the plasma processing, resulting in a surface with anti-soiling capabilities which would decrease the washing frequency and therefore have a further water saving effect.

9.1 Theory

Anti-soiling technology in the CSP field is most commonly using hydrophobic surfaces, that work to reduce adhesion of soiling onto mirrors through a combination of low surface energy and also the physical structure interfering with contact forces between the soiling and the surface and increasing rebound rate of soiling particles [210].

Previous investigations have suggested that hydrophilic surfaces are more susceptible to soiling [211], however these have investigated surfaces with hydrophilicity induced by application of a coating, and not pure glass surface where hydrophilicity is instead induced directly from the glass. Therefore, it is not known if a glass surface with plasma induced hydrophilicity will also increase soiling adhesion.

9.2 Methodology

In order to investigate the impact of plasma processing on soiling adhesion, anti-soiling trials were conducted where soiled samples were subject to complete

cleaning to meet Criteria A as in Chapter 8.6, allowed to dry fully, then subject to resoiling as in Chapter 5.4.

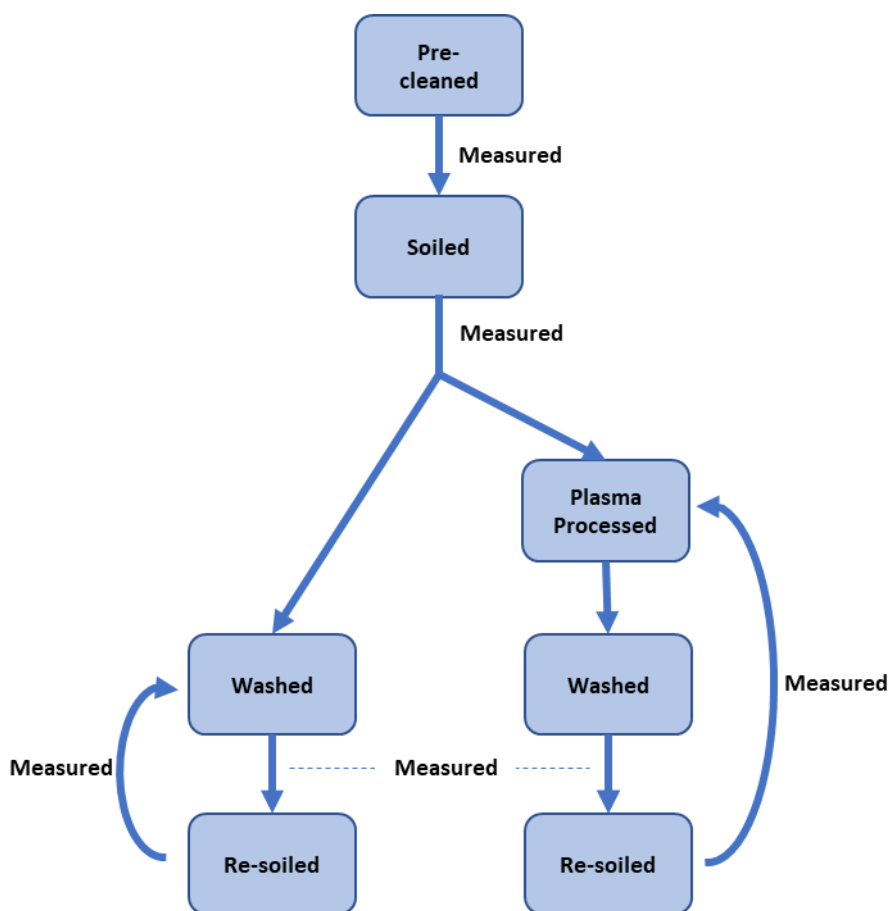


Figure 9-1 Chart showing anti-soiling methodology steps.

Half of the samples were plasma processed at standard plasma parameters and washed at a speed of 2 m/min at 0.06 L/min, the equivalent of 0.375 L/m². The other half of the samples were not plasma processed before being washed at a speed of 0.25 m/min at 0.06 L/min, or 3 L/m². This is shown in Figure 9-1.

The samples were then subject to another round of washing, with or without plasma processing, and again resoiling, to investigate if there is a cumulative effect.

9.3 Results

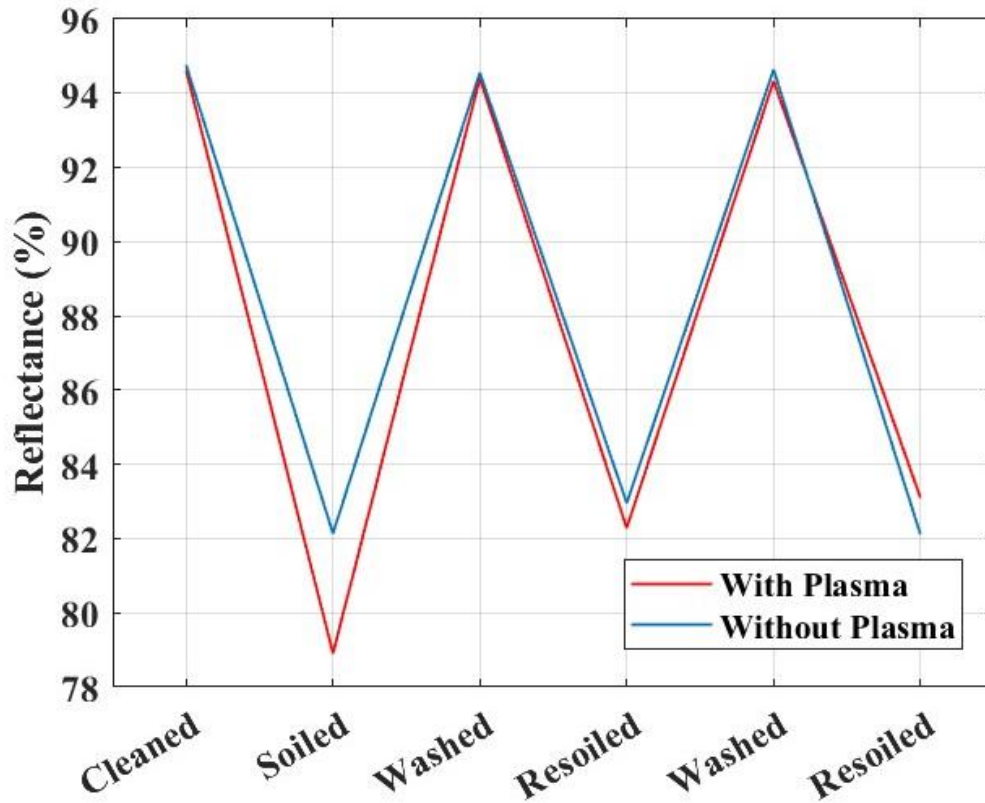


Figure 9-2 Average reflectance of samples with and without plasma processing prior to washing.

As seen in Figure 9-2 and Table 9-1, the average reflectance value of the plasma processed samples and the unprocessed samples remain similar after each resoiling step. This indicates that plasma processing followed immediately by water washing does not result in a surface that is any more or less susceptible to soiling, therefore the frequency of washing may not need to change in an industrial application.

Table 9-1 Average reflectance (%) of samples with and without plasma processing prior to washing.

	Cleaned	Soiled	Washed	Resoiled	Washed	Resoiled
With Plasma	94.6	78.9	94.4	82.3	94.3	83.1
Without Plasma	94.8	82.1	94.6	83.0	94.6	82.1

After the first resoiling, the average reflectance of the plasma processed samples was marginally lower than on unprocessed samples, at 82.3% and 83.0% respectively. After the second resoiling, the opposite is observed, with plasma processed samples being slightly higher at 83.1% reflectance compared to 82.1% for unprocessed samples. The difference after the first soiling run of 78.9% compared to 82.1% occurs before the plasma processing, as seen in Figure 9-1, and therefore is not as a result of the plasma processing resulting in greater soiling adhesion, and is instead due to the random nature of the soiling.

When all datapoints are plotted, as seen in Figure 9-3 this random nature of the soiling is seen, where after the initial soiling the set of samples to be plasma processed has many measurement points of low reflectance. After washing the range of values for both plasma and non-plasma processed samples is significantly smaller. After the second resoiling, the non-plasma processed samples this time have points of low reflectance, showing that the effect is not as a result of whether the sample is or isn't subject to plasma, rather it is as a result of the random nature of soiling distribution on the mirror surface.

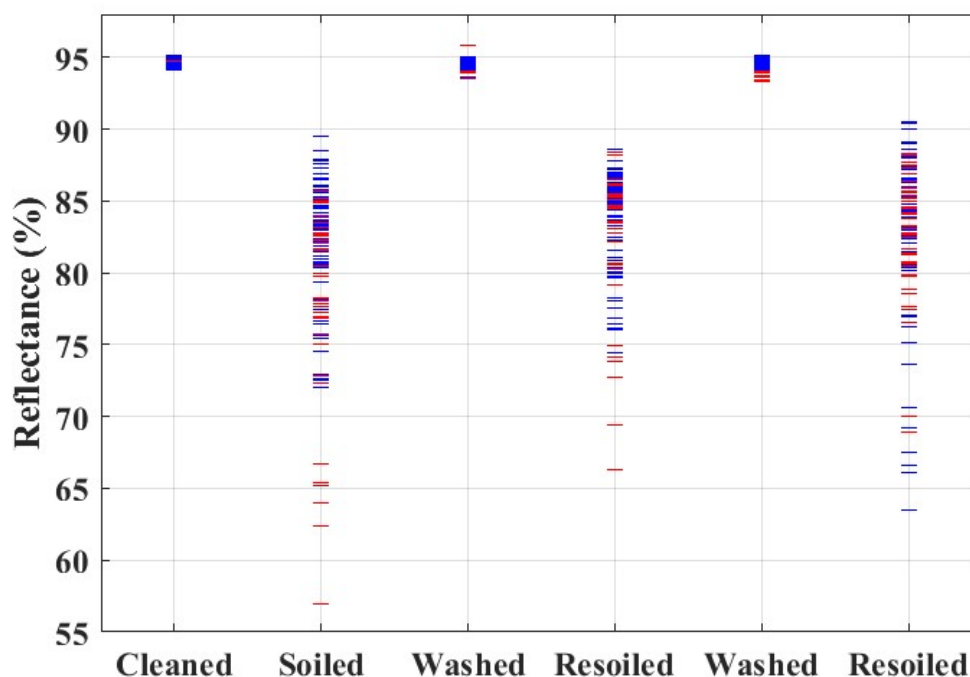


Figure 9-3 Average reflectance of samples with (red) and without (blue) plasma processing prior to washing.

These trials show the plasma processing does not have an effect on resoiling rates, either positively or negatively, that is significant enough to be detected over the already varied soiling of the mirror surface. It is therefore unlikely that plasma processing will require an increased frequency of washing due to higher soiling rates, and therefore water saved during washing is not then used during more frequent washing.

10 Self-Cleaning

Self-cleaning of a surface can be considered as a removal of soiling or contamination without active intervention. Such surfaces exist already in a variety of applications, such as in domestic ovens.

Technologies that induce self-cleaning often utilise hydrophobicity or lipophobicity, to encourage liquid rolling off and preventing soiling on the surface [212]; or the embedding of chemicals that undergo catalytic breakdown of the surface contamination, in the case of self-cleaning ovens assisted by the heat generated in the oven cavity during regular use [213].

Self-cleaning in solar applications has had some research interest. Previously mentioned research into EDS (Electro Dynamic Screen) technology can be considered to be partially self-cleaning, as it still requires an active input, albeit with little human intervention. Other self-cleaning approaches include applying a coating impregnated with a photocatalytic material, typically metal oxides such as TiO_2 , ZnO , and SnO_2 , which facilitate photochemical degradation of contaminants, but is effective only against organic contaminants and has little effect on inorganic mineral soiling typically seen in CSP plants [214]. Other self-cleaning technologies focus on harnessing the condensation that forms on the mirrors during the cold desert nights. Typically, this is in the form of hydrophobic coatings that encourage beading of the water, which then rolls down the mirror surface taking with it the soiling, as described in Chapter 2.5.

10.1 Theory

Self-cleaning of surfaces can be an extremely beneficial quality to surfaces in a variety of industrial and domestic applications. Whilst many focus on harnessing the properties of hydrophobic surfaces, it is hoped that the superhydrophilic surfaces created in this work may also have a self-cleaning effect.

The acceleration a felt by a droplet on a surface is

$$a = g \cdot \sin \alpha \quad (10-1)$$

Where g is acceleration due to gravity and α is the angle of tilt of the surface.

Using $F = ma$, this is related to the critical force F_C , at which point the droplet begins to move down the surface

$$F_C = mg \cdot \sin \alpha_C \quad (10-2)$$

Where m is the mass of the droplet and α_C is the critical angle.

Considering flat heliostats, when the mirrors are angled close to vertical, $\alpha \rightarrow 90^\circ$ and therefore F is maximised $F \rightarrow mg$. Larger droplets with greater mass therefore experience greater downward force and are more likely to roll down the surface. This effect is utilised by self-cleaning surfaces that employ hydrophobicity to increase droplet mass.

The net force acting on each droplet can further be defined as

$$F = F_r - F_a \quad (10-3)$$

Which is the difference between the retentive force F_r acting on the rear edge of the droplet, and the advancing force F_a at the front of the droplet [215]. This can further be defined by

$$F = \frac{4}{\pi} R \gamma_l (\cos \theta_r - \cos \theta_a) \quad (10-4)$$

Where R is the contact area of the droplet, γ_l is the surface tension of the liquid, and θ_r and θ_a are the angles of the receding and advancing edge respectively. When the droplet begins the move, it can be assumed the receding angle becomes 0, $\theta_r \rightarrow 0^\circ$, and therefore

$$F = \frac{4}{\pi} R \gamma_l (1 - \cos \theta_a) \quad (10-5)$$

Considering Young's equation, surface forces acting on the boundary of a droplet not subject to an external force is

$$\gamma_s - \gamma_l \cos \theta - \gamma_{sl} = 0 \quad (10-6)$$

Where γ_s , γ_l , and γ_{sl} are the surface tension components of the solid, liquid, and solid-liquid interface respectively and θ is the contact angle. This was modified by Adam and Jessop to account for the influence of an external force to create

$$\gamma_s - \gamma_l \cos \theta_a - \gamma_{sl} - f = 0 \quad (10-7)$$

And

$$\gamma_s - \gamma_l \cos \theta_r - \gamma_{sl} + f = 0 \quad (10-8)$$

At the advancing and receding edges respectively, where f is the force resisting movement.

Taking the Owens-Wendt approach, total surface energy (σ_s) is considered a sum of a polar (σ^P) and non-polar (dispersive) (σ^D) component. This is related to the interfacial solid-liquid tension by

$$\gamma_{SL} = \sigma_s + \sigma_L - 2 \left(\sqrt{\sigma_s^D \sigma_L^D} + \sqrt{\sigma_s^P \sigma_L^P} \right) \quad (10-9)$$

Plasma processing of surfaces greatly increases the polar part of the surface tension [216][217], which in turn reduces the interfacial tension, allowing the water to travel and spread over the surface more readily. On an inclined plane, this results in a lower force needed to induce droplet movement, which induces self-cleaning.

The work in this chapter investigates if this is indeed the effect, and if plasma processing can help reduce water consumption by utilising dew formation to provide self-cleaning of samples without active washing.

10.2 Methodology

To investigate potential self-cleaning effects, samples were placed into the condensation chamber as described in Chapter 5.7. All samples were subject to the same condensation parameters.

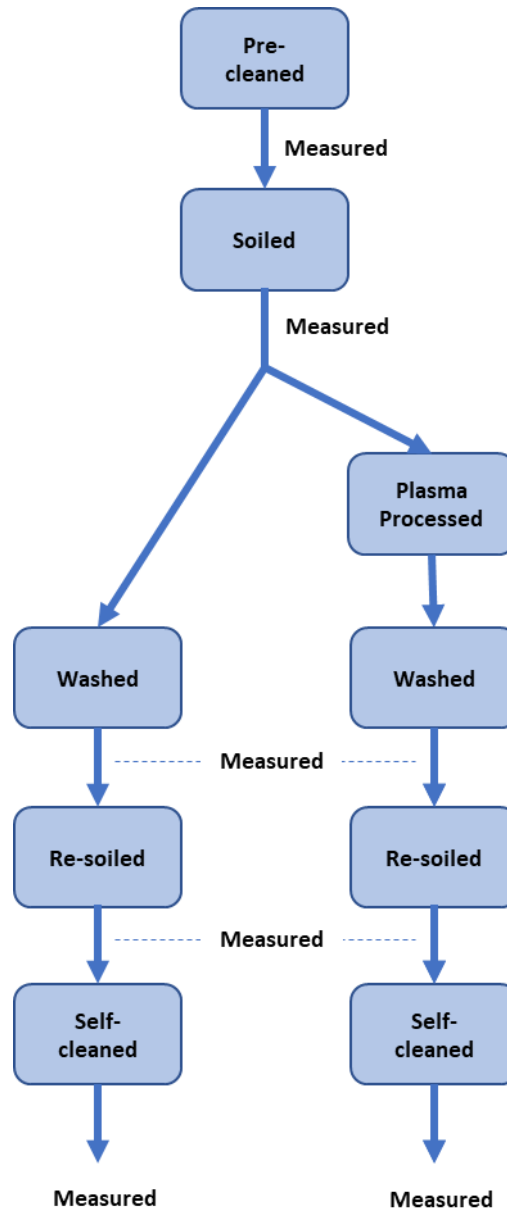


Figure 10-1 Flow chart showing self cleaning trial methodologies.

For each set of trials, two mirror samples were used, one of which was plasma processed according to standard parameters immediately before water washing, and one of which was not subject to plasma. Both samples underwent the same

procedure of pre cleaning, soiling, washing, resoiling, as shown in Figure 10-1, then placed onto the cooled block in the condensation chamber side by side.

10.3 Results

There was considerable visual difference between the behaviour of the condensation on plasma processed and unprocessed samples.



Figure 10-2 Mirror samples that have (left) and have not (right) been plasma processed, after being in the condensation chamber for 30 minutes.

On plasma processed samples, water condensed more easily onto the surface (Figure 10-2) and also had a far higher chance of travelling down the mirror (Figure 10-3) such that at the parameters investigated the unprocessed sample did not have any tracks form at all, whereas on plasma processed samples there was frequent formation, completion, and reformation of tracks.

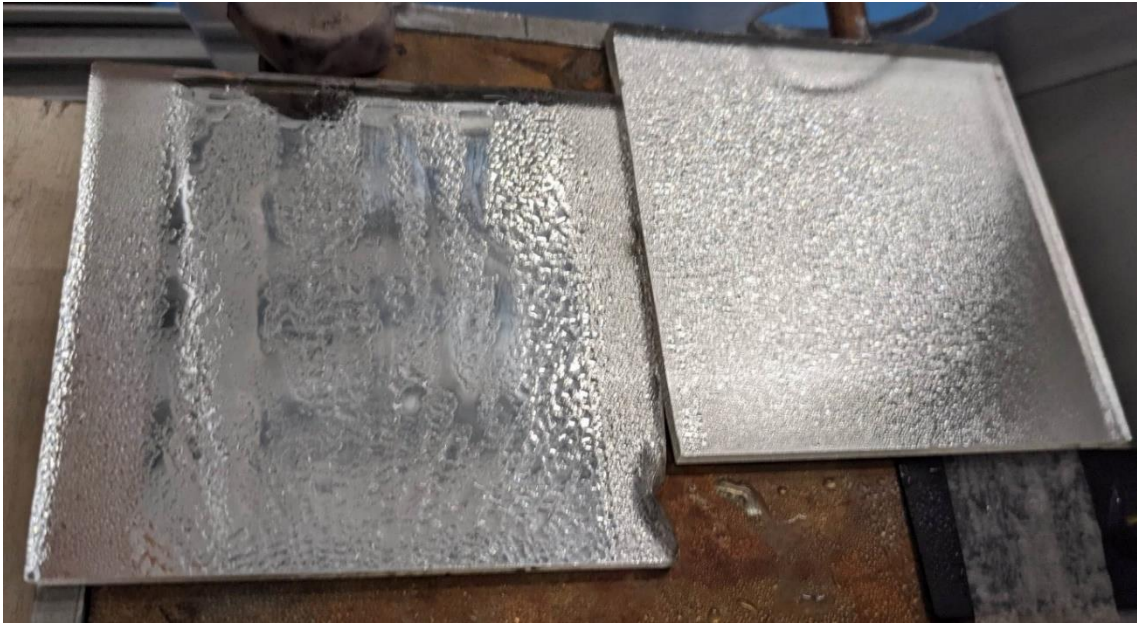


Figure 10-3 Mirror samples that have (left) and have not (right) been plasma processed, after being in the condensation chamber for 60 minutes.

After drying, plasma processed samples showed greater cleaning in areas where the tracks travelled, whereas the unprocessed samples showed more “soiling herding”, where water that condensed onto the mirror surface formed beads that then dried in place, leaving patches of higher and lower soiling but there being no overall removal of soiling from the surface, seen in Figure 10-4.



Figure 10-4 Mirror samples that have (left) and have not (right) been plasma processed, after being in the condensation chamber for 90 minutes then allowed to dry completely.

After self-cleaning, plasma processed samples had an average increase in reflectance of 2.8%, from 84.2% to 87.0%. This was greater both in increase and final reflectance than the change observed in unprocessed samples, increasing only 1.3% from 85.5% to 86.8%, as shown in Table 10-1.

Table 10-1 Average reflectance of samples after self-cleaning trials.

	Pre-Cleaned	Soiled	Washed	Re-soiled	Self-cleaned
With Plasma	94.7	82.3	94.7	84.2	87.0
Without Plasma	94.8	84.2	94.8	85.5	86.8

Reflectance measurements do not represent this self-cleaning capability optimally, as the measurement rig allowed for measurement of small areas and therefore it is random chance as to whether the tracks fall within the measurement area. This is shown in Figure 10-5 where each datapoint from each set of samples is displayed, showing the large range of reflectance values. For plasma processed the lowest value is 81.5% and the highest value is 94.1%, above the 93% threshold for adequate cleanliness. For the samples not subject to plasma processing, the lowest value is 81.5% and the highest is 92.1%.

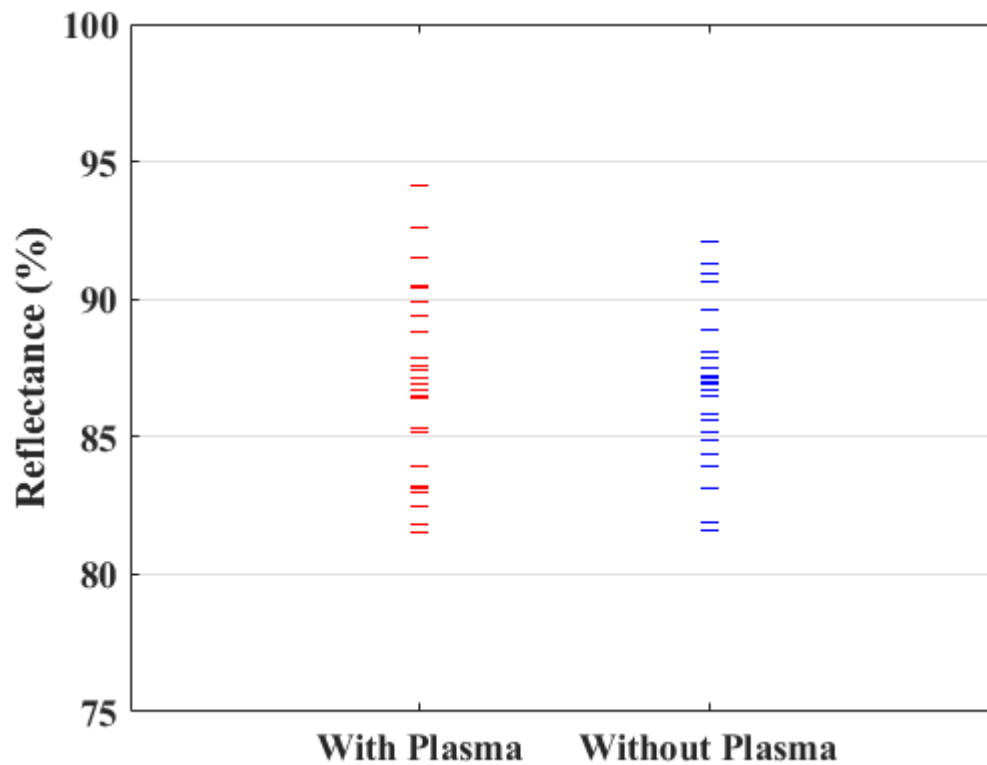


Figure 10-5 Reflectance values of plasma processed (red) and unprocessed (blue) samples after self-cleaning.

Consequently, whilst it is observed visually that plasma processed samples undergo self-cleaning in the presence of condensation, reflectance measurements do not show a significant difference between the samples, seen in Table 10-1 and Figure 10-6.

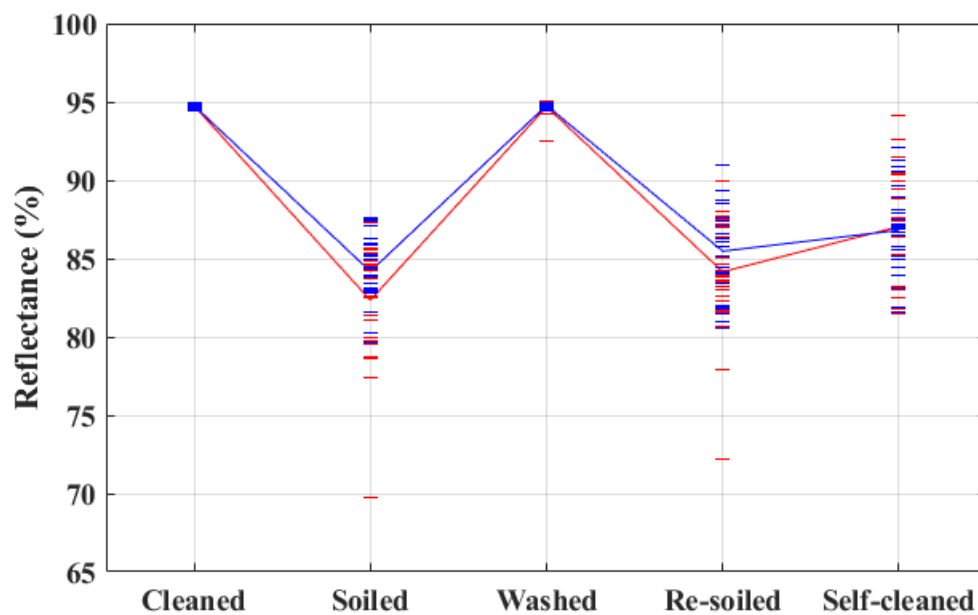


Figure 10-6 Reflectance values of plasma processed (red) and unprocessed (blue) samples throughout the self-cleaning testing procedure.

Samples left for longer periods of time, for example to simulate one nightly dew cycle, may undergo more consistent cleaning as more tracks form across the sample.

11 Discussions and Conclusion

Work presented in this thesis investigates the potential use of plasma in the application of concentrating solar power, with the intent to reduce water consumption of the plant for mirror washing purposes.

Initial trials aiming to investigate plasma only cleaning of mirrors, which would result in a total elimination of water for washing purposes, showed that whilst the plasma used did remove some soiling from the mirror surface, it was not effective enough for the application. The difficulty of plasma only cleaning in this application is that the plasma must be low temperature and unreactive, as the mirrors are relatively fragile and can suffer from melting and thermal shock damage. The mirrors also are chemically similar to the soiling, therefore reactive plasmas risk damaging the bonds on the surface of the mirror, resulting in a reduction in reflectance, which is not appropriate for this application. It is possible that more effective plasma only cleaning could be developed, for example by changing the processing parameters such as the plasma torch configuration. A surface discharge DBD may be more appropriate as the mirror surface and attached soiling could be in the plasma generation region itself, which could induce soiling removal mechanisms not possible with the volume discharge torch used.

Instead, hybrid plasma water washing was investigated, whereby the soiled mirrors are plasma processed immediately before water washing. Investigations of plasma processing on clean mirrors was found to induce a superhydrophilic surface with water contact angles below 2° , which resulted in larger areas being covered with set volumes of water, allowing for more efficient water use as less water is required to cover an area of mirror. Plasma processing also increases the rate of evaporation of the water from the sample surface, which may reduce resoiling rates as soiling adhesion is higher when the surface is wet, and as such rapid drying of the mirror after washing is preferable to reduce the window of such increased soiling. Resoiling trials were conducted only when the mirror samples were completely dry, and thus this potential effect and benefit was not investigated. Such resoiling trials did not show a significant difference in soiling

rates between processed and unprocessed mirror samples, and so whilst there is no particular benefit of the plasma processing in this aspect of the application, there is importantly no increase in soiling, meaning any water saved during washing is not negated by the need for more frequent washing as a result of higher resoiling rates.

Another advantage of the plasma processing was in altering the behaviour of dew formation on the mirrors when placed in a condensation chamber, where on plasma processed samples the water that condensed onto the mirror rolled down the mirror surface much more readily, taking with it soiling.

The work presented here has not been fully optimised, and therefore the beneficial aspects of the plasma processing may be far greater than demonstrated here.

Whilst plasma processing is not a new concept, it has not previously been used in this application, and therefore it was unknown how the processing would affect behaviour of the water, soiling, and condensation on the mirrors. This is particularly the case when the plasma was applied to an already soiled mirror surface, rather than the clean surfaces typically used for surface energy modification investigations.

Considering the Aims and Objectives as defined in Chapter 2.1:

Aim:

Investigate an atmospheric pressure plasma system that can be used in situ to reduce water consumed during cleaning of Concentrating Solar Power mirrors

Objectives:

- Investigate the temporal and spatial stability of the produced plasmas
- Determine if plasma can be used to remove soiling from CSP mirror segments
- Determine if plasma can modify surface energy of CSP mirror segments
 - And what effect this has on washing efficiency, anti-soiling, and water use

- Understand the fundamental processes behind any cleaning and anti-soiling effects

The stability of the plasma spatially and temporally was conducted primarily using optical emission spectroscopy, which showed how the intensity of the plasma varied with different plasma parameters of gas flow and power. This work also showed the uneven spatial distribution of the plasma generated with some torch types, and the implications this would have on processing. In this case, that the processing needed to be rastered in order to process the areas that would not be exposed to the plasma in a single pass treatment.

Plasma only cleaning was investigated, however was not satisfactory in restoring the mirrors' cleanliness to acceptable levels. The energy in the plasma was not sufficient to overcome soiling adhesion bonds, and higher energy or chemically reactive approaches were decided to be impractical due to the high risk of damaging bonds of the mirror itself, owing to the similar chemical structure of primarily quartz soiling and silica mirrors. A higher kinetic energy of the plasma, which could result in greater physical sputtering of soiling, may be achieved through changing of the gas flow rate or intentional manipulation of the flow distribution, however an increased flow would also result in less energy in the plasma due to reduced residence time in the plasma generating region of the torch. Therefore, plasma only cleaning was determined to be not possible with the equipment studied here, and further investigation of this approach terminated.

Consequently, a hybrid approach was investigated, utilising the surface energy modification effect of the plasma to change the behaviour of the water used during cleaning. This surface energy modification resulted in an induced temporary superhydrophilic surface, and the influence of parameters such as speed and power on this effect investigated. The effect of this superhydrophilic surface on water was investigated and it was found that water spread farther and also more evenly on the surface, with contact angles below 2° . Water droplets on the plasma induced hydrophilic surface also took less time to dry than on the untreated surface. With relation to washing, the water directed onto the sample

from the nozzle spread more evenly on the plasma treated surface, and fell down the vertically aligned mirrors in an even sheet, as opposed to the beading and rolling seen on untreated surfaces. This effected the cleaning mechanisms of the water, with beading in some cases being more beneficial as the dragging forces are greater, allowing more soiling to be removed, in particular the smaller particles of soiling. However, beading results in less area being cleaned, and so the water is not used efficiently over larger surfaces. In complete cleaning trials, this hybrid washing resulted in water savings of up to 87.5%.

Potential anti-soiling and self-cleaning has been investigated. There was not found to be a significant difference in soiling rates when the mirrors were exposed to an artificial soiling procedure.

The fundamental processes behind the above effects and implications have been discussed alongside the theory and results sections of each chapter.

Surface energy modification was found to be due to breaking of surface bonds by high energy electrons produced in the plasma, creating polar surface hydroxyl groups which result in hydrophilicity of the surface. This effect is not permanent, and these hydroxyl groups eventually are “capped off” with other molecules or return to their positions on the surface.

This induced hydrophilicity effects how the water behaves on the surface, and has been discussed from perspective of water spreading and evaporating on a flat surface, as well as the downward travel of water on a vertical surface. The surface energy modification also effects the process of dew formation on the mirrors, and changes how water condenses on the surface from an atmosphere of high humidity, which with sufficient mass will also roll down the surface, resulting in self-cleaning.

The unique contribution to knowledge of this work has been in the application of plasma in the washing procedure of concentrating solar power mirrors. Resulting in a gained knowledge of how this affects the behaviour of the water then used during cleaning, which has not previously been studied.

12 Future Work

The work undertaken is early stage research for the use of plasma in CSP, there is much potential for its application and further possibility of optimisation of the technologies and techniques used.

Whilst it has been shown the plasma processing does induce a superhydrophilic surface and that this does result in different behaviour of water on the surface, it was also shown that this induced hydrophilicity is not permanent and does undergo ageing. For this reason, the work here used water washing immediately after plasma processing, however it may not be necessary to do plasma process every time before washing. The surface can retain some hydrophilic properties for weeks after the initial plasma processing, and so washing with water alone in between plasma processing may also be more efficient than if plasma processing is not used at all. The balance of plasma processing for greater hydrophilicity versus the water saved must be determined.

Another important step towards commercialisation is in consideration of the energy balance. Generation of plasma can require considerable energy in order to ionise the feed gas, and therefore it must be considered that the increase in energy generation gained by mirrors of higher cleanliness is not negated by the energy required in the generation and application of the plasma. Work on optimisation of parameters, both in plasma generation and mirror processing, would increase the understanding and likelihood of the feasibility of plasma use on CSP mirrors.

Considering the journey of this work towards commercialisation, physical scaling and practical application of the plasma torch to process the large and numerous mirrors seen in CSP plants is necessary. Some work has already been conducted in this aspect, in which an articulated robot arm, rail guided robot, and a free roaming robot were investigated for their potential application. Considering factors such as simplicity, sustainability, and cost, the free roaming surface robot

was deemed to be the most appropriate and a design was proposed for the application [218].

Overall, this work is an important early step in proof of concept of plasma assisted mirror washing. The basic principle and effect has been demonstrated and understood, with further work necessary to take the concept forward to a commercial and industrial application.

REFERENCES

1. International Energy Agency. World Energy Outlook. 2022.
2. IEA., AIE. World Energy Outlook 2018. 2018. Available at: DOI:10.1787/weo-2018-en
3. Fernández-García A., Álvarez-Rodrigo L., Martínez-Arcos L., Aguiar R., Márquez-Payés JM. Study of different cleaning methods for solar reflectors used in CSP plants. Energy Procedia. Elsevier B.V.; 2014; 49: 80–89. Available at: DOI:10.1016/j.egypro.2014.03.009
4. Solargis. Longterm yearly average of direct normal irradiation - United Kingdom - Global Solar Atlas 2.0. 2019.
5. Henner D., REN21. Renewables 2022 global status report 2022. 2022.
6. China prioritizes Concentrated Solar Power connection and dispatch in new rule. HelioCSP. 2023. Available at: <https://helioscsp.com/china-prioritizes-concentrated-solar-power-connection-and-dispatch-in-new-rule/> (Accessed: 20 April 2023)
7. Bracken N., Macknick J., Tovar-hastings A., Komor P., Gerritsen M., Mehta S., et al. Concentrating Solar Power and Water Issues in the U. S. Southwest. 2015; (March).
8. Seckler D., Barker R., Amarasinghe U., Seckler D., Barker R., Amarasinghe U. Water Scarcity in the Twenty-first Century. International Journal of Water Resources Development. 1999; 15(1–2): 29–42. Available at: DOI:10.1080/07900629948916
9. Duvenhage DF., Brent AC., Stafford WHL. The need to strategically manage CSP fleet development and water resources : A structured review and way forward. Renewable Energy. Elsevier Ltd; 2019; 132: 813–825. Available at: DOI:10.1016/j.renene.2018.08.033
10. Kearney DW., Drive C., Mar D., Kolb GJ. Final report on the operation and maintenance improvement program for concentrating solar power plants.

1999.

11. Woerlen I. Mouchot's sun engine. Available at: <http://hotairengines.org/solar-engine/mouchot-1865> (Accessed: 12 May 2023)
12. Ericsson J. Sun Power - The Solar Engine. Contributions to the Centennial Exhibition. 1876. pp. 558–577.
13. Fernández-García A., Zarza E., Valenzuela L., Pérez M. Parabolic-trough solar collectors and their applications. Renewable and Sustainable Energy Reviews. 2010; 14(7): 1695–1721. Available at: DOI:10.1016/j.rser.2010.03.012
14. World Energy Council. World Energy Resources 2016. World Energy Council 2016. 2016; : 6–46. Available at: DOI:http://www.worldenergy.org/wp-content/uploads/2013/09/Complete_WER_2013_Survey.pdf
15. Kraemer S. Solar Thermal Power Prices have Dropped an Astonishing 50% in Six Months. SolarPACES. 2017. Available at: <https://www.solarpaces.org/solar-thermal-energy-prices-drop-half/> (Accessed: 5 March 2019)
16. Romero M., Martínez D., Zarza E. Terrestrial Solar Thermal Power Plants: On the verge of commercialization. European Space Agency, (Special Publication) ESA SP. 2004; (567): 81–89.
17. Ziuku S., Seyitini L., Mapurisa B., Chikodzi D., van Kuijk K. Potential of Concentrated Solar Power (CSP) in Zimbabwe. Energy for Sustainable Development. Elsevier Ltd; 2014; 23(December): 220–227. Available at: DOI:10.1016/j.esd.2014.07.006
18. Llorente García I., Álvarez JL., Blanco D. Performance model for parabolic trough solar thermal power plants with thermal storage: Comparison to operating plant data. Solar Energy. 2011; 85(10): 2443–2460. Available at: DOI:10.1016/j.solener.2011.07.002

19. Weinstein LA., Loomis J., Bhatia B., Bierman DM., Wang EN., Chen G. Concentrating Solar Power. *Chemical Reviews*. 2015; 115(23): 12797–12838. Available at: DOI:10.1021/acs.chemrev.5b00397
20. Walston Jr. LJ., Rollins KE., Smith KP., LaGory KE. A Review of Avian Monitoring and Mitigation Information at Existing Utility- Scale Solar Facilities. 2015. Available at: DOI:<https://doi.org/10.2172/1176921>
21. Fairley P. Solar Towers Don't Seem to Be the Bird Destroyers Once Thought. *IEEE Spectrum*. 2015. Available at: <https://spectrum.ieee.org/reassessing-bird-deaths-from-solar-power-towers> (Accessed: 9 April 2023)
22. Hersch P., Zweibel K. Basic photovoltaic principles and methods. Golden, Colorado: Solar Energy Research Institute; 1982. Available at: DOI:10.2172/5191389
23. DECC. UK solar PV strategy part 2: Delivering a brighter future. Department of energy and climate change. 2014; Available at: www.gov.uk/decc
24. Dower B. Solar Panels in the Landscape. *A Comprehensive Guide to Solar Energy Systems*. Elsevier Inc.; 2018. 373–389 p. Available at: DOI:10.1016/b978-0-12-811479-7.00019-1
25. Maghami MR., Hizam H., Gomes C., Radzi MA., Rezadad MI., Hajighorbani S. Power loss due to soiling on solar panel: A review. *Renewable and Sustainable Energy Reviews*. Elsevier; 2016; 59: 1307–1316. Available at: DOI:10.1016/j.rser.2016.01.044
26. Karim M., Naamane S., Delord C. Evaluation of the behaviour of different solar mirrors against soiling phenomenon. *Proceedings of 2016 International Renewable and Sustainable Energy Conference, IRSEC 2016*. IEEE; 2017; : 326–329. Available at: DOI:10.1109/IRSEC.2016.7984008
27. King P., Sansom C., Comley P. Photogrammetry for concentrating solar

- collector form measurement, validated using a coordinate measuring machine. *Sustainability (Switzerland)*. 2020; 12(1): 1–20. Available at: DOI:10.3390/su12010196
28. Christian JM., Ho CK. Finite Element Modeling and Ray Tracing of Parabolic Trough Collectors. *Proceedings of the ASME 2011 5th International Conference on Energy Sustainability*. 2011; : 1–9.
 29. Fend T., Hoffschmidt B., Jorgensen G., Küster H., Krüger D., Pitz-Paal R., et al. Comparative assessment of solar concentrator materials. *Solar Energy*. 2003; 74(2): 149–155. Available at: DOI:10.1016/S0038-092X(03)00116-6
 30. Wiesinger F., Sutter F., Fernández-García A., Reinhold J., Pitz-Paal R. Sand erosion on solar reflectors: Accelerated simulation and comparison with field data. *Solar Energy Materials and Solar Cells*. 2016; 145: 303–313. Available at: DOI:10.1016/j.solmat.2015.10.036
 31. Kennedy CE., Terwilliger K. Optical durability of candidate solar reflectors. *Journal of Solar Energy Engineering, Transactions of the ASME*. 2005; 127(2): 262–269. Available at: DOI:10.1115/1.1861926
 32. Costa SCS., Diniz ASAC., Kazmerski LL. Solar energy dust and soiling R&D progress: Literature review update for 2016. *Renewable and Sustainable Energy Reviews*. 2018; 82(November 2017): 2504–2536. Available at: DOI:10.1016/j.rser.2017.09.015
 33. Water Saving for Concentrated Solar Power. Available at: <https://wascop.eu/>
 34. Picotti G., Borghesani P., Cholette ME., Manzolini G. Soiling of solar collectors – Modelling approaches for airborne dust and its interactions with surfaces. *Renewable and Sustainable Energy Reviews*. Elsevier Ltd; 2018; 81(June 2017): 2343–2357. Available at: DOI:10.1016/j.rser.2017.06.043
 35. Ilse KK., Figgis BW., Naumann V., Hagendorf C., Bagdahn J. Fundamentals of soiling processes on photovoltaic modules. *Renewable*

- and Sustainable Energy Reviews. Elsevier Ltd; 2018; 98(January): 239–254. Available at: DOI:10.1016/j.rser.2018.09.015
36. Engelbrecht JP., Moosmüller H., Pincock S., Jayanty RKM., Lersch T., Casuccio G. Technical note: Mineralogical, chemical, morphological, and optical interrelationships of mineral dust re-suspensions. *Atmospheric Chemistry and Physics*. 2016; 16(17): 10809–10830. Available at: DOI:10.5194/acp-16-10809-2016
 37. Sansom C., Almond H., King P., Endaya E., Bouaichaoui S. Airborne sand and dust soiling of solar collecting mirrors. *AIP Conference Proceedings*. 2017; 1850(June). Available at: DOI:10.1063/1.4984505
 38. Ilse K., Micheli L., Figgis BW., Lange K., Daßler D., Hanifi H., et al. Techno-Economic Assessment of Soiling Losses and Mitigation Strategies for Solar Power Generation. *Joule*. 2019; 3(10): 2303–2321. Available at: DOI:10.1016/j.joule.2019.08.019
 39. Martin-Sanchez PM., Gebhardt C., Toepel J., Barry J., Munzke N., Günster J., et al. Monitoring microbial soiling in photovoltaic systems: A qPCR-based approach. *International Biodeterioration and Biodegradation*. Elsevier Ltd; 2018; 129(December 2017): 13–22. Available at: DOI:10.1016/j.ibiod.2017.12.008
 40. Ghazi S., Sayigh A., Ip K. Dust effect on flat surfaces - A review paper. *Renewable and Sustainable Energy Reviews*. Elsevier; 2014; 33: 742–751. Available at: DOI:10.1016/j.rser.2014.02.016
 41. Xu C., Wang Z., Li X., Sun F. Energy and exergy analysis of solar power tower plants. *Applied Thermal Engineering*. Elsevier Ltd; 2011; 31(17–18): 3904–3913. Available at: DOI:10.1016/j.applthermaleng.2011.07.038
 42. Trieb F., Schillings C., Sullivan MO., Pregger T., Hoyer-klick C. Global Potential of Concentrating Solar Power. *SolarPACES*. 2009. pp. 1–11.
 43. Figgis B., Ennaoui A., Ahzi S., Rémond Y. Review of PV soiling particle mechanics in desert environments. *Renewable and Sustainable Energy*

- Reviews. Elsevier Ltd; 2017; 76(March): 872–881. Available at: DOI:10.1016/j.rser.2017.03.100
44. Cuddihy EF. Theoretical considerations of soil retention. *Solar Energy Materials*. 1980; 3(1–2): 21–33. Available at: DOI:https://doi.org/10.1016/0165-1633(80)90047-7
 45. Wu Z., Yan S., Wang Z., Ming T., Zhao X., Ma R., et al. The effect of dust accumulation on the cleanliness factor of a parabolic trough solar concentrator. *Renewable Energy*. 2020; 152: 529–539. Available at: DOI:10.1016/j.renene.2020.01.091
 46. Conceição R., González-Aguilar J., Merrouni AA., Romero M. Soiling effect in solar energy conversion systems: A review. *Renewable and Sustainable Energy Reviews*. 2022; 162. Available at: DOI:10.1016/j.rser.2022.112434
 47. El-Nashar A. The Effect of Dust Accumulation on the Performance of Evacuated Tube Collectors. 1986; 36(2): 139–146.
 48. Sansom C., Comley P., King P., Almond H., Atkinson C., Endaya E. Predicting the Effects of Sand Erosion on Collector Surfaces in CSP Plants. *Energy Procedia*. Elsevier B.V.; 2015; 69: 198–207. Available at: DOI:10.1016/j.egypro.2015.03.023
 49. Hunter SR., Smith DB., Polizos G., Schaeffer DA., Lee DF., Datskos PG. Low cost anti-soiling coatings for CSP collector mirrors and heliostats. *High and Low Concentrator Systems for Solar Energy Applications IX*. 2014; 9175(865): 91750J. Available at: DOI:10.1117/12.2061845
 50. Aranzabe E., Azpitarte I., Fernández-García A., Argüelles-Arízcan D., Pérez G., Ubach J., et al. Hydrophilic anti-soiling coating for improved efficiency of solar reflectors. *AIP Conference Proceedings*. 2018; 2033(November): 1–6. Available at: DOI:10.1063/1.5067223
 51. Sansom C., Fernández-García A., Sutter F., Almond H., King P., Martínez-Arcos L. Soiling and cleaning of polymer film solar reflectors. *Energies*. 2016; 9(12). Available at: DOI:10.3390/en9121006

52. Sansom C., King P., Fernández-García A., Almond H., Kayani T., Boujjat H. The design of dust barriers to reduce collector mirror soiling in CSP plants. AIP Conference Proceedings. 2018; 2033(November). Available at: DOI:10.1063/1.5067033
53. Sarver T., Al-Qaraghuli A., Kazmerski LL. A comprehensive review of the impact of dust on the use of solar energy: History, investigations, results, literature, and mitigation approaches. Renewable and Sustainable Energy Reviews. Elsevier; 2013; 22: 698–733. Available at: DOI:10.1016/j.rser.2012.12.065
54. Bouaddi S., Fernández-García A., Sansom C., Sarasua JA., Wolfertstetter F., Bouzekri H., et al. A review of conventional and innovative- sustainable methods for cleaning reflectors in concentrating solar power plants. Sustainability (Switzerland). 2018; 10(11). Available at: DOI:10.3390/su10113937
55. Cleaning Vehicles for Concentrated Solar Power. Available at: <http://www.ecilimp.com/termosolar.php> (Accessed: 6 May 2020)
56. Kolb GJ., Davenport R., Gorman D., Lumia R., Thomas R., Donnelly M. Heliostat cost reduction study. Proceedings of the Energy Sustainability Conference 2007. 2007; (June): 1077–1084. Available at: DOI:10.1115/ES2007-36217
57. Notice of proposed action: Application for a Groundwater Discharge permit NS2015505. Nevada Division of Environmental Protection; 2015.
58. Hardt M., Martínez D., González A., Garrido C., Aladren S., Villa JR., et al. HECTOR – heliostat cleaning team-oriented robot. SolarPaces Conference. 2011; (July).
59. Zhu G., Kearney D., Mehos M. On characterization and measurement of average solar field mirror reflectance in utility-scale concentrating solar power plants. Solar Energy. Elsevier Ltd; 2014; 99: 185–202. Available at: DOI:10.1016/j.solener.2013.11.009

60. Roth EP., Pettit RB. Effect of soiling on solar mirrors and techniques used to maintain high reflectivity. *Solar Materials Science*. 1980; (June): 199–227. Available at: DOI:10.1016/b978-0-12-511160-7.50013-2
61. Sarasua JA., Sandá A., Villasante C., Aranzabe E. Non-immersion ultrasonic cleaning for heliostats. *AIP Conference Proceedings*. 2018; 2033(November). Available at: DOI:10.1063/1.5067071
62. BRU P., BULLIARD SAURET O., COUTURIER R. WO2016046278A1: System and method of ultrasonic cleaning of a soiled surface, comprising an ultrasonic wave generation device. 2016.
63. Stark J., Heiling C., Hudelson JN., Yellowhair J., Horenstein M. Electrodynamic removal of dust from solar mirrors and its applications in concentrated solar power (CSP) plants. *IEEE*; 2014; (4): 1–7.
64. Peratt AL. Electric space: Evolution of the plasma universe. *Astrophysics and Space Science*. 1996; 244(1–2): 89–103. Available at: DOI:10.1007/BF00642283
65. Lerner EJ. Two World Systems Revisited: A Comparison of Plasma Cosmology and the Big Bang. *IEEE Transactions on Plasma Science*. 2003; 31(6 I): 1268–1275. Available at: DOI:10.1109/TPS.2003.821478
66. Yahnin AG., Sergeev VA. Simultaneous satellite and ground-based observations of polar cap Aurora. *Advances in Space Research*. 1996; 18(8): 111–114. Available at: DOI:10.1016/0273-1177(95)00977-9
67. Howlader MK., Yang Y., Roth JR. Time-resolved measurements of electron number density and collision frequency for a fluorescent lamp plasma using microwave diagnostics. *IEEE Transactions on Plasma Science*. 2005; 33(3): 1093–1099. Available at: DOI:10.1109/TPS.2005.848623
68. Shinoda T., Awamoto K. Plasma display technologies for large area screen and cost reduction. *IEEE Transactions on Plasma Science*. 2006; 34(2 II): 279–286. Available at: DOI:10.1109/TPS.2006.872453

69. Tendero C., Tixier C., Tristant P., Desmaison J., Leprince P. Atmospheric pressure plasmas: A review. *Spectrochimica Acta - Part B Atomic Spectroscopy*. 2006; 61(1): 2–30. Available at: DOI:10.1016/j.sab.2005.10.003
70. Boulos MI. Thermal Plasma Processing. *IEEE Transactions on Plasma Science*. 1991; 19(6): 1078–1089. Available at: DOI:10.1109/27.125032
71. Mehdizadeh M., Mehdizadeh M. Plasma applicators at RF and microwave frequencies. *Microwave/RF Applicators and Probes*. William Andrew Publishing; 1 January 2015; : 335–363. Available at: DOI:10.1016/B978-0-323-32256-0.00010-5 (Accessed: 7 April 2020)
72. Annemie., Bogaerts., Neyts E., Gijbels R., Mullen J Van der. Gas Discharge Plasmas and Their Applications. *Spectrochimica Acta Part B*. 2002; 57: 609–658.
73. Wong CS., Mongkolnavin R. Elements of Plasma Technology. 2016. 133 p. Available at: DOI:10.1007/978-981-10-0117-8
74. Morozov AI. Introduction to plasma dynamics. *Introduction to Plasma Dynamics*. 2012. 1–808 p. Available at: DOI:10.1201/b13929
75. Gryziński M. Classical theory of electronic and ionic inelastic collisions. *Physical Review*. 1959; 115(2): 374–383. Available at: DOI:10.1103/PhysRev.115.374
76. Verboncoeur JP. Particle simulation of plasmas: Review and advances. *Plasma Physics and Controlled Fusion*. 2005; 47(5 A). Available at: DOI:10.1088/0741-3335/47/5A/017
77. Pai S-I. Magnetogasdynamics and plasma dynamics. *Journal of the Franklin Institute*. 1962. 323 p. Available at: DOI:10.1016/0016-0032(62)90846-3
78. Stenson E V., Horn-Stanja J., Stoneking MR., Pedersen TS. Debye length and plasma skin depth: two length scales of interest in the creation and

- diagnosis of laboratory pair plasmas. *Journal of Plasma Physics*. 2017; 83(1). Available at: DOI:10.1017/s0022377817000022
79. Bellan PM. *Fundamentals of Plasma Physics*. Cambridge University Press; 2008.
 80. Boyd TJM., Sanderson JJ. *The Physics of Plasmas*. Cambridge University Press; 2003.
 81. Inan U., Gołkowski M. *Principles of Plasma Physics for Engineers sand Scientists*. Cambridge University Press; 2011.
 82. Marode E., Djermoune D., Dessante P., Deniset C., Ségur P., Bastien F., et al. Physics and applications of atmospheric non-thermal air plasma with reference to environment. *Plasma Physics and Controlled Fusion*. 2009; 51(12). Available at: DOI:10.1088/0741-3335/51/12/124002
 83. Smirnov BM. *Physics of Ionized Gases*. John Wiley & Sons; 1963.
 84. DREICER H. Electron and Ion Runaway in a Fully Ionized Gas. *Physical Review*. 1959; 115(2).
 85. Fridman A. *Plasma Chemistry*. Plasma Chemistry. 2008. 1–978 p. Available at: DOI:10.1017/CBO9780511546075
 86. Bruggeman PJ., Iza F., Brandenburg R. Foundations of atmospheric pressure non-equilibrium plasmas. *Plasma Sources Science and Technology*. IOP Publishing; 2017; 26(12). Available at: DOI:10.1088/1361-6595/aa97af
 87. Isbary G., Shimizu T., Li YF., Stolz W., Thomas HM., Morfill GE., et al. Cold atmospheric plasma devices for medical issues. *Expert Review of Medical Devices*. 2013; 10(3): 367–377. Available at: DOI:10.1586/erd.13.4
 88. Morent R., De Geyter N., Verschuren J., De Clerck K., Kiekens P., Leys C. Non-thermal plasma treatment of textiles. *Surface and Coatings Technology*. 2008; 202(14): 3427–3449. Available at: DOI:10.1016/j.surfcoat.2007.12.027

89. Schütze A., Jeong JY., Babayan SE., Park J., Selwyn GS., Hicks RF. The atmospheric-pressure plasma jet: A review and comparison to other plasma sources. *IEEE Transactions on Plasma Science*. 1998; 26(6): 1685–1694. Available at: DOI:10.1109/27.747887
90. Boulos MI., Fauchais P., Pfender E. *Thermal Plasmas: Fundamentals and Applications*. 1994. Available at: DOI:10.1007/978-1-4899-1337
91. Chang JS., Lawless PA., Yamamoto T. Corona Discharge Processes. *IEEE Transactions on Plasma Science*. 1991; 19(6): 1152–1166. Available at: DOI:10.1109/27.125038
92. Pattanadech N., Potivetkul S., Yuttagowith P. Corona phenomena of various high voltage shielding types. *2006 International Conference on Power System Technology, POWERCON2006*. 2006; (1). Available at: DOI:10.1109/ICPST.2006.321552
93. Mizuno A. Electrostatic Precipitation. *IEEE Transactions on Dielectrics and Electrical Insulation*. 2000; 7(5): 615–624. Available at: DOI:10.1109/94.879357
94. Chen J., Davidson JH. Ozone Production in the Positive DC Corona Discharge: Model and Comparison to Experiments. *Plasma Chemistry and Plasma Processing*. 2002; 22(4): 495–522. Available at: DOI:10.1023/A:1021315412208
95. Lieberman MA., Lichtenberg AJ. *Principles of Plasma Discharges and Materials Processing: Second Edition*. Principles of Plasma Discharges and Materials Processing: Second Edition. 2005. 1–757 p. Available at: DOI:10.1002/0471724254
96. Emeleus KG., Carmichael NM. The Aston Dark Space. *Nature*. 1928; 121(3036): 14.
97. Waldmann T., Iturrondobeitia A., Kasper M., Ghanbari N., Aguesse F., Bekaert E., et al. Review—Post-Mortem Analysis of Aged Lithium-Ion Batteries: Disassembly Methodology and Physico-Chemical Analysis

- Techniques. *Journal of The Electrochemical Society*. 2016; 163(10): A2149–A2164. Available at: DOI:10.1149/2.1211609jes
98. Aronsson BO., Lausmaa J., Kasemo B. Glow discharge plasma treatment for surface cleaning and modification of metallic biomaterials. *Journal of Biomedical Materials Research*. 1997; 35(1): 49–73. Available at: DOI:10.1002/(SICI)1097-4636(199704)35:1<49::AID-JBM6>3.0.CO;2-M
 99. Mickan M., Helmersson U., Horwat D. Effect of substrate temperature on the deposition of Al-doped ZnO thin films using high power impulse magnetron sputtering. *Surface and Coatings Technology*. Elsevier; 2018; 347(October 2017): 245–251. Available at: DOI:10.1016/j.surfcoat.2018.04.089
 100. Inaba T., Watanabe Y., Nagano M., Ishida T., Endo M. Ar torch plasma characteristics and its application to waste treatment. *Thin Solid Films*. 1998; 316(1–2): 111–116. Available at: DOI:10.1016/S0040-6090(98)00399-X
 101. Ramakrishnan S., Rogozinski MW. Properties of electric arc plasma for metal cutting. *Journal of Physics D: Applied Physics*. 1997; 30(4): 636–644. Available at: DOI:10.1088/0022-3727/30/4/019
 102. Kogelschatz U. Atmospheric-pressure plasma technology. *Plasma Physics and Controlled Fusion*. 2004; 46(12 B). Available at: DOI:10.1088/0741-3335/46/12B/006
 103. Wei X., Xu F., Bennett A., Swan J., Pulsford J., Chen G., et al. Numerical analysis of direct-current (DC) plasma processing for high-efficient steel surface modification. *International Journal of Advanced Manufacturing Technology*. 2023; 124(7–8): 2215–2228. Available at: DOI:10.1007/s00170-022-10548-x
 104. Lieberman MA., Ashida S. Global models of pulse-power-modulated highdensity, low-pressure discharges. *Plasma Sources Science and Technology*. 1996; 5(2): 145–186. Available at:

DOI:<https://doi.org/10.1088/0963-0252/5/2/006>

105. Sproul WD., Christie DJ., Carter DC. Control of reactive sputtering processes. *Thin Solid Films*. 2005; 491(1–2): 1–17. Available at: DOI:10.1016/j.tsf.2005.05.022
106. Rossnagel SM., Cuomo JJ., Westwood WD. *Handbook of Plasma Processing Technology: Fundamentals, Etching, Deposition, and Surface Interactions*. William Andrew Publishing; 1990. Available at: https://app.knovel.com/web/toc.v/cid:kpHPPTFED3/viewerType:toc//root_slug:handbook-plasma-processing/url_slug:introduction-references?q=capacitive&issue_id=kt005H7JU8&hierarchy= (Accessed: 6 April 2020)
107. Yin Y., Bilek MMM., McKenzie DR. The origins of self-bias on dielectric substrates in RF plasma processing. *Surface and Coatings Technology*. 2006; 200(12–13): 3670–3674. Available at: DOI:10.1016/j.surfcoat.2004.09.015
108. Tang YY., Wang XJ., Liu L., Zhao LM., Liu FK. Design of high power microwave ceramic windows in C-band. *Journal of Fusion Energy*. 2014; 33(1): 68–73. Available at: DOI:10.1007/s10894-013-9640-y
109. Gower SA. Electrical properties of an un-cooled microwave waveguide applicator - VSWR. *Journal of Physics D: Applied Physics*. 2003; 36(16): 1931–1935. Available at: DOI:10.1088/0022-3727/36/16/303
110. Fleisch T., Kabouzi Y., Moisan M., Pollak J., Castãos-Martínez E., Nowakowska H., et al. Designing an efficient microwave-plasma source, independent of operating conditions, at atmospheric pressure. *Plasma Sources Science and Technology*. 2007; 16(1): 173–182. Available at: DOI:10.1088/0963-0252/16/1/022
111. Bennett A., Yu N., Castelli M., Chen G., Balleri A., Urayama T., et al. Characterisation of a microwave induced plasma torch for glass surface modification. *Frontiers of Mechanical Engineering*. 2020; Available at: DOI:10.1007/s11465-020-0603-5

112. Moisan M., Beaudry C., Leprince P. A small microwave plasma source for long column production without magnetic field. *IEEE Transactions on Plasma Science*. 1975; PS-3(2): 55–59.
113. Bennett A., Yu N., Castelli M., Chen G., Fang F. Etching characteristics of crystal quartz by surface wave microwave induced plasma. 2020; : 10. Available at: DOI:10.1117/12.2574947
114. Yu N., Jourdain R., Gourma M., Xu F., Bennett A., Fang F. Power dissipation of an inductively coupled plasma torch under e mode dominated regime. *Micromachines*. 2021; 12(7). Available at: DOI:10.3390/mi12070834
115. Connor JW., Wilson HR. A review of theories of the L-H transition. *Plasma Physics and Controlled Fusion*. 2000; 42(1).
116. Lee JK., Lee HC., Chung CW. E-H mode transition in inductively coupled plasma using Ar, O₂, N₂, and mixture gas. *Current Applied Physics*. Elsevier B.V; 2011; 11(5 SUPPL.): S149–S153. Available at: DOI:10.1016/j.cap.2011.04.009
117. Chaudhary K., Rizvi SZH., Ali J. Laser-Induced Plasma and its Applications. *Plasma Science and Technology - Progress in Physical States and Chemical Reactions*. InTech; 2016. p. 13. Available at: DOI:10.5772/61784
118. Colao F., Lazic V., Fantoni R., Pershin S. A comparison of single and double pulse laser-induced breakdown spectroscopy of aluminum samples. *Spectrochimica Acta-Part B Atomic Spectroscopy*. 2002; 57(7): 1167–1179. Available at: DOI:10.1016/S0584-8547(02)00058-7
119. Rai VN., Thakur SN. Physics of Plasma in Laser-Induced Breakdown Spectroscopy. *Laser-Induced Breakdown Spectroscopy*. 2007. 83–111 p. Available at: DOI:10.1016/B978-044451734-0.50007-7
120. Meger RA., Blackwell DD., Fernsler RF., Lampe M., Leonhardt D., Manheimer WM., et al. Beam-generated plasmas for processing

- applications. *Physics of Plasmas*. 2001; 8(5 II): 2558–2564. Available at: DOI:10.1063/1.1345506
121. Gross RA., Miller B. 5. Plasma Heating by Strong Shock Waves. 1971. pp. 169–212. Available at: DOI:10.1016/S0076-695X(08)60842-X
 122. Katagiri K., Hasegawa J., Nishinomiya S., Ikagawa H., Oguri Y. Development of a coaxial tapered electromagnetic shock tube for beam-plasma non-linear interaction experiments. *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms*. 2008; 266(10): 2161–2164. Available at: DOI:10.1016/j.nimb.2008.02.056
 123. Griffiths RW., Sandeman RJ., Hornung HG. The stability of shock waves in ionizing and dissociating gases. *Journal of Physics D: Applied Physics*. 1976; 9(12): 1681–1691. Available at: DOI:10.1088/0022-3727/9/12/006
 124. Djurović S., Mijatović Z., Vujičić B., Kobilarov R., Savić I., Gavanski L. Measurement of the shock front velocity produced in a T-tube plasma. *Physics of Plasmas*. 2015; 22(1). Available at: DOI:10.1063/1.4905645
 125. Mohamed Salem M., Loiseau JF., Held B. Impedance matching for optimization of power transfer in a capacitively excited RF plasma reactor. *EPJ Applied Physics*. 1998; 3(1): 91–95. Available at: DOI:10.1051/epjap:1998208
 126. Zhang C., Ordóñez R. Extremum-Seeking Control and Applications. 2012; : 31–45. Available at: DOI:10.1007/978-1-4471-2224-1
 127. Werner F., Korzec D., Engemann J. Slot antenna 2.45 GHz microwave plasma source. *Plasma Sources Science and Technology*. 1994; 3(4): 473–481. Available at: DOI:10.1088/0963-0252/3/4/004
 128. Kogelschatz U., Eliasson B., Egli W. From ozone generators to flat television screens: history and future potential of dielectric-barrier discharges. *Pure and Applied Chemistry*. 2007; 71(10): 1819–1828. Available at: DOI:10.1351/pac199971101819

129. Gibalov VI., Pietsch GJ. Dynamics of dielectric barrier discharges in different arrangements. *Plasma Sources Science and Technology*. 2012; 21(2). Available at: DOI:10.1088/0963-0252/21/2/024010
130. Brandenburg R. Dielectric barrier discharges: progress on plasma sources and on the understanding of regimes and single filaments. *Plasma Sources Science and Technology*. IOP Publishing; 2018; 27(7). Available at: DOI:https://doi.org/10.1088/1361-6595/aa6426
131. Gibalov VI., Pietsch GJ. Development of dielectric barrier discharges in gas gaps and on surfaces. *Journal of Physics D: Applied Physics*. 2000; 33(20): 2618–2636. Available at: DOI:10.1088/0022-3727/33/20/315
132. Uytdenhouten Y., Van Alphen S., Michielsen I., Meynen V., Cool P., Bogaerts A. A packed-bed DBD micro plasma reactor for CO₂ dissociation: Does size matter? *Chemical Engineering Journal*. Elsevier; 2018; 348(December 2017): 557–568. Available at: DOI:10.1016/j.cej.2018.04.210
133. Chirokov A., Gutsol A., Fridman A. Atmospheric pressure plasma of dielectric barrier discharges. *Pure and Applied Chemistry*. 2005; 77(2): 487–495. Available at: DOI:10.1351/pac200577020487
134. Kogelschatz U. Dielectric-barrier Discharges: Their History, Discharge Physics, and Industrial Applications. *Plasma Chemistry and Plasma Processing*. 2003; 23(1).
135. Kang WS., Park JM., Kim Y., Hong SH. Numerical study on influences of barrier arrangements on dielectric barrier discharge characteristics. *IEEE Transactions on Plasma Science*. 2003; 31(4 II): 504–510. Available at: DOI:10.1109/TPS.2003.815469
136. Braun D., Kuchler U., Pietsch G. Microdischarges in air-fed ozonizers. *Journal of Physics D: Applied Physics*. 1991; 24(4): 564–572. Available at: DOI:10.1088/0022-3727/24/4/007
137. Ráhel J., Sherman DM. The transition from a filamentary dielectric barrier

- discharge to a diffuse barrier discharge in air at atmospheric pressure. *Journal of Physics D: Applied Physics*. 2005; 38(4): 547–554. Available at: DOI:10.1088/0022-3727/38/4/006
138. Becker KH., Schoenbach KH., Eden JG. Microplasmas and applications. *Journal of Physics D: Applied Physics*. 2006; 39(3). Available at: DOI:10.1088/0022-3727/39/3/R01
 139. Meiners S., Salge JGH., Prinz E., Förster F. Surface modification of polymer materials by transient gas discharges at atmospheric pressure. *Surface and Coatings Technology*. 1998; 98(1–3): 1121–1127. Available at: DOI:10.1016/S0257-8972(97)00234-X
 140. Pochner K., Neff W., Lebert R. Atmospheric pressure gas discharges for surface treatment. *Surface and Coatings Technology*. 1995; 74–75(PART 1): 394–398. Available at: DOI:10.1016/0257-8972(95)08325-1
 141. Kostov KG., Nishime TMC., Castro AHR., Toth A., Hein LRO. Surface modification of polymeric materials by cold atmospheric plasma jet. *Surface and Coatings Technology*. 2014; 314. Available at: DOI:10.1016/j.apsusc.2014.07.009
 142. Kostov KG., Nishime TMC., Hein LRO., Toth A. Study of polypropylene surface modification by air dielectric barrier discharge operated at two different frequencies. *Surface and Coatings Technology*. Elsevier B.V.; 2013; 234(February 2018): 60–66. Available at: DOI:10.1016/j.surfcoat.2012.09.041
 143. Dimitrakellis P., Gogolides E. Atmospheric plasma etching of polymers: A palette of applications in cleaning/ashing, pattern formation, nanotexturing and superhydrophobic surface fabrication. *Microelectronic Engineering*. Elsevier; 2018; 194(February): 109–115. Available at: DOI:10.1016/j.mee.2018.03.017
 144. Heidemann HM., Dotto MER., Laurindo JB., Carciofi BAM., Costa C. Cold plasma treatment to improve the adhesion of cassava starch films onto PCL

- and PLA surface. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2019; 580(August). Available at: DOI:10.1016/j.colsurfa.2019.123739
145. Pinheiro MJ. Plasma: the genesis of the word. 2007; : 6–7. Available at: <http://arxiv.org/abs/physics/0703260>
 146. Siemens W von. Ueber die elektrostatische Induction und die Verzögerung des Stroms in Flaschendrahten. *Annalen der Physik*. 1857; 178(9): 66–122. Available at: DOI:10.1002/andp.18571780905
 147. Zhang X., Lee BJ., Im HG., Cha MS. Ozone Production with Dielectric Barrier Discharge: Effects of Power Source and Humidity. *IEEE Transactions on Plasma Science*. IEEE; 2016; 44(10): 2288–2296. Available at: DOI:10.1109/TPS.2016.2601246
 148. Song CL., Bin F., Tao ZM., Li FC., Huang QF. Simultaneous removals of NO_x, HC and PM from diesel exhaust emissions by dielectric barrier discharges. *Journal of Hazardous Materials*. 2009; 166(1): 523–530. Available at: DOI:10.1016/j.jhazmat.2008.11.068
 149. Li S., Huang Y., Wang F., Liu J., Feng F., Shen X., et al. Fundamentals and environmental applications of non-thermal plasmas: Multi-pollutants emission control from coal-fired flue gas. *Plasma Chemistry and Plasma Processing*. 2014; 34(3): 579–603. Available at: DOI:10.1007/s11090-013-9517-x
 150. Hübner M., Brandenburg R., Neubauer Y., Röpcke J. On the Reduction of Gas-Phase Naphthalene Using Char-Particles in a Packed-Bed Atmospheric Pressure Plasma. *Contributions to Plasma Physics*. 2015; 55(10): 747–752. Available at: DOI:10.1002/ctpp.201510014
 151. Zhang J., Duan Y., Zhao W., Zhu C., Zhou Q., She M. Removal of Elemental Mercury from Simulated Flue Gas by Combining Non-thermal Plasma with Calcium Oxide. *Plasma Chemistry and Plasma Processing*. Springer US; 2016; 36(2): 471–485. Available at: DOI:10.1007/s11090-

152. Montoro-Damas AM., Brey JJ., Rodríguez MA., González-Elípe AR., Cotrino J. Plasma reforming of methane in a tunable ferroelectric packed-bed dielectric barrier discharge reactor. *Journal of Power Sources*. 2015; 296: 268–275. Available at: DOI:10.1016/j.jpowsour.2015.07.038
153. Shimizu K., Sugiyama T., Samaratunge MNL. Study of Air Pollution Control by Using Micro Plasma Filter. 2008; 44(2): 506–511.
154. Jögi I., Erme K., Levoll E., Raud J., Stamate E. Plasma and catalyst for the oxidation of NO_x. *Plasma Sources Science and Technology*. IOP Publishing; 2018; 27(3). Available at: DOI:10.1088/1361-6595/aaae3c
155. Hilsum C. Flat-panel electronic displays: A triumph of physics, chemistry and engineering. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*. 2010; 368(1914): 1027–1082. Available at: DOI:10.1098/rsta.2009.0247
156. Liu Q., Ding G., Yang Z., Zhu B., Wang Y. Development of an ac plasma display panel with a low discharge voltage utilizing an electrophoretic carbon nanotube as a field emission layer. *Journal of Micromechanics and Microengineering*. 2012; 22(7). Available at: DOI:10.1088/0960-1317/22/7/075014
157. Liston EM., Martinu L., Wertheimer MR. Plasma surface modification of polymers for improved adhesion: A critical review. *Journal of Adhesion Science and Technology*. 1993; 7(10): 1091–1127. Available at: DOI:10.1163/156856193X00600
158. Abe H., Yoneda M., Fujiwara N. Developments of plasma etching technology for fabricating semiconductor devices. *Japanese Journal of Applied Physics*. 2008; 47(3 PART 1): 1435–1455. Available at: DOI:10.1143/JJAP.47.1435
159. Shenton MJ., Stevens GC. Surface modification of polymer surfaces: Atmospheric plasma versus vacuum plasma treatments. *Journal of Physics*

- D: Applied Physics. 2001; 34(18): 2761–2768. Available at: DOI:10.1088/0022-3727/34/18/308
160. Law VJ., Tait D. Microwave plasma cleaning of ion implant ceramic insulators. Vacuum. 1998; 49(4): 273–278. Available at: DOI:10.1016/s0042-207x(98)00108-0
 161. Isabell TC., Fischione PE., O’Keefe C., Guruz MU., Dravid VP. Plasma cleaning and its applications for electron microscopy. Microscopy and Microanalysis. 1999; 5(2): 126–135. Available at: DOI:10.1017/S1431927699000094
 162. Jidenko N., Bourgeois E., Borra JP. Temperature profiles in filamentary dielectric barrier discharges at atmospheric pressure. Journal of Physics D: Applied Physics. 2010; 43(29). Available at: DOI:10.1088/0022-3727/43/29/295203
 163. Lowe HJ., Lucas DH. The physics of electrostatic precipitation. British Journal of Applied Physics. 1953; 4(S2). Available at: DOI:10.1088/0508-3443/4/S2/317
 164. Scholtz V., Pazlarova J., Sousova H., Khun J., Julak J. Nonthermal plasma - A tool for decontamination and disinfection. Biotechnology Advances. Elsevier Inc.; 2015; 33(6): 1108–1119. Available at: DOI:10.1016/j.biotechadv.2015.01.002
 165. Arndt S., Unger P., Berneburg M., Bosserhoff AK., Karrer S. Cold atmospheric plasma (CAP) activates angiogenesis-related molecules in skin keratinocytes, fibroblasts and endothelial cells and improves wound angiogenesis in an autocrine and paracrine mode. Journal of Dermatological Science. 2018; 89(2): 181–190. Available at: DOI:10.1016/j.jdermsci.2017.11.008
 166. Martin JW. Glasses and ceramics. Materials for Engineering. 2006; : 133–158. Available at: DOI:10.1533/9781845691608.2.133
 167. Belkind A., Gershman S. Plasma Cleaning of Surfaces. Vacuum

Technology and coating. 2008;

168. Iwasaki M., Matsudaira Y., Takeda K., Ito M., Miyamoto E., Yara T., et al. Roles of oxidizing species in a nonequilibrium atmospheric-pressure pulsed remote O₂/N₂ plasma glass cleaning process. *Journal of Applied Physics*. 2008; 103(2). Available at: DOI:10.1063/1.2830982
169. Homola T., Matoušek J., Kormunda M., Wu LYL., Černák M. Plasma treatment of glass surfaces using diffuse coplanar surface barrier discharge in ambient air. *Plasma Chemistry and Plasma Processing*. 2013; 33(5): 881–894. Available at: DOI:10.1007/s11090-013-9467-3
170. Yamamoto T., Okubo M., Imai N., Mori Y. Improvement on hydrophilic and hydrophobic properties of glass surface treated by nonthermal plasma induced by silent corona discharge. *Plasma Chemistry and Plasma Processing*. 2004; 24(1): 1–12. Available at: DOI:10.1023/B:PCPP.0000004878.61688.4d
171. Múgica-Vidal R., Alba-Elías F., Sainz-García E., Pantoja-Ruiz M. Atmospheric pressure air plasma treatment of glass substrates for improved silver/glass adhesion in solar mirrors. *Solar Energy Materials and Solar Cells*. Elsevier B.V.; 2017; 169(May): 287–296. Available at: DOI:10.1016/j.solmat.2017.05.034
172. Terpilowski K., Rymuszka D. Surface properties of glass plates activated by air, oxygen, nitrogen and argon plasma. *Glass Physics and Chemistry*. 2016; 42(6): 535–541. Available at: DOI:10.1134/S1087659616060195
173. Sairem. Available at: <https://www.sairem.com/solutions-for-microwave-plasma-generation/surface-wave-microwave-plasma-sources/> (Accessed: 2 December 2023)
174. Brown S., Leach R., Sun W. An overview of industrial X-ray computed tomography. NPL REPORT ENG 32. 2012.
175. Winter J., Dünnebier M., Schmidt-Bleker A., Meshchanov A., Reuter S., Weltmann KD. Aspects of UV-absorption spectroscopy on ozone in

- effluents of plasma jets operated in air. *Journal of Physics D: Applied Physics*. 2012; 45(38). Available at: DOI:10.1088/0022-3727/45/38/385201
176. Hong D., Rabat H., Bauchire JM., Chang MB. Measurement of ozone production in non-thermal plasma actuator using surface dielectric barrier discharge. *Plasma Chemistry and Plasma Processing*. 2014; 34(4): 887–897. Available at: DOI:10.1007/s11090-014-9527-3
 177. Walsh JL., Shi JJ., Kong MG. Contrasting characteristics of pulsed and sinusoidal cold atmospheric plasma jets. *Applied Physics Letters*. 2006; 88(17). Available at: DOI:10.1063/1.2198100
 178. Bruggeman P., Brandenburg R. Atmospheric pressure discharge filaments and microplasmas: Physics, chemistry and diagnostics. *Journal of Physics D: Applied Physics*. 2013; 46(46). Available at: DOI:10.1088/0022-3727/46/46/464001
 179. Merlino RL. Understanding Langmuir probe current-voltage characteristics. *American Journal of Physics*. 2007; 75(12): 1078–1085. Available at: DOI:10.1119/1.2772282
 180. Destefani CA., Murphy AB., Siores E., Elchinger MF. Enthalpy probe diagnostics of an atmospheric pressure argon microwave induced plasma. *Journal of Physics D: Applied Physics*. 2000; 33(16): 1996–2003. Available at: DOI:10.1088/0022-3727/33/16/311
 181. Feng X. Enthalpy probe technique for thermal plasma diagnostics. *Plasma Science and Technology*. 2003; 5(4): 1909–1914. Available at: DOI:10.1088/1009-0630/5/4/012
 182. Mauer G., Vaen R., Stöver D. Plasma and particle temperature measurements in thermal spray: Approaches and applications. *Journal of Thermal Spray Technology*. 2011; 20(3): 391–406. Available at: DOI:10.1007/s11666-010-9603-z
 183. Walsh JL., Iza F., Janson NB., Law VJ., Kong MG. Three distinct modes in a cold atmospheric pressure plasma jet. *Journal of Physics D: Applied*

- Physics. 2010; 43(7). Available at: DOI:10.1088/0022-3727/43/7/075201
184. Hanson RK., Spearrin RM., Goldenstein CS. Spectroscopy and Optical Diagnostics for Gases. Spectroscopy and Optical Diagnostics for Gases. 2016. Available at: DOI:10.1007/978-3-319-23252-2
 185. OceanOptics. HR4000 Operation Manual. 2009. p. 36.
 186. OceanOptics. USB2000+ Operation Manual. 2005; (170).
 187. Pearse RWB., Gaydon AG. The Identification of Molecular Spectra. 1963.
 188. Lofthus A., Krupenie PH. The spectrum of molecular nitrogen. Journal of Physical and Chemical Reference Data. 1977; 6(1): 113–307. Available at: DOI:10.1063/1.555546
 189. Krstulović N., Labazan I., Miloević S., Cvelbar U., Vesel A., Mozeti M. Optical emission spectroscopy characterization of oxygen plasma during treatment of a PET foil. Journal of Physics D: Applied Physics. 2006; 39(17): 3799–3804. Available at: DOI:10.1088/0022-3727/39/17/014
 190. Walkup RE., Saenger KL., Selwyn GS. Studies of atomic oxygen in O₂+CF₄ rf discharges by two-photon laser-induced fluorescence and optical emission spectroscopy. The Journal of Chemical Physics. 1985; 84(5): 2668–2674. Available at: DOI:10.1063/1.450339
 191. Li Y., Niu G., Wang X., Tang J., Duan Y. Effects of Air/H₂O Discharge Plasma on Propane Combustion Enhancement Using Dielectric Barrier Discharges. Plasma Chemistry and Plasma Processing. Springer US; 2018; 38(4): 831–850. Available at: DOI:10.1007/s11090-018-9896-0
 192. Kwok DY., Li D., Neumann AW. Fowkes' surface tension component approach revisited. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 1994; 89(2–3): 181–191. Available at: DOI:10.1016/0927-7757(94)80117-7
 193. Huanxiyl. Available at:
<https://www.huanxiyl.com/upfile/201611/2016110947491413.jpg>

194. Steenland K., Sanderson W. Lung Cancer among Industrial Sand Workers Exposed to Crystalline Silica. *American Journal of Epidemiology*. 1 April 2001; 153(7): 695–703. Available at: DOI:10.1093/aje/153.7.695
195. Brown K., Narum T., Jing N. Soiling test methods and their use in predicting performance of photovoltaic modules in soiling environments. *Conference Record of the IEEE Photovoltaic Specialists Conference*. 2012; : 1881–1885. Available at: DOI:10.1109/PVSC.2012.6317960
196. Fernández-García A., Sutter F., Martínez-Arcos L., Sansom C., Wolfertstetter F., Delord C. Equipment and methods for measuring reflectance of concentrating solar reflector materials. *Solar Energy Materials and Solar Cells*. 2017; 167(August): 28–52. Available at: DOI:10.1016/j.solmat.2017.03.036
197. Sansom C., Fernández-García A., King P., Sutter F., Garcia Segura A. Reflectometer comparison for assessment of back-silvered glass solar mirrors. *Solar Energy*. 2017; 155(October): 496–505. Available at: DOI:10.1016/j.solener.2017.06.053
198. Meyen S., Fernández-García a., Kennedy C., Lüpfer E. Standardization of solar mirror reflectance measurements--round robin test. 16th SolarPACES Conference. 2010; (October). Available at: <http://www.nrel.gov/docs/fy11osti/49189.pdf>
199. Bennett A., Jourdain R., Mackay P., Morantz P., Nicholls J. Atmospheric Pressure Plasma Etching of Crystal Quartz. *euspen's 18th International Conference & Exhibition*. 2018; (June): 10–11.
200. Birdi KS., Vu DT., Winter A. A study of the evaporation rates of small water drops placed on a solid surface. *Journal of Physical Chemistry*. 1989; 93(9): 3702–3703. Available at: DOI:10.1021/j100346a065
201. Dhavaleswarapu HK., Migliaccio CP., Garimella S V., Murthy JY. Experimental investigation of evaporation from low-contact-angle sessile droplets. *Langmuir*. 2010; 26(2): 880–888. Available at:

DOI:10.1021/la9023458

202. Figgis B., Nouviaire A., Wubulikasimu Y., Javed W., Guo B., Ait-Mokhtar A., et al. Investigation of factors affecting condensation on soiled PV modules. *Solar Energy*. 2018; 159(December 2017): 488–500. Available at: DOI:10.1016/j.solener.2017.10.089
203. Nayshevsky I., Xu Q., Lyons AM. Hydrophobic-Hydrophilic Surfaces Exhibiting Dropwise Condensation for Anti-Soiling Applications. *IEEE Journal of Photovoltaics*. 2019; 9(1): 302–307. Available at: DOI:10.1109/JPHOTOV.2018.2882636
204. AGC Solar. Sunmax Premium Reflect Factsheet. 2022.
205. McMillan P., Piriou B. Raman spectroscopic studies of silicate and related glass structure: a review. *Bulletin de Mineralogie*. 1983; 106(1–2): 57–75. Available at: DOI:10.3406/bulmi.1983.7668
206. Götze J. Chemistry, textures and physical properties of quartz — geological interpretation and technical application. *Mineralogical Magazine*. 2009; 73(4): 645–671. Available at: DOI:10.1180/minmag.2009.073.4.645
207. Haji A., Naebe M. Cleaner dyeing of textiles using plasma treatment and natural dyes: A review. *Journal of Cleaner Production*. Elsevier Ltd; 2020; 265: 121866. Available at: DOI:10.1016/j.jclepro.2020.121866
208. Zille A., Oliveira FR., Souto PAP. Plasma treatment in textile industry. *Plasma Processes and Polymers*. 2015; 12(2): 98–131. Available at: DOI:10.1002/ppap.201400052
209. Ranieri P., Sponsel N., Kizer J., Rojas-Pierce M., Hernández R., Gatiboni L., et al. Plasma agriculture: Review from the perspective of the plant and its ecosystem. *Plasma Processes and Polymers*. 2021; 18(1). Available at: DOI:10.1002/ppap.202000162
210. Yuan W zhi., Liao Z., He K., Huang SM. Mechanism of photovoltaic module soiling in the presence of dew. *Solar Energy Materials and Solar Cells*.

- Elsevier B.V.; 2022; 248(September): 111962. Available at: DOI:10.1016/j.solmat.2022.111962
211. Huang ZS., Shen C., Fan L., Ye X., Shi X., Li H., et al. Experimental investigation of the anti-soiling performances of different wettability of transparent coatings: Superhydrophilic, hydrophilic, hydrophobic and superhydrophobic coatings. *Solar Energy Materials and Solar Cells*. Elsevier B.V.; 2021; 225(March): 111053. Available at: DOI:10.1016/j.solmat.2021.111053
 212. Peng J., Zhao X., Wang W., Gong X. Durable Self-Cleaning Surfaces with Superhydrophobic and Highly Oleophobic Properties. 2019; Available at: DOI:10.1021/acs.langmuir.9b01507
 213. Palmisano P., Faraldi P., Fino D., Russo N. Household oven self-cleaning surfaces via catalytic thermal oxidation. 2009; 154: 251–257. Available at: DOI:10.1016/j.cej.2009.03.028
 214. Adak D., Bhattacharyya R., Barshilia HC. A state-of-the-art review on the multifunctional self-cleaning nanostructured coatings for PV panels , CSP mirrors and related solar devices. *Renewable and Sustainable Energy Reviews*. Elsevier Ltd; 2022; 159(June 2021): 112145. Available at: DOI:10.1016/j.rser.2022.112145
 215. Extrand CW., Gent AN. Retention of liquid drops by solid surfaces. *Journal of Colloid And Interface Science*. 1990; 138(2): 431–442. Available at: DOI:10.1016/0021-9797(90)90225-D
 216. Wolkenhauer A., Avramidis G., Hauswald E., Militz H., Viöl W. Sanding vs. plasma treatment of aged wood: A comparison with respect to surface energy. *International Journal of Adhesion and Adhesives*. 2009; 29(1): 18–22. Available at: DOI:10.1016/j.ijadhadh.2007.11.001
 217. O’Kell S., Henshaw T., Farrow G., Aindow M., Jones C. Effects of low-power plasma treatment on polyethylene surfaces. *Surface and Interface Analysis*. 1995; 23(5): 319–327. Available at: DOI:10.1002/sia.740230508

218. Benito Moreno A. Autonomous Plasma Robot: The Future of Maintenance in Solar Energy Plants. 2021. Available at: <http://hdl.handle.net/2117/359630>