Proceedings
Physics with Industry 2013
Lorentz Center Leiden, the Netherlands, 18 - 22 November
Colophon

Text
Participants and organisation workshop.

Cover photo
Technicians are inspecting a mirror that will fly aboard NASA’s James Webb Space Telescope. Image credit: NASA / Chris Gunn.

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Thanks to
The organisation is particularly grateful for the excellent service and facilities of the Lorentz Center, the effort of the senior researchers (from the preparation phase onwards) and the enthusiastic contribution of all participants during the week. The workshop ‘Physics with Industry’ was organised by Marcel Bartels and Martijn de Jager of the Foundation for Fundamental Research on Matter (FOM) and Floor Paauw of the Technology Foundation STW in collaboration with İkrám Cakır of the Lorentz Center. The event was funded by the Lorentz Center (which is partly funded by FOM and STW) and the participating companies. FOM is part of the Netherlands Organisation for Scientific Research (NWO). STW is funded by NWO and the Dutch Ministry of Economic Affairs.

Edition November 2013
Foreword

It is our great pleasure to present to you the proceedings of the fourth 'Physics with Industry' workshop that was organised by the Foundation FOM and Technology Foundation STW at the Lorentz Center in the Netherlands. The main aim of the 'Physics with Industry workshop' is to obtain creative solutions for industrial problems and to bring (young) physicists in contact with industrial R&D.

The first 'Physics with Industry workshop' was organized in 2010 and was inspired by the 'Mathematics with Industry' workshops, which have regularly been organised by the 'International Study Group Mathematics with Industry' since 1968. As well as enabling excellent scientific research, both FOM and STW focus on contributing to the Dutch knowledge economy, for example through public-private research collaborations and the training of young scientists. The 'Physics with Industry workshop' is therefore a natural extension of FOM's and STW's ambition to help companies and to inspire (young) physicists.

60 physicists participated in the workshop 2013, ranging from PhD students to professors. These scientists spent a week working in groups on five industrial problems, which were selected by a programme committee from proposals put forward by industry. Following an introduction to the various problems by the companies on Monday, the participants worked on these in groups for the rest of the week. On the last day, the groups presented their findings to the companies. A novelty in the 2013 workshop was that for most of the companies site-visits before the workshop took place so that the participants could become acquainted with the problem in a 'real-life' setting. Also various experiments took place during the workshop week.

Besides the scientific outcomes, the workshop also resulted in new public private contacts that may lead to future collaborations. Participants were mostly driven by the sheer pleasure of applying their physics knowledge to new problems, the desire to enrich their scientific network and the interest in gaining hands on experience with industrial R&D processes. Companies benefited from the scientific input they received and participating in the workshop enlarged their academic network. Two of the companies indicated to have the intention to apply for patent based on the outcome of the workshop.

These proceedings provide an overview of the scientific results obtained during the fourth 'Physics with Industry' workshop. We hope you enjoy reading it!

Wim van Saarloos
Director FOM

Eppo Bruins
Director STW
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Introduction

The fourth workshop Physics with Industry was organized in 2013 by the Foundation FOM and Technology Foundation STW at the Lorentz Center at Leiden, the Netherlands.

The five industrial problems discussed during the week were collected via an open call for proposals in spring 2013. A programme committee selected the five 'best problems' for the workshop. The selection criteria used by the committee were:

- it must be possible to solve the problems (or a major solution must be within reach) within one week and physics can make a clear contribution to the solution;
- it should be an urgent problem;
- the company should be willing to share detailed information.

The committee aimed at a mix of contributions from small, medium and large companies. The committee consists of seven researchers with different backgrounds in physics:

- Prof. Marileen Dogterom, FOM Institute AMOLF
- Prof. Ute Ebert, Centrum Wiskunde & Informatica
- Prof. Erik van der Giessen, University of Groningen
- Prof. Fred MacKintosh, VU Amsterdam
- Dr. Jacco Snoeijer, Twente University
- Dr. Peter Steeneken, NXP Semiconductors
- Prof. Lucas van Vliet, Delft University of Technology

The committee selected problems from the companies Ingenieursbureau Oranjewoud, Océ Technologies, PamGene International, Tata Steel, and RGS Development. Together a well balanced mix of SME’s and larger industries posing different challenges ranging from fundamental questions to more applied problems in a wide variety of industries. As soon as the five workshop problems had been selected, senior researchers from academia who are familiar with the specific subjects involved were recruited. They helped the companies to prepare their questions for the workshop and they joined the workshop week to guide the progress of the discussions.

These proceedings contain five chapters, one for each company case. Each chapter starts with a description of the case and a profile of the company, followed by a detailed description of the results obtained in the single workshop week.
Ingenieursbureau Oranjewoud

The fine dust problem near urban highways - optimization of the electrostatic precipitator device

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1. Abstract

Emission of fine dust from vehicle traffic on urban highways is a major health concern. Oranjewoud has therefore proposed to place electrostatic precipitators (ESP) on top of highway noise barriers in order to capture a significant amount of it before it escapes into densely populated areas. In this report we analyse the optimal design, placement and operating conditions of these ESPs. Concerning the design, we discuss in particular the capture efficiency for small particles with a half-micrometer diameter. We also discuss the flow resistance present in the conventional ESP design and propose an open air design that should be more optimal for the considered application. Regarding the placement of the ESPs, we give an estimate for their efficiency when placed on top of the noise barriers that follows from aerodynamic simulations of a typical highway configuration. Furthermore, we use our simulations to motivate an alternative upwind placement, which is more efficient in the presence of a significant cross wind. Finally, after considering several operating conditions, such as energy cost and safety, we conclude that the proposed solution to the fine dust problem is feasible.

2. Company profile

Oranjewoud is one of the major engineering and consultancy companies in the Netherlands with around 10,000 employees within the total Group (Oranjewoud N.V.) in which the engineering and consultancy part of the group counts approximately 3,000 employees. They want to be at the forefront of the development and application of sustainable and integral solutions in our living environment. They play a responsible role by using their expertise to ensure a sustainable future. Oranjewoud has adopted the following core values: enterprising, people-focused, evolutionary and characterful. These values determine how their firm and staff behave and interact with the environment and one another. Oranjewoud takes personal responsibility for providing society with high-value and sustainable solutions in a way that is both socially and economically responsible. Their projects are carried out in various areas
3. Problem description

3.1 Motivation

Fine dust particles created by vehicle traffic on urban highways is a major health concern. Specifically, exposure to fine dust can lead to asthma, lung cancer, respiratory diseases and birth complications [1]. The sources of fine dust from highways are primarily soot, from the incomplete combustion of fuel inside car engines, and rubber, released from the contact of car tires with the road. The harm of fine dust can be related in particular to its particle size. Of chief concern is particulate matter with a diameter less than ten micrometers, which is commonly referred to as PM10. Whereas larger particles can be filtered by the cilia and mucus in a person's nose and throat, PM10 penetrates deeply into the bronchi and lungs. Furthermore, particulate matter with a diameter less than 2.5 micrometers, similarly referred to as PM2.5, can even enter the gas exchange regions of the lungs. In Europe it is not uncommon for highways to pass through densely populated areas. In particular, if the wind is directed from the highway to a populated area, it will disperse the fine dust into these areas. It would therefore be very desirable to be able capture the fine dust emitted from highways before it can pollute these populated areas.

A solution proposed by Oranjewoud is to install a line of electrostatic precipitators (ESPs) on top of the noise barriers of a highway, a so-called Line ESP. Their principal assumption is that a significant amount of fine dust escapes the highway canyon (as formed by the noise barriers) by passing directly over the noise barrier with a proximity of about a meter. Because an ESP is designed to capture fine dust (we will elaborate on its working mechanisms in Section 4.1) a line of ESP's should therefore greatly help to reduce the amount of fine dust that would disperse into the urban areas. The fine dust captured by the ESP is collected onto grounded plates, and Oranjewoud has postulated that rain water should be sufficient to periodically wash it away. Existing work towards the design and commissioning of the Line ESP is summarised in Ref. [2].

The “problem” as defined by Oranjewoud for the Physics with Industry workshop is to:

Determine and examine all variables that need to be taken into account for the development of a working full scale prototype of the Line ESP.

To this end, a key question is how the fine dust is affected by the aerodynamics of the highway canyon, particularly in the presence of a cross wind. If this can be answered, the efficiency of the Line ESP can be quantified and its placement and dimensions can be optimized. Other specific questions posed by Oranjewoud included the acoustic properties of the Line ESP, its energy usage, how to operate it safely and how to maintain it. As a case study, the A13 highway between Delft and Rotterdam was proposed. This six lane highway passes 3.5km of densely populated areas at which the noise barriers have a height of six metres. For extra motivation, it was pointed out that the exposure to fine dust for people living along the A13 is equivalent to smoking 17 cigarettes a day.

3.2 Problem solving strategy

Our strategy for addressing the problems defined in Section 3.1 is to divide them into the three different scales present: the micro-scale, at which the fine dust is captured by the ESP, the meso-scale, describing the aerodynamics of the highway canyon creating the fine dust entering
the ESP, and the **macro-scale**, encompassing the practical operating conditions of the setup. Specifically, a synopsis of how we will proceed is as follows:

1. **Micro-scale** – capturing of the fine dust with the ESP device (Section 4).
   A key problem is the reduced efficiency of the proposed ESP design to capture small particles with a diameter of about half a micrometer. To this end, we discuss the mechanisms at play within the ESP that affect their capture efficiency. We also analyse the pressure drop of the proposed ESP design and propose a different design that we believe to be more optimal.

2. **Meso-scale**: – aerodynamics of the highway canyon (Section 5).
   ESPs are typically used in factories, where the flow of air is contained in a chimney. This is not so in the present configuration, where the device will be operated in open air, introducing important considerations regarding the flow topology over the highway canyon. One of the main points of interest is the optimal location, as well as dimensions, of the ESP inside the canyon. We will show that the optimal placement is intimately related to the flow field of air inside the canyon.

3. **Macro-scale**: – optimal operating conditions (Section 6).
   We address various parameters such as the amount of fine dust production by a typical highway, weather data, safety, cleaning and maintenance, and energy cost. Our main finding in this section is that there are no “deal breakers”, i.e. from an operational standpoint the Line ESP appears to be a feasible project.

4. Microscale: Optimization of ESP device

4.1 Working principle of industrial ESP device

In this section the working principles of an electrostatic precipitator (ESP) are explained. A typical ESP device used in industry is a plate-type ESP. It consists of a set of grounded parallel plates of length $L$, spaced a distance $D$ apart, creating a duct through which the polluted gas flows. Between the plates are thin wires which are put to a high voltage. If the voltage is high enough, gas molecules very close to the wire are ionized. This is called a corona discharge. The initiation voltage can be both positive and negative, but a negative voltage is more commonly used. The presence of a strong electric field causes the electrons to move away from the wire and from positive gas ions. They follow the electric field lines extending from the wire to the grounded plates. Close to the wire, the electronic kinetic energy is higher than the ionization energy of the gas molecules, so the electrons can ionize other gas molecules in their path. In this way, an ionization avalanche is created close to the wire. This is called the active zone. Further away from the wire, the electrons do not cause ionization. However, they attach themselves to other objects in their path, both neutral gas molecules and dust particles, making them negatively charged. Consequently, these particles are accelerated by the electric field, and finally obtain a steady-state velocity, the drift velocity. If charged gas ions encounter a dust particle, a transfer of the negative charge to the dust takes place. The charged dust follows the electric field lines, which are typically homogeneous far from the wire. The dust is attached to the grounded collection plates by the Van der Waals force. In this way, the dust is collected at the plates and the gas passing through the ESP is cleaned from the pollutant. The distribution of electric field lines depends strongly on the geometry of the ESP. The corona-initiating field strength depends i.e. on the composition of the gas and the radius of the wire. A blue light and crackling sound can be heard during the operation. This is caused by recombination of the electrons and positive ions, in which a photon is emitted. The sound is caused by shock waves formed because the electron mobility is very different from the ion mobility.
Collection efficiency

The diameter-resolved collection efficiency $\eta$ is defined for each particle diameter $d_p$ as the ratio of the particle mass collected $M_{\text{coll}}$ and the mass entering the ESP $M_{\text{in}}$, i.e.

$$\eta(d_p) = \frac{M_{\text{coll}}(d_p)}{M_{\text{in}}(d_p)}.$$  

(1)

Various models for the collection efficiency have been proposed, the most basic by Deutsch [3]. It assumes “infinite mixing”, which means that turbulent flow causes the dust particles to be homogeneously distributed in the duct and is given by

$$\eta = 1 - e^{-\frac{wL}{vD}}.$$  

(2)

Here, $v$ is the velocity component of the gas parallel to the plates and $w$ is the so-called migration velocity, which is defined as the steady-state velocity component perpendicular to the plate surface. This quantity depends strongly on the microscopic details such as the diameter $d_p$ of a dust particle and the electric field strength. The quantity $wL/(vD)$ is often called the Deutsch number, and can be interpreted as the product of the “aspect ratios” of ESP geometry and velocities. The higher the Deutsch number, so, the higher the migration velocity and plate length $L$, and the smaller the wind velocity and distance $D$, the larger the efficiency.

![Figure 1. Diameter-resolved collection efficiency under typical conditions and at a temperature of 150° C. Notice in particular the drop in efficiency. This figure is adapted from Ref. [3].](image)

The fractional collection efficiency of a plate-type ESP is plotted in Figure 1 for specific values of operational conditions. For large particles the collection efficiency is usually very high, above 90%. There is a remarkable dip in the efficiency for particles sized between 0.01 and 1 μm which is explained now. According to the Deutsch equation (2), for fixed geometry and wind speed, the dependence of $\eta$ on the particle size is through the migration velocity $w(d_p)$. It can be found by considering a force balance in the region far away from the wire, assuming that the particle is fully charged to its saturation charge $Q$ and that the electric field is homogeneous and in the direction of the plates. Here, two forces work on the dust particles. The first is the electric force $F_e$, which is proportional to the charge of the dust and the electric field strength,

$$F_e = Q \vec{E}.$$  

(3)

The saturation charge depends strongly on the diameter of the particle as can be seen in Figure 2. If the dust particles have a large diameter ($\geq 10 \mu m$), their surface area is relatively large and can accommodate a lot of field lines, which results in a large saturation charge. This is the so-called “field charging”. However, if the particle diameter becomes of the order of the...
mean free path of the gas ions, \( \lambda \), the dust particles obtain their charge from gas ions undergoing Brownian motion, a mechanism named “diffusion charging”. This results in significantly less charge. In short, smaller particles obtain less charge than larger ones, so the electric force has less effect on them. The second force is the effective drag force experienced by particles moving through a viscous fluid. Under ESP circumstances the drag force can be obtained from Stokes’ law. There is a catch however, which is the fact that the continuum description breaks down when the particle diameter approaches (again) the mean free path of the gas ions\(^1\). Then, Stokes’ law can be used, but with a slight alteration that accounts for the non-continuum effects, called the Cunningham correction factor \( C \). Including the correction factor, the drag force is given by

\[
\vec{F}_d = 6\pi \mu \frac{d_p}{2} \frac{1}{C},
\]

where \( \mu \) is the dynamic viscosity of the gas, and \( C \) is the Cunningham correction factor, which is a lengthy expression and a function of the Knudsen number. This factor becomes large for diameters \( d_p < 2\lambda \) and basically expresses that the particles small compared to \( \lambda \) experience effectively less drag force from the surrounding medium, because of the lower probability that the particle receives a hit during its Brownian motion.

Writing down the force balance in the \( y \)-direction,

\[
m_p \dot{w} = -F_{e,y} - F_{d,y},
\]

which is easily solved to give the velocity in the \( y \)-direction as a function of time. The particle approaches its steady-state velocity, the migration velocity, after a typical timescale

\[
\tau_p = m_p C/(3\pi \mu d_p),
\]

and the steady-state velocity is given by

\[
w = \frac{Q E_y}{3\pi \mu d_p C}.
\]

This migration velocity has precisely the same behaviour as described in the force balance above. In short, the largest particles experience a very large electric force so their migration velocity will be large. For the smallest particles the migration velocity is again large, because they experience very little drag. The particles with diameter of the order of \( \lambda \) receive less charge than the larger particles, but they also experience a larger drag force than the smallest particles, so their migration velocity drops. With a diameter of the order of \( \lambda \), they are precisely in the crossover region where the two advantageous effects both begin to decrease.

Now we refer again to Figure 1. The mean free path in air is about \( \lambda = 0.065 \) µm at room temperature. The figure is taken at a temperature of 150\(^\circ\)Celsius, for which the mean free path is slightly larger, 0.1 µm. It can be seen that the efficiency dip indeed occurs at this length scale. Now that we understand where the decrease in efficiency for capturing smaller particles arises from, it seems unavoidable that the PM\(_{2.5}\) are difficult to collect. We can change the geometry a little, e.g. make the ESP device longer, or place the plates closer apart, but we cannot really change or remove the minimum in their migration velocity. Therefore, alternatives to the plate ESP have to be considered.

### 4.2 Open air ESP

A typical ESP installation in industry is installed in a air conduit to filter outgoing process gasses. In this setting, there is a forced flow of air, so a relatively high flow resistance can be tolerated. To use a ESP along a highway, the flow resistance must be as low as possible to maximize the flow rate of fine dust through the ESP. In addition, since the wind plays a

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\(^1\)When the Knudsen number \( 2\lambda/d_p \) is high.
dominant role in an outdoor environment, there is a lot of variation in flow direction and this needs to be accommodated for.

We therefore propose a new design for an ESP, optimized for installation in open air, based on wire grids rather than parallel plates. Figure 3 shows, with increasing novelty, the various proposed designs. The wire diameter and wire pitch have to be chosen such that the grid is sufficiently open for air, but sufficiently close to define a homogeneous electric field. Vertical grids between the high voltage cathodes will increase the capture efficiency, by minimizing the deflection needed before a particle is trapped. Replacing the parallel plates by grids will significantly decrease the flow resistance when the airflow is not perfectly aligned to the ESP. Finally, a more dense configuration based on a honeycomb lattice can be used to achieve higher efficiency without increasing the outside dimensions of the device.

Figure 2. Saturation charge of dust particles as a function of their diameter. This figure is adapted from [3].

Figure 3. Novel suggestions for improving the ESP design, focused on application in the open field rather than in a conduit. All sketches are crosssections, black lines are grounded, the red points are at high voltage. (a) A common ESP design, as used in the Oranjewoud prototype. (b) Extra vertical wire grids to increase capture efficiency. (c) Wire grids instead of horizontal plates to decrease flow resistance if the oncoming flow is not parallel to the ESP device. (d) Like case c, but using a more dense packing of the grid tubes in a hexagonal pattern to increase efficiency without increasing the footprint.
Design considerations

The wire thickness and pitch are the most important parameters for the wire grids. For this it is useful to define the openness $B$ of the mesh by

$$B = (1 - d/p)^2$$

for square grid with wire diameter $d$ and pitch $p$.

From an aerodynamic perspective, the flow resistance through the mesh needs to be minimal, corresponding to a maximal openness and a minimal wire diameter. However, the capture efficiency goes down when the openness is too large or the wire diameters too small, since the dust particles might not be deflected sufficiently by the electric field to precipitate on the mesh. A third consideration is that it is undesirable to have ionization of air induced by the field around the mesh. This means that the wire diameter should not be too small, nor should the ratio of the wire pitch to the distance between mesh and high voltage cathode be too large.

To summarize, it is an optimization process with two variables, where the figure of merit, the total device efficiency, scales with the capture efficiency but inversely with the flow resistance.

- Flow resistance: $B$ large, $d$ small
- Capture efficiency: $B$ small, $d$ large
- Avoid ionization on grid: $p$ small, $d$ large

These considerations will be investigated in more detail in the next paragraphs.

Flow resistance

In order to estimate the efficiency gain of the new concept, first of all an aerodynamic calculation of the pressure drop over the ESP is made. The original ESP design is compared against the new wire grid design. Some basic assumptions are made. The initial concept is basically an array of parallel plates through which the air flows. From basic aerodynamic theory the pressure drop over the ESP can be calculated. The Reynolds number based on the half channel height is given as:

$$Re_h = \frac{hU_\infty}{\nu}.$$  \hspace{1cm} (7)

For typical operating conditions ($U_\infty = 5 \text{ m/s}$, $h = 0.05 \text{ m}$ and $\nu = 15.68 \cdot 10^{-6} \text{ m}^2/\text{s}$) this yields a Reynolds number of $Re_h \approx 15,000$. This indicates that the flow through the ESP is turbulent.

From the momentum balance over the ESP the pressure drop can be related to the wall shear stress ($\tau_w$) as:

$$\tau_w = h \frac{\partial p}{\partial x},$$  \hspace{1cm} (8)

where the wall shear stress can be related to the bulk velocity between the plates ($U_b \approx 5 \text{ m/s}$) as:

$$\tau_w \approx \frac{U_b \rho}{225}.$$  \hspace{1cm} (9)

Combining (9) with (8) and integrating over the depth of the ESP ($L$) gives the pressure drop as:

$$\Delta p = \frac{\rho U_b L}{225h}.$$  \hspace{1cm} (10)
which yields for an $1 \times 1 \, \text{m}^2$ ESP of 0.5 m thickness a pressure loss of $3 \text{N/m}^2$. However also the form drag should be considered as the frontal area is relatively large and blunt. This can be estimated as:

$$F_D = 0.5 \, \rho \, U_\infty^2 \, C_D \, A.$$  \hspace{1cm} (11)

The frontal area $A$ has been estimated to be 0.12m$^2$ whereas the drag coefficient of a blunt body is approximately $C_D \approx 1.3$. The only contributing elements to the form drag are the supporting beams at the edge of the ESP which adds approximately 1 N to the total drag. So the total flow resistance of a typical ESP configuration in the present case is approximately $4 \, \text{N/m}^2$. In Ref. [8] an estimation for the non-dimensional pressure drop $K$ over a wire mesh is given as:

$$K = f(R_eD) \frac{1 - (1 - \sigma)^2}{(1 - \sigma)^2},$$  \hspace{1cm} (12)

in which $\sigma$ is the solidity of the screen and $f(R_eD)$ is approximately 0.45 for a typical wire screen at design operating conditions. For a typical wire screen with a wire diameter of 1 mm and a spacing of 2 cm the solidity is calculated as $\sigma = 0.10$. Finally, the pressure drop over such a wire screen can be estimated as $\Delta p = 1.7 \text{N/m}^2$. Assuming that a similar supporting construction is used as in the original design, the total flow resistance of the wire screen is approximately $2.7 \, \text{N/m}^2$. With respect to the original design, theoretically a gain of 32% can be obtained. However it should be noted that in case the oncoming flow is not parallel to the ESP, the drag of the conventional ESP configuration significantly increases with respect to the wire mesh design.

**Ionization and capture efficiency**

We will now propose some modifications in the ESP geometry. Our aim is to optimize the devices operation in an open environment, such as on top of highway noise barriers, as well as reducing the operation costs. In Figure 4 we show a sketch of a single stage ESP with typical geometrical parameters$^2$: a wire-to-plate gap of 10 cm, a wire-to-wire pitch of 4 cm, a wire diameter of 1 mm. A positive voltage of 50 kV on the wires produces a high field ($> 40 \, \text{kV/cm}$) region around the wires with a diameter of about 2.4 mm. The red lines show the path of the positive ions produced in this region towards the collection plates. The ion flow affects with a smaller extent the region between two adjacent wires, which is therefore less effective in charging the dust. This region can be removed by the introduction of a high-transparency mesh at ground potential between two wires. The modified ion flow is shown in Figure 5. The cross section of the mesh (2 cm pitch, 2 mm wire diameter) is depicted in purple. The volume results arranged in multiple cells with a pitch of 10 cm.

Though the effect of multiple meshes on the flow resistance must be evaluated, we observe several advantages in this new design:

- **Higher electric field.** The introduction of the mesh has the same effect of reducing the distance between the wire and the parallel plate. A wire voltage of only 25 kV is sufficient to produce a similar high-field region as wide as in the standard design.

- **Additional collection surface.** The surface of the meshes increases the total surface available for the dust collection.

- **Enhanced collection probability.** The charged dust flows through the meshes, hence very close to a collection electrode. In addition, the fraction that crosses a mesh is affected by an opposite electric field pushing back to the collection electrode.

$^2$The electrostatical configurations have been calculated and visualised with Garfield, see Ref. [5].
Figure 4. Sketch of a single stage ESP (wire-to-plate gap of 10 cm, wire-to-wire pitch 4 cm, wire diameter 1 mm, positive voltage of 50 kV on wires). The red lines show the path of the positive ions produced in the high field region towards the collection plates.

Figure 5. Sketch of a single stage ESP with a mesh between the wires (wire-to-plate gap of 10 cm, wire-to-wire pitch 10 cm, wire diameter 1 mm, wire-to-mesh distance of 5 cm, meshes with 2 cm pitch and 2 mm diameter, positive voltage of 25 kV on wires).

The last two bullet points are especially promising for the collection of the dust with diameter smaller than 2 μm that is characterised by a lower efficiency in the standard design. A further modification in this direction brings the device to the innovative “Open-air ESP” configuration shown in Figure 6. Parallel plates are substituted by meshes, obtaining a modular device with cells composed by a high voltage wire surrounded by meshes at ground potential. Though the collection surface is reduced, we will discuss the effect on flow resistance in Section 4.2.

Particle resuspension

Once a particle is stuck on a capture electrode, it is very difficult for it to get off again. Figure 7 compares the relative strength of the aerodynamic drag to the adhesion, neglecting any effects of humidity. For rather extreme wind speeds (25 m/s or 10 Beaufort) particles with a diameter less than 7 micrometer will stick to the surface. For more modest wind speeds and relevant humidities, it is expected that particles up to 100 micrometer will not resuspend. Compared to a traditional ESP in an industrial setting, the amount of fine dust in the air near a busy highway is several orders of magnitude lower. Therefore the much smaller surface area of a mesh compared to a plate should not impose problems of dust build-up and a cleaning interval of once or twice a year should be sufficient.

4.3 Alternative geometry

In addition to the ESPs described earlier, there is class of devices that operate without an explicit capture electrode, Figure 8. Ions are generated by a high voltage on a thin wire or at the tip of a sharp needle. The ions charge dust particles, and the dust will eventually precipitate on all surfaces nearby. In ambient conditions, the charge will be carried away by humid air.
Figure 6. Sketch of a “Open air ESP” with a modular structure of pitch of 10 cm. Parallel plates are removed.

Figure 7. Comparison of adhesion versus aerodynamic drag, as a function of particle size. Adhesion is caused by the Van der Waals force (plotted here) and hydrostatic force (not included). The latter force increases with increasing humidity and will effectively move the adhesion curve upwards. Adapted from Ref [4].
This type of system has been applied in poultry farms, where dust and airborne pathogens are an issue, and it is reported to lower the particle concentration in the air by 50% [6]. These devices can be mounted on the ceiling, or at any location where there is sufficient circulation of air, and can optionally be backed by a ventilator. The lack of a capture electrode makes this type of device less suitable for an application in an unconfined space. It is expected that the fine dust particles, even when charged, will remain airborne long enough to travel from the highway into the urban area around it.

5. Meso-scale: aerodynamics

In this paragraph the results of the simulations and experiments are discussed. First of all, a short overview of the important aspects of the current flow configuration is given here. The important non-dimensional parameter that governs the flow dynamics is the Reynolds number:

\[ Re = \frac{UL}{\nu}, \]  

(13)

in which \( U \) is characteristic velocity scale, \( L \) a typical length scale and \( \nu \) is kinematic viscosity of the working fluid. This number is very important when performing experiments on a scaled model. Once the Reynolds number is kept constant (by either increasing velocity or decreasing viscosity) both flows are geometrically similar. In general in wind tunnel experiments or simulations it is not possible to obtain a Reynolds number that is in the same order of magnitude as the real life case. This is also the case in the current research. Based on previous research however, it is noted that it is not always necessary to match the Reynolds number exactly. Castro [7] could not find any significant Reynolds number dependence for

\[ Re_H = \frac{U\infty H}{\nu} \geq 5000, \]  

(14)

where \( H \) is the height of the sound barrier and \( U\infty \) is the freestream velocity.

A second important parameter that governs the general flow field is the ratio between the height of the sound barrier \( h \) and the width between the sound barriers \( w \). Figure 9 shows that when the ratio of \( W \) and \( H \) is about 1, the so called d-type roughness exists. Increasing the \( w/h \) ratio the so-called k-type roughness is present. In the d-type roughness case, almost no eddy shedding into the free-stream flow is present which is in contrast with the k-type roughness. This greatly influences the mechanism of dispersion of pollutants that have been generated in between the sound barriers. For the current case \( w/h = 5 \). Hence, the current case is of the k-type roughness.

5.1 Experiment

In order to investigate the flow field around sound barriers consisting of a impermeable wall with a semi-permeable top part we constructed a flow tunnel. This consists of a 1.5 m long, 4.5 cm wide and 10 cm high channel. The outflow is kept constant by siphoning over a fixed
Figure 9. Flow type depending on ratio between width of channel $W$ and height $H$. Mean streamlines are shown superimposed on instantaneous passive scalar contours. Figure adapted from Leonardi et al [9]

height drop. The level in the tank is kept at 8 cm height, and adjusted by varying the inflow. The sound barrier is modeled by a 2 cm high 1 wide obstruction spanning the width of the entire channel, and the ESP is modeled with a coarse messing grid. Ink was injected with a dropper at relevant positions, to model the diffusion of pollutant and observe the fraction passing through the ESP. The diffusion was recorded with a 30 frames per second camera. We varied the distance between the two barriers so the $w/h$ ratio was either 3, 4 or 5. This corresponds to a 5 meter barrier around a 15, 20 or 25 meter wide motorway. Three different ESP geometries were tested. Firstly no ESP was added, secondly a vertical ESP was added, either on only the downwind or only the upwind barrier, and finally a larger sloping ESP was added.

Plain barriers

The flow over the two plain barriers shows very clear features. The flow along the bottom of the gap moves up towards the upwind barrier, and along the top the flow is directed downstream. From the upwind barrier vortices are shed, moving downstream and mixing the polluted air from the highway with the clean upwind air. In the literature such a flow is called a “street canyon flow”.

The concentration flux over the downstream wall is largely dominated by the effect of the shear layer that has been shed from the upstream sound barrier. As this shear layer is approximately independent of the Reynolds number, also the concentration flux profile can be regarded as Reynolds independent. Hence, although we are at a much smaller Reynolds number still the experiment captures the most important flow features.

ESP on sound barrier

In subsequent flow experiments a messing grid was placed on top of the barriers. The wire width was 0.75 mm, wire spacing 2 mm. The porosity of the grid is larger than one expects from a well-designed ESP, but this system still can show what the effect is of a semi-permeable structure on top of an impermeable wall. Such a situation is very challenging to implement in
Figure 10. Effect of an ESP on the downwind barrier. A filament of ink caught in an eddy is seen as it is partly transmitted through the ESP and partly is forced down past it, creating an effectively higher street canyon.

a numerical simulation. Therefore, this configuration was tested in this relatively simple experiment.

Figure 10 shows the effect of an ESP on the downwind barrier. A filament of ink is seen in two frames, taken shortly after each other. This filament can be seen to travel over the ESP, and down along it, while there is not so much transmitted through. Effectively the added ESP can be seen to create the flow-field of a canyon with a larger height, namely that of the barrier with the ESP.

The open to closed area of the grid is significantly larger than that of an optimally designed ESP, but this experiment shows clearly how essential a low flow resistance is to the flowfield of the highway. The higher the resistance gets, the more the flow will shape to a canyon of height barrier + ESP, causing all pollutant to pass by the ESP.

Overhanging ESP

As a last experiment we tested a configuration where the ESPs overhang the highway. This will have several positive effects. Firstly the region where mixing between clean over-blowing air and polluted highway air takes place is shorter, secondly the sloping barrier helps to contain the pollutant to the highway as it escapes from the downwind ESP, and finally the larger area of the ESP also increases efficiency.
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Figure 11. The flow of pollutant with two sloped ESP’s. The majority of the pollutant travels through the downwind ESP

Figure 11 shows an image of the flow around this configuration. It is seen that a very large portion of the pollutant travels through the downwind grid. There is still much room to optimize the geometry of the ESP, possibly by adding flow-enhancing structures, but this experiment already shows that even with a grid with a much higher flow resistance than an ESP, the majority of pollutant can still be directed through it.

5.2 Simulations with DALES-urban

In order to get insight in the dispersion of fine dust generated on a highway numerical simulations are performed by using the DALES-urban code. DALES-urban solves the Large-Eddy equations for incompressible fluids. It is a modified version of DALES [10] that allows the addition of obstacles in the flow. It uses a finite-volume method with second-order accurate discretizations in space and a third-order Runge-Kutta method to integrate the equations in time. For the pollutant the advective term is modeled with a flux-limited scheme (first-order accurate in space in case of strong gradients) to enforce positivity. The simulations are used to answer the following questions:

- How is fine dust dispersed into the atmosphere when a highway is located in between two sound barriers?
- What is the best location to place an ESP?

Description of the test case

A two-way highway is assumed to be located in between two sound barriers of height $h$. The sound barriers have a typical distance of $5h$ in between each other. The domain has a height of $H = 10h$ and its length is $L = 20h$. The width is $W = 4h$. The domain contains a total of 608256 cells; 144 cells in the streamwise direction, 88 cells in the vertical and 48 cells in spanwise direction. Along the height of the sound barriers 24 cells of equal size are used. From $0.5h$ above the sound barriers up to the top of the domain the grid is stretched starting from the cell height of $0.042h$. In horizontal direction the grid is stretched with a minimum cell size of $0.04h$ adjacent to the sound barriers walls. The thickness of the sound barriers is one cell of $0.04h$. Temperature effects are neglected because the atmosphere is assumed to be neutrally stratified. In addition, it is assumed that the traffic does not induce large scale forcings on the
flow and that the turbulence due to the presence of the sound barriers is the dominant over the turbulence induced by traffic. For the flow field periodic boundary conditions are assumed in the horizontal directions. In this way the simulated boundary layer will approximate the ‘urban boundary layer’ in which surrounding obstacles around sound barriers are of the same height as the sound barriers. The fine dust is modeled as a passive tracer; the emitted pollutant is neutrally buoyant and is advected with the flow. There are no chemical reactions. For the pollutant periodic boundary conditions are applied in the direction parallel to the sound barriers, while for the streamwise direction in- and outflow conditions are used; zero pollutant is imposed at the inflow boundary. The bottom, top and sound barrier walls have no-slip boundary conditions. In addition, as a driving force the top boundary moves with a velocity $U_{\infty}$, similar to a Couette flow setting. The upper boundary layer is not fully resolved to reduce computational costs. The Reynolds number based on the sound barrier height and the mean velocity near the top boundary is 3300.

Two line sources of constant mass flux of fine dust are added to resemble the emission from traffic; the sources are along the spanwise direction. Source 1 is located at a distance of 0.77$h$ downstream of the first sound barrier. Source 2 is located at that same distance upstream of the second sound barrier. Both sources are located a height of 0.5$h$. The sources are distributed over the surrounding cells by a normal distribution with a standard deviation of 0.6$h$ in the horizontal and 0.14$h$ in the vertical direction.

![Figure 12. Mean velocity magnitude and streamlines.](image)

**Results**

In all simulations the flow is integrated in time until the turbulent flow field achieved a steady-state. Subsequently, the velocity components and the concentrations are averaged over a time period of $100T$, where $T$ is the time scale based on the sound barrier height and the free stream velocity.

Figure 12 shows the mean velocity magnitude contours together with the associated streamlines. Several recirculation areas are visible of which the one in between the sound barriers is the largest. Both experiments and simulations show the large recirculation area which might suggest that mounting an ESP close to the upwind sound barrier could be an effective measure for pollutant removal. To investigate this concept an additional simulation is
performed in which the pollutant is captured when it passes the volume close to the upwind sound barrier. The volume has a length of $0.42h$ and a height of $0.33h$. It is located adjacent to the upwind sound barrier at the inside of the canyon. Figure 13 shows the contours of concentration originating from Source 1. Figure 14 shows the same contours for the case in which the pollutant is captured. The presence of this pollutant sink does not influence the flow; the mean flow fields are the same. It is clearly visible that the concentration is lower due to the capture. Figure 15 shows the concentration contours generated by Source 2 for the baseline case and Figure 16 shows the same contours for the case when the pollutant is captured. Again, a decrease in concentration levels is visible. To quantify the effect of the pollutant capture the vertical profile of pollutant mass flux at the downstream barrier location is plotted in Figure 17 for Source 1 (left figure) and Source 2 (right figure). The difference of these profiles integrated over the height gives an estimate of the captured pollutant. For Source 1 this efficiency is 27% and for Source 2 this is 13%.

Assuming that all pollutant that passes the top of the downstream barrier will not pass a second time, the maximum efficiency of pollutant capture at the top of the downstream barrier can also be predicted. Just as for the case of capturing at the upstream sound barrier we assume that the capturing device does not alter the flow field and captures all pollutant passing its volume. At this location, the height of the device will be the parameter that determines how much pollutant will be captured. Table 1 shows the prediction of the percentage of emitted concentration that is captured for several device heights for the simulated case.

**Reynolds number dependence**

In order to investigate the dependence on the Reynolds number the case needs to be studied at higher Reynolds numbers. In addition, a grid sensitivity study needs to be performed to investigate if the resolution of the simulations is adequate. A first step has been made by increasing the Reynolds number by a factor four. The simulations are done on the same grid. Because increasing the Reynolds number results in smaller boundary layers near walls these boundary layers will be underresolved. Therefore a “wall function” has been used which
Figure 14. Pollutant capture close to upwind sound barrier; emission from source 1; orange circles represent source locations; Source 1 is the left circle.

<table>
<thead>
<tr>
<th>Device height</th>
<th>$\eta_{h1}$</th>
<th>$\eta_{h2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25h</td>
<td>11%</td>
<td>12%</td>
</tr>
<tr>
<td>0.5h</td>
<td>26%</td>
<td>28%</td>
</tr>
<tr>
<td>0.73h</td>
<td>41%</td>
<td>43%</td>
</tr>
<tr>
<td>1.00h</td>
<td>60%</td>
<td>62%</td>
</tr>
</tbody>
</table>

Table 1. Maximum efficiency of pollutant capture for ESP mounted on downstream sound barrier
assumes the boundary layer fits a logarithmic profile found empirically. These extra simulations show the same large scale structures as the previous simulations. However, the mass flux that is captured in the volume at the upstream barrier is about a factor two larger; the efficiency for source 1 is 47% and for source 2 this is 28%, while the efficiency of capturing pollutant at the downstream barrier is the same as for the lower Reynolds number case (see Table 1).

5.3 Conclusions

Numerical simulations show the same large-scale structures as where visible in the experiments. A strong shear layer emerges at the top of the sound barriers. In the time-avered results several recirculation areas are visible. The results show that the capture of fine dust at the top of the downstream sound barrier requires a rather high device. Capturing the pollutant when it is still present within the area in between the two sound barriers appears to be more effective according to the results from the simulation in which the pollutant is captured close to the top of the upstream sound barrier. To get a more detailed prediction of the maximum mass flux of captured pollutant at the two capturing locations additional simulations and/or experiments are required. Furthermore, the experiments suggest that placing an ESP under an angle on top of a sound barrier higher efficiencies can be reached. It is recommended that these results are also numerically verified in a high Reynolds number simulation.

6. Macro-scale: Operating conditions

In this section we elaborate on the operating conditions of an ESP that is placed along a highway. What are the implications of a functional ESP with respect to cleaning, safety, and power consumption? It is helpful to be aware of the types of fine dust that are encountered in the neighbourhood of urban highways. The fine dust that is produced by vehicle traffic is composed of carbon based material, mainly soot and rubber particles. Soot is produced from the incomplete combustion of petrol and diesel. Rubber particles originate from the friction between the car tires and the asphalt. In order to elaborate on the cleaning of these materials,
we make a rough estimation of the amount of fine dust that is captured by an ESP along a highway.

6.1 The amount of fine dust collected

For the sake of convenience, we assume that all the fine dust that is produced on the highway is captured by the ESP device. Furthermore, the following approximations are made: i) the fine dust production per meter highway is 10 g/day; ii) the density of the collected fine dust is 1 g/cm³; iii) per meter of highway, the open air ESP has a surface area of 1 m² on which it collects the fine dust. Given these approximations, the layer of fine dust per month increases with $3 \times 10^{-4}$ m, i.e. three tenth of a millimetre, per unit area. On yearly basis the layer of fine dust has increased approximately a few millimetres on the surface of an open air ESP.

6.2 Cleaning

The layer of fine dust is expected to adhere to the grounded framework of an ESP due to short-range Van der Waals forces. Because of the non-stop accumulation, the layer of fine dust eventually needs to be removed. Rainfall emerges as a convenient candidate to act as a natural cleaning source to wash away the fine dust of the ESP framework. In the Netherlands, a dry period (no rainfall) typically lasts for a few days up to two weeks. During these dry intervals, the layer of fine dust increases two tenth of a millimetre at most (see above paragraph).

However, considering that the most important types, soot and rubber particles, are the carbon based, we may assume that the fine dust is hydrophobic and not likely to dissolve in or be attracted to water. Consequently, we cannot exclude whether the fine dust will be completely, partly, or not at all washed away by rainfall. This can best be empirically determined by, for example, placing a soot-covered ESP prototype outdoors for several weeks. In the case the prototype is not cleaned by rainfall, we advise a twice-a-year cleaning maintenance for an ESP device that is placed along a highway. Since the layer of fine dust that accumulates in one month (few tenths of a millimetre) is two orders of magnitude smaller than the distance between the high-voltage wire and the grounded framework (centimetres), the chance of a
Figure 17. Vertical profile of pollutant mass flux at the downstream barrier location for Source 1 (left) and Source 2 (right)

short circuit in such time periods is limited. If the chance of short circuit due to the layer of fine dust needs to be further reduced, one can accomplish this by increasing the surface area of the ESP and/or increasing the number of cleaning maintenances per year. A coating could be applied to the ESP framework that reduces the adhesive forces of the fine dust, causing the fine dust to be more easily washed away by rainfall. Hence, repetitive cleaning services become redundant. Such a coating seems to be an interesting prospect. However, we did not further elaborate on this option.

6.3 Safety

If an ESP device is placed along a highway it may pose hazards, of which the most obvious is electrocution due to the high-voltage components. People driving on the highway may get out of their cars and come in close proximity of an ESP device. Therefore, we advise to place an ESP out of reach from humans, preferably 4 meters from the ground, or higher. Also, when an ESP is placed high from the ground, it will be less prone to car accidents compared to when it is close to the ground. Birds are a serious problem. Since their size is of the same length scale as the distance between the high-voltage wire and the grounded framework (centimetres), they run the risk of getting electrocuted. Furthermore, droppings left by birds will add to the filthiness on the ESP device and may even cause a short circuit. We expect that simple bird spikes, see Figure 18, will be effective in keeping birds from entering or sitting on top of an ESP device. The structure of bird spikes can be made as “open” as desired so that it has little influence on the flow resistance of an ESP device. Typical insects (ants, flies, wasps, etc.) are relatively small and will therefore not be able to cause a short circuit. However, we cannot predict if a high electric field is a health hazard for insects and whether there is a risk of dead insects accumulating in an ESP device. Again, this is best empirically determined by placing an operational ESP prototype outdoors for several weeks. Finally, during rainfall the ESP high voltage should be turned off so that no short circuit can occur. We assume that during rainfall any dust particles will be removed from the air due to contact with rain droplets and consequently will be deposited on the ground.

6.4 Power consumption

The estimation of the power consumption of an ESP along a highway is based on the ESP prototype that was at our disposal during the workshop. The prototype (∼0.5 m in length) consumes 5.4 W. Assuming that an ESP per metre of highway is about four times larger, we
estimate its power consumption is 20 W/m. This amount of power should be in the same order of magnitude as the power consumption per metre of the 242 W LED lightposts that were recently placed along the A44 highway [12].

7. Conclusions and outlook

Fine dust reduction near highways using an Electrostatic Precipitator is feasible. The open air ESP proposed here is likely to be a much more efficient way to the capture fine dust particles for this application than a conventional ESP. From an aerodynamic perspective, there is much to be gained by choosing the optimal position for the device, and the circulation within a street canyon can be used to capture dust near the upwind noise barrier.

To proceed, we propose that initial tests need to be performed to prove the working principle of the open air ESP. A combination of electrical field calculations and lab tests should be used to optimize the grid geometry. Further aerodynamic simulations have to be performed on more realistic noise barrier shapes to get a definitive answer where to install an ESP device. The next step is a small scale field test, not necessarily near a highway, to test the prolonged operation of the open air ESP in Dutch weather conditions, followed by a large scale test where the effectiveness of an ESP along a section of a highway is measured.

If these field tests prove to be successful, the installation of an ESP along highways in densely populated urban areas is likely to be a very cost effective measure that dramatically improves the air quality.

8. References


[12] Website: http://www.rijkswaterstaat.nl/wegen/plannen_en_projecten/a_wegen/A44/ledverlichting_a44/
Analyzing liquid penetration in paper by electrical impedance spectroscopy (EIS)

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1. Abstract

In this paper we aim to understand how Electrical Impedance Spectroscopy (EIS) measurements, combined with other techniques, can be used to characterize the morphology of penetration of water in paper. We interpreted EIS data of water absorption in paper by constructing an equivalent circuit model, which show general agreement with the timescales from the measurements, however the data can not easily be interpreted. Furthermore we suggested improvements to the current experimental setup, such as permeable electrodes and a confined environment for the sample. Finally we proposed a few complementary analysis techniques, such as optical coherence spectroscopy and white light microscopic imaging. None of the alternatives gives us the desired ease in measuring and analysis, but could be used complementary.

2. Company profile

Océ, a Canon Group company [2], is an international leader in digital printing and document management for professionals. Océ printers (see figure 1) are commonly used for wide format printing, high-speed production printing and document-related business services. Océ has a long history in developing, manufacturing and selling printing technology. Nowadays, Océ employs 4 000 specialists at innovation and technology centers in Europe, North America and Asia. The largest R&D site is in Venlo with about 800 employees, mostly highly educated engineers in physics, mechanics, electronics, chemistry, information technology and industrial design.
3. Problem description

3.1 Introduction

Océ’s inkjet printer systems are water based. They are able to operate on a large variety of media, including paper, textiles and plastics. The physico-chemical processes involved in printing include water evaporation from complex fluids, the interaction of fluids and soft solids with structured substrates, the control of liquid-solid transitions like gelling and crystallization in confined geometries, etc. Paper is a random, closely packed arrangement of cellulose fibers; the process of liquid penetration into porous paper in time is complicated and develops over multiple length and time scales. The liquid flows through the pores between the fibers and is absorbed into the fibers. Liquid sorption causes deformation and swelling of the fibers, which is macroscopically observed as curling of the sheet. The fibers also have varying wettabilities and, during the forming of paper sheets, they arrange preferentially along the machine direction. When fluid flows through the porous medium certain parts of the flow will advance faster than the average, which is known as viscous fingering. The water-air interface within the paper is ‘pinned’ by the local roughness and varying surface composition, which gives rise to discontinuous, avalanche-like imbibition dynamics.

At the moment we are investigating a common method, that is used for analysis of electrochemical and transport processes, known as Electrical Impedance Spectroscopy (EIS). Océ is searching for a quick and simple analysis of imbibition in paper and is looking into the possibilities EIS offers here.

3.2 Challenge

The challenge of Océ for the workshop is based the following questions:

1. How can one measure real time liquid penetration in paper?
2. What information about liquid penetration can be extracted from EIS?
3. Are there alternatives to EIS?

Specifically, the present work focused on:

1. The EIS measurement method should satisfy the following requirements:
   - Capability to quantify the depth of penetration of water in printing-grade paper.
   - Measurements with a time resolution of \( \leq 0.1 \text{s} \).
   - Off-the-shelf technology, easily adjustable for specific experiments.
2. The evaluation of EIS should incorporate the following questions

- What information does EIS spectra give on the morphology of the liquid front?
- What adjustments are necessary to the existing EIS setup?
- How unique can EIS spectra be interpreted in terms of fluid distributions?

3. What alternative imaging/tomography techniques might be implemented, while satisfying the above-mentioned requirements.

3.3 Theory of Electrical Impedance Spectroscopy (EIS)

Measuring the magnetic and electric field components of a field that propagates through a sample can allow to deduce the distribution of its material properties. Maxwell’s equations are the most general description of the electromagnetic field in an inhomogeneous medium [3]. Here we specialize the treatment to linear, time-invariant (the changes in the medium are much slower than the field frequency), non-magnetic media:

\[
\epsilon \frac{\partial \mathbf{E}}{\partial t} - \nabla \times \mathbf{H} + \sigma \mathbf{E} = -\mathbf{J}^e \tag{1}
\]

\[
\mu \frac{\partial \mathbf{H}}{\partial t} + \nabla \times \mathbf{E} = -\mathbf{J}^m \tag{2}
\]

Applying the Fourier transform

\[
\tilde{\mathbf{E}}(x, \omega) = \int_{-\infty}^{\infty} \mathbf{E}(x, t)e^{-j\omega t} \, dt \tag{3}
\]

to both the electric and magnetic fields, one obtains the frequency-domain system

\[
-\nabla \times \tilde{\mathbf{H}} + \mathbf{Y}\tilde{\mathbf{E}} = -\tilde{\mathbf{J}}^e \tag{4}
\]

\[
j\omega \mu \tilde{\mathbf{H}} + \nabla \times \tilde{\mathbf{E}} = -\tilde{\mathbf{J}}^m \tag{5}
\]

where \(\mathbf{Y} = \sigma - j\omega\epsilon\) is the electric admittance of a (locally homogeneous) medium with permeability \(\epsilon\) and conductivity \(\sigma\). The reciprocal of the admittance, \(Z(\omega) = 1/\mathbf{Y}(\omega) = R(\omega) + jX(\omega)\) defines the impedance \(\mathbf{Z}(\omega)\), resistivity \(R(\omega)\) and the reactance \(X(\omega)\). The concept of impedance, models the opposition that a circuit presents to a current when a voltage is applied across the testing electrodes (the ‘port’). The phase of the impedance shows the shift by which the current lags behind the voltage [3, 4]. The reactance can either be capacitive \(X_C = 1/(\omega C)\) (electrostatic storage of charge induced by voltages between capacitors) or inductive \(X_L = \omega L\) (caused by current loops). Electric impedance spectroscopy models describe the medium contained between the electrodes as an equivalent electric circuit composed of lumped resistive, capacitive and possibly inductive components.

The first model is sketched in figure 2. Two layers are distinguished: dry and wet paper. The imbibition front is considered to be advancing uniformly. In reality, the liquid penetration front is rough over different length scales (see figure 2, right). This raises the question to which extent actual EIS data can be modeled with equivalent electric circuits. At low frequencies electrode polarization can influence the impedance measurements. It will be caused by the saturation of the sample, because at the boundary between the sample and the electrodes, an electric charge double layer is formed. A variety of electrode polarization techniques exist [3]. An electrode correction can be described for a two electrode system [3], where \(Z_{se} = Z_s + Z_{el}\). Here \(Z_{se}\) represents the measured signal, from which the electrode polarization \(Z_{el}\) needs to be removed to obtain \(Z_s\), the impedance without electrode polarization. [3].
3.4 Paper as a porous medium

Paper is a closely-packed network of chemically-treated fibers, obtained from a wet pulp of cellulose and a number of compounds that improve its mechanical properties and define its color. Quantifying the shape of the imbibition front within this porous structure is challenging, either through imaging techniques or direct numerical integration of the free energy equation. Another approach is to model the paper at the macroscopic scale, in which the porous medium is considered as an effective medium using a Lagrangian approach. Within poromechanics, characteristic values for the medium are used to investigate the general behavior of the porous medium. Important values that can be measured with standard tests are porosity $\phi$ (using a pycnometer) and the absolute permeability $k$ (which describes the interconnection of pores [7, 5]).

The flow behavior can be described by Darcy’s law for multiphase flow conditions

$$u_\alpha = \frac{-K_\alpha}{\eta_\alpha} \nabla p_\alpha,$$  \hspace{1cm} (6)

where $u_\alpha$ is the fluid flux, $\eta_\alpha$ the viscosity, $K_\alpha$ the effective permeability ($K_\alpha = k \cdot k_{\text{relative}}$), $\alpha = [w, a]$ stands for water and air respectively. When mass conservation is applied

$$\frac{d\phi}{dt} \rho_\alpha S_\alpha + \nabla \cdot (\rho_\alpha u_\alpha) = 0,$$  \hspace{1cm} (7)

where $\rho_\alpha$ is the density of the considered fluid phase, $S_{w} + S_{a} = 1$ are the water and air saturation respectively. Mass conversation together with Darcy’s law gives, after some algebraic operations [6]

$$\phi \frac{dS_\alpha}{dt} - V \cdot (D(S) \nabla S) = 0$$  \hspace{1cm} (8)

with

$$D(S) = \frac{K_\alpha}{\eta_\alpha} \frac{dp}{dS}$$  \hspace{1cm} (9)

which describes that flow through porous media will become diffusive.

The Lucas-Washburn equation describes capillary wetting of porous materials. Letting $\eta$ be the viscosity and $\gamma$ the surface tension between fluids, the total infiltrated volume evolves in time following a power law:

$$V = \left( \frac{\gamma t^1}{\eta} \right)^{1/2}$$  \hspace{1cm} (10)

which has been verified experimentally for a wide range of fluid and porous media combinations.
4. EIS setup

The EIS experiments performed at Océ (by N. Tomozeiu) are executed with the setup as shown in figure 3. Paper is fixed between the electrodes, the impedance measurement started and then water is let to infiltrate through the inlet at the bottom. As soon as the water level in the reservoir, below the sample, reaches the paper, changes in the impedance are recorded. This provides the reference time of the impedance measurement. This measurement should then be interpreted in terms of an advancing front of water and its fingerlike behaviour.

![Experimental setup](image1)

![Sketch of principle](image2)

Figure 3. The original measurement setup, as used by Océ in the experiments. The paper is held between the electrodes, then the water is brought into contact with the bottom surface of the sheet [1].

Unfortunately the obtained results raise several questions. The miniscus of the water in the reservoir can not be considered to be a straight line. Vibrations, imperfections in the inlet velocity and the wettability of the basin lead to a preferential initial wetting of the paper. Due to the ‘undisturbed’ paper approach (clamping the paper between two electrodes) the fluid will probably, before full saturation, already start to flow sideways, having some affect on the measured result. Furthermore fluid can start to leak outside the electrode system. The paper extends the measurement area and the area where it is clamped. This causes an unequal stress effect at the bottom fibres on the corners, before the paper is fully saturated. When the paper is not fully saturated, it will tend to curve (due to sorption of the liquid and expansion of the material). This will cause additional stresses at the outer edges of the clamped electrodes on the paper. Also the pressure within the setup will rise once it approaches full saturation, due to the no-flow condition at the top electrode. Because the top and bottom electrode are not both flat and similar, the electrical field will probably not be uniform, as assumed in standard theory for identical flat electrodes in capacitor systems.

To determine the extend of asymmetry in the electric field, due to asymmetry in the setup, finite element simulations of this setup were performed using the commercially available Comsol software. Sections of the results are shown in figure 4. As described above, the flat electrode is on top and the ‘u’ shape electrode is at the bottom. For computational efficiency, only the right part of the axisymmetric setup is considered. For figure 4, left, the water conductivity was chosen to be $\sigma = 5.5 \times 10^{-6} \text{ S m}^{-1}$ and the relative water permittivity of $\varepsilon = 80$, which is comparable to ultra pure water [8], to reproduce the beginning of the experiment. In this case the electric field is not uniform. In the area on the right, the fluid will only penetrate the paper from the side. Additionally the measured impedance in this area will most likely be very different. This
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Figure 4. Electric field magnitude within the sample, radially symmetric finite element simulation at $\omega = 1 \times 10^4$ Hz (Océ setup) (figure 3). The water’s conductance is Left: $5.5 \times 10^{-6}$ S m$^{-1}$, comparable to ultra pure water and Right: $5.5 \times 10^{-4}$ S m$^{-1}$, comparable to distilled water.

makes the time evaluated impedance hard to interpretate. In a second computation, the water impedance was increased to $\sigma = 5.5 \times 10^{-4}$ S m$^{-1}$ (using the same dielectric permittivity), a value comparable to that of distilled water [8]. (see figure 4, right). The divergence in the electric field is almost unrecognizable, however when frequencies go up from DC to higher AC values, the electric permittivity will differ between the copper and fluid, causing different electric fields again (especially at higher frequencies permittivity changes will become significant). Also the problem with the uneven fluid penetration remains.

To improve the sample holder, the holder in figure 5 was designed. Here the electrodes do not consist of corrosive copper, but of sintered monel or a gold coated porous medium.

Without the need to include a reservoir, the electrodes can simply be parallel plates. With the appropriate electrode pore size, the paper will be approached by a transversally uniform front of water, thus improving the reliability of the measurements.

An alternative aproach would be to use the Bristow method [12], as shown in figure 6. The paper is brought into contact with liquid and dragged sideways with a constant velocity. In this version of the setup, the distance between the nozzle and the electrodes determines the advancement of the imbibition front before the EIS measurement can start. The setup can be equipped with a broadband source and detector, to characterize a range of frequencies at a time.
**Figure 5.** Proposed alternative setup. Here an enclosed sample is set up in between porous, symmetric electrodes (based on [3, 9, 10, 11]).

**Figure 6.** An alternative sampling method, using the Bristow setup, to allow measurement of a quasi-static droplet.
5. EIS interpretation

To interpret the EIS data we simulate it with a simple electrical circuit representing the dry and wet part of paper, see figure 7.

![Electrical Circuit Diagram](image)

**Figure 7.** Paper wetting representation by electrical circuit.

The dry paper is represented by the capacitor $C_{\text{dry}}$, in series with the wet paper as represented by a parallel RC-circuit (resistor $R_{\text{wet}}$ and capacitor $C_{\text{wet}}$). The thickness of the wet part is defined by $0 \leq \delta \leq 1$, which may be interpreted as a normalized depth of the average water front penetration.

\[
C_{\text{dry}} = \frac{\varepsilon_{\text{dry}} \varepsilon_0 A}{d \cdot (1 - \delta)} \quad \text{(11)}
\]

\[
C_{\text{wet}} = \frac{\varepsilon_{\text{wet}} \varepsilon_0 A}{d \cdot \delta} \quad \text{(12)}
\]

\[
R_{\text{wet}} = \frac{\rho_{\text{wet}} d \cdot \delta}{A} \quad \text{(13)}
\]

where $A$ is the electrode area (disk with a radius of 1 cm) and $d$ is the paper thickness. Depending on the paper type $d$ varies from 110 to 270 $\mu$m. The total impedance of the circuit can be presented as a sum of the impedances of the dry and wet part:

\[
Z_{\text{total}} = Z_{\text{dry}} + Z_{\text{wet}} \quad \text{(14)}
\]

\[
Z_{\text{dry}} = \frac{1}{j \omega C_{\text{dry}}} \quad \text{(15)}
\]

\[
Z_{\text{wet}} = \frac{1}{1/R_{\text{wet}} + j \omega C_{\text{wet}}} = \frac{R_{\text{wet}} - j R_{\text{wet}}^2 \omega C_{\text{wet}}}{1 + R_{\text{wet}}^2 \omega^2 C_{\text{wet}}^2} \quad \text{(16)}
\]

the measurements have been done with the frequency $\omega = 10$ kHz. To compare our results with the experimental data, we present the final value of calculated impedance $Z_{\text{total}}$ through its modulus and argument and using the total resistance $R_{\text{total}}$ and capacitance $C_{\text{total}}$:

\[
\|Z\| = \sqrt{\Re(Z_{\text{total}})^2 + \Im(Z_{\text{total}})^2} \quad \text{(17)}
\]

\[
\angle Z = \arctan \frac{\Im(Z_{\text{total}})}{\Re(Z_{\text{total}})} \quad \text{(18)}
\]
\[ R_{\text{total}} = \Re(Z_{\text{total}}) \]  
\[ C_{\text{total}} = -\frac{1}{\Im(Z_{\text{total}})\omega} \]  

The results of our simulations are shown in figure 8.

\begin{figure}[h]
\centering
\begin{subfigure}{0.45\textwidth}
\centering
\includegraphics[width=\textwidth]{figure8a}
\end{subfigure}
\begin{subfigure}{0.45\textwidth}
\centering
\includegraphics[width=\textwidth]{figure8b}
\end{subfigure}
\begin{subfigure}{0.45\textwidth}
\centering
\includegraphics[width=\textwidth]{figure8c}
\end{subfigure}
\begin{subfigure}{0.45\textwidth}
\centering
\includegraphics[width=\textwidth]{figure8d}
\end{subfigure}
\caption{Top: experimental results of measuring the impedance of the paper (110\,\mu m thickness) while it is wetted by water. Bottom: the simulation of the described experiments. Left figures shows the behavior of the impedance modulus $|Z|$ during the experiment, middle figures - impedance argument $\angle Z$, right figures - resistance and capacitance.}
\end{figure}

As seen from the experimental figures most of the changes in the impedance behavior happens during the initial stage of the experiment in the first 5 seconds. To achieve good agreement with experimental data two things must be fitted in our simulation. First, to simulate fast processes in the initial experimental stage we assume the $\delta$ changes from 0 to 0.9 during the first 5 seconds of the simulation and for the remaining duration there is only a slow change from 0.9 to 1. The time step where the $\delta$ rate changes from fast to slow is our fitting parameter. Secondly, for the experiments, ultra pure water is used, and during the water penetration into the medium the liquid can accumulate salt from the paper. We have to compensate for the changes in the capacitance $C_{\text{wet}}$ and resistance $R_{\text{wet}}$ due to the changes in the water. From the experiment the approximate change rate of $C_{\text{wet}}$ and $R_{\text{wet}}$ can be estimated, but the exact time dependence of the $C_{\text{wet}}$ and $R_{\text{wet}}$ is another set of our fitting parameters. For the simulation presented in figure 8 the best fit has been achieved by exponentially increasing the capacity $C_{\text{wet}}$ by 1.8 orders of magnitude and exponentially decreasing the resistance $R_{\text{wet}}$ by 4.5 orders of magnitude during the initial stage of the experiment. By using the parameters described above we can achieve reasonable well agreement with experimental data (see figure 8).
However the physical interpretation of the described fitting parameters suggests that we do not have a smooth water penetration front. First, to achieve good fitting we should introduce ‘fast’ and ‘slow’ rates of $\delta$ changes. Very fast changes of $\delta$, during the first seconds of experiments, may suggest a non-linear process occurring during the initial stages of wetting. To eliminate uncertainty in $\delta$ changes, which is essentially the average water front behavior, an independent measurement of water transmission into paper is required. Secondly, the increase of water conductivity due to the increase of salt concentration may not fully explain the large drop of the total resistance during the initial stage of the experiment. However such behavior may be explained by the fact that the water front is not actually smooth, but dominated by the fingering process. When individual fingers reach the top electrode, they create a conductance (parallel) band, thus increasing the overall conductivity. Direct imaging of wetted paper surface suggests that individual fingers may reach the surface much earlier than the average water front. Such a rapid fingering process explains the large drop in resistance during the initial stage of the experiment. This assumption is also supported by the behavior of impedance argument (see middle part in figure 8). $\angle Z$ has a peak with values reaching towards 0 during the initial stages of the experiment, meaning that over a short period of time the conductivity dominates over the total paper thickness, suggesting the finger penetration from the bottom to top electrode. Later relaxation of $\angle Z$ to intermediate values suggest that the average water front eventually ‘catches up’ with individual fingers.

To accurately determine the degree of front roughening, caused by imbibition, an independent measurement of the average water level is required. If the measured average water front moves with the same speed indicated by sharp changes in the impedance then we are dealing with extremely fast water penetration with a relatively smooth front. However if the average water front moves slower than indicated by impedance changes then we may assume that water front is dominated by ‘fingers’, which does not greatly change the water consumption levels from reservoir, but create paths with high conductance in the paper and thus changing the impedance. Impedance measurements at low frequencies are sensitive to conductivity effects, mainly viscous fingering, while at high frequencies permittivity effects dominate (the average water front). So by scanning over a broad frequency range, it is possible to obtain more information about viscous fingering.
5.1 Improving the EIS in interpretation through multielectrode setup

To improve the spacial resolution of water penetration in the original experimental setup, shown in figure 3, we propose a multielectrode setup, as used by others [24, 25]. Figure 9(a) shows in a diagram the new experimiental configuration, where the upper electrode is now divided into 5 different electrodes. This improves the spacial resolution, over the whole sample, but decreases the time resolution.

We assume that, like in figure 7, we can model our system with an equivalent electric circuit, as shown in figure 10.

As seen before, the capacitance and resistance change as a function of water uptake and waterfront. This correlation remains, when increasing the number of electrodes.

The contribution of the capacitance and resistance is well known in usual impedance measurements, as well as in a multielectrode setup. The proximity of the electrodes could create anomalies or interferces in the electric field. In order to prevent this, the electrodes should have a lateral distance of about 1.5× the electodes size [13]. We propose the use of square electodes of 5 mm × 5 mm. The lateral spacing of the output electrodes increases the spatial discrimination and should be chosen to minimize capacitive coupling.

To avoid interference of the electrodes, we propose to use time multiplexing. In figure 9, square pulses represent the data acquisition time of each channel. With an acquisition time $dt$, a datapoint can be measured every $5dt$, where $dt$ is dependent on frequency and number of averages, as well as possible necessary relaxation times. Using commercial ADC boards (e.g. by National Instruments), this can be done in high precision via a Matlab or Labview interface.

While, in this way, time resolution is decreased, this setup allows measurement on multiple smaller locations during one experiment.

Figure 9. Multi-electrode setup and channel multiplexing scheme

Figure 10. Circuit equivalent in the case of multielectrodes setup
6. Alternative measurement techniques

Electric Impedance Spectroscopy usually involves representing the sample as an equivalent circuit. In the case under consideration, the sample is composed of a sheet of paper in which liquid infiltrates by capillary suction. The interface between fluids (ambient atmosphere and the invading liquid), within the bulk of the disordered host medium, is a rough, correlated process.

Direct, real-time imaging of a microscopic diffusive phenomenon that takes place in the bulk of a random medium is complicated by many factors, and the following sections illustrate the tradeoffs required by various existing techniques. Depending on the ratio of the probing wavelength $\lambda$ and the characteristic scattering dimensions $a$, one can generally distinguish between the ray-optics limit ($\lambda/a \ll 1$) and the effective medium limit ($\lambda/a \gg 1$), in which the discontinuities of the medium are not ‘sensed’ by the incident field.

The ideal method for imaging ink penetration in paper has spatial resolution, both in the axial and transversal directions, and is also time resolved. The requirements for this project are a spatial resolution on the order of a $\mu$m, and a time resolution $\leq 0.1$ s. In our study, we will restrict the discussion to non-destructive analysis techniques, i.e. those that do not alter the sample before or during the measurement.

In the literature, one can find a number of experiments in which paper has been measured. An overview of these studies is given in [14]. Techniques that are suitable to measure the bulk of paper are listed in table 1.

Table 1. Techniques for imaging the bulk of paper. Adapted from [14].

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbrev.</th>
<th>Resolution ($\mu$m)</th>
<th>2D / 3D</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray micro-tomography</td>
<td>X-\mu CT</td>
<td>0.7–1.0</td>
<td>3D analysis</td>
<td>Low contrast between different components. Poor availability of equipment. Same resolution in the x, y and z direction</td>
</tr>
<tr>
<td>Confocal laser scanning</td>
<td>CSLM</td>
<td>0.2–0.7</td>
<td>3D reconstruction</td>
<td>Low contrast between paper components. Decreasing intensity and resolution in the z-direction.</td>
</tr>
<tr>
<td>microscopy</td>
<td></td>
<td></td>
<td></td>
<td>3D reconstruction possible, when using microtome slices.</td>
</tr>
<tr>
<td>Light microscopy</td>
<td>LM</td>
<td>0.2</td>
<td>2D</td>
<td></td>
</tr>
<tr>
<td>Focused-ion-beam scanning</td>
<td>FIB</td>
<td>0.01</td>
<td>3D reconstruction</td>
<td></td>
</tr>
<tr>
<td>electron microscopy</td>
<td>SEM</td>
<td>0.0001–0.02</td>
<td>2D</td>
<td></td>
</tr>
<tr>
<td>Transmission electron</td>
<td>TEM</td>
<td>0.0002</td>
<td>2D</td>
<td>2D representation of a tiltable 3D sample</td>
</tr>
<tr>
<td>microscopy</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

An example of an ink penetration experiment with focused-ion-beam imaging is given in figure 11. In this example one can clearly see the difference between the coating and the fiber layer of the sample. It is shown that a CaCO$_3$ coating gives a different penetration pattern than clay coating.
Figure 11. Penetration of ink in paper, 3D reconstruction based on Focussed Ion Beam imaging. Left: CaCO$_3$ coating, Right: Clay coating. Image from [15].

6.1 Confocal microscopy

As one alternative we propose time resolved confocal microscopy. The steady state situation of a paper with fluorescent ink has been measured by Li and He [16], see figure 12. In their data the difference of ink patterns can be seen between kaolin coating, CaCO$_3$ coating and uncoated paper. The cellulose fibers absorb part of the laser light. To increase the z-range of the measurement Li and He use fluorescent ink.

Figure 12. Confocal microscopy image of fluorescent ink in (a) kaolin coated paper, (b) CaCO$_3$ coated paper and (c) uncoated paper. Images from [16].

In confocal imaging, one usually measures the x-y plane at various depths z. We propose to perform the measurement only in the x-z direction to gain a higher time resolution. If an area of 100 $\mu$m $\times$ 100 $\mu$m is measured, we estimate a time resolution of 1 s.

Another challenge of this method is how to apply the ink droplet. The objective is usually very close to the sample leaving very little space to introduce the droplet. Once the droplet is there it will absorb a large portion of the applied light. Probably only the paper below the edge of the droplet can be imaged. Alternative to having both time and spatial resolution in one method, one could separate the investigation into a time resolved and a spatially resolved measurement. In this case the spatially resolved measurements will give the shape of an ink-drop that has penetrated paper, while the time resolved measurement gives the speed on which this penetration takes place.
6.2 Gamma ray transmission

The principle of this method is to derive the extent of water imbibition from the attenuation of an X-ray beam that crosses the paper sheet during the wetting process. This technique relies on wet fibers having a measurably higher specific extinction coefficient than dry paper. We propose a ‘cup’ with a diameter of 2 cm, and depth of 200 μm as a sample holder. This cup has an inlet and an outlet for the introduction and removal of water. All parts but the bottom surface are made of Plexiglas, and the bottom surface is a 100 μm thick glass plate. A sketch of the cup can be seen in figure 13.

Paper is meant to be put on top of the cup, and a ring can be mounted on top of it. Both the cup and the ring have a thread on their side, so as to be able to firmly tighten paper between them, while still being able to adjust the height.

**Figure 13.** Gamma ray transmission setup. Left: Sample holder, Right: Schematic setup.

Fe$^{55}$ is a very well-known low-energy radioactive source. It emits at the energy of 5.9 keV, which corresponds to a wavelength of about 20.1 nm (soft X-rays), with a half-life time equal to 2.737 years. A scintillation probe allows to measure the beam intensity passing through the sample. This can be a Thermo Scientific 9000 model, type 44B, which is ideal for measurements with Fe$^{55}$. The active surface of the probe is circular with a diameter of 2 cm. Regarding the measurement protocol, the cup is filled with water up to its rim (200 μm), with the use of a high precision syringe pump (Harvard Apparatus Elite 11 Plus). Then, a measurement of the total attenuation of the radiation beam is taken, with all the components present, except paper. This gives the reference intensity ($I_0$) for all subsequent measurements. The beam intensity within a linearly attenuating medium is expressed by the Beer-Lambert law:

\[ I = I_0 e^{-\alpha x} \]  

where $I_0$ is the initial beam intensity, $I$ is the intensity measured after the beam has travelled for $x$ length in the attenuating medium, $\alpha$ is the extinction coefficient of the medium.

Then, paper should be put on top of the cup and mounted with the ring, at which point the measurement is started. There are two options for the measurements. The first one is the following: with the setup shown in figure 13, the attenuation is measured for the whole area of the paper. The acquisition time is relatively fast, as described in the scintillation probe manual, and it is around 50 to 80 ms. As water will start to penetrate into paper, its average penetration depth will start to grow. This will create extra attenuation to the already existing one, which will be measured by the probe. Given the acquisition time of the probe, there will be enough time for a number of attenuation measurements until paper gets fully saturated with water, which allows a time-resolved acquisition. With these measurements we can plot attenuation versus penetration depth, and from this graph, we will be able to correlate the absorbed amount of liquid with time, as shown in figure 14.

At any given time, with the measurement of the attenuation of the beam, we will be able to have an estimate on the volume of water that has penetrated into paper. As a second option,
instead of taking advantage of the whole cross section of the beam source, one can use a pinhole to increase the lateral resolution. Accordingly, the scintillation probe should be replaced with one with a smaller cross section. We repeat the measurements in the same way, and then we get information on the local uptake of water, within the area of interest. However, given the smaller cross-sectional area, the acquisition time will increase. This can be tackled with the use of a more active source (higher count-rate). While the full beam crossection is a comparison to the measured overall water uptake, the pinhole allows to measure local variations in full saturation. With a different source it might be possible to improve the time resolution for the pinhole.

6.3 Optical Coherence Tomography

The technique commonly referred to as OCT yields depth-resolved images from low-coherence interferometry. A low-temporal-coherence light source is connected to one arm of a $2 \times 2$ fiber directional coupler (FC). The two opposite ports feed the probe module and a reference mirror. The backreflection from the two ports is recombined at the FC and the interference signal is measured by a photodetector. The reference mirror is scanned in the axial direction to yield depth-resolved scans, and the probe module can include galvanometric mirrors to achieve lateral scans.

The lateral resolution is limited by the focal spotsize, whereas the axial resolution is ultimately given by the (short) coherence length of the source: the intensity envelope FWHM of the interference signal is inversely proportional to the spectral width of the source, which can be improved with broader-band light such as femtosecond pulsed lasers, superluminescent diodes etc. This technique has been initially employed in biomedical imaging, e.g. for the imaging of the back of the eye or dermal tissue but is increasingly applied to materials testing [19] and to characterize buried defects in turbid media [17, 18]. This technique has gone through very active development and enhancements in resolution and speed have been discussed by many [20], and was also previously used on paper [21].

6.4 Speckle correlometry

When illuminated with highly coherent light (e.g. CW laser beams), media which exhibit randomness or inhomogeneity on a lengthscale comparable to the wavelength diffract a seemingly random pattern of beams, called speckle. The far-field speckle pattern however can be

![Figure 14. Gamma-ray beam intensity vs penetration depth.](image)

- 39 -
used to retrieve information about the scattering object surface statistics, and perhaps some of its internal composition as well. Due to its interferometric nature, speckle is extremely sensitive to the smallest changes in diffracting object, and as such is a valuable tool for assessing relative changes of a sample.

Much of the recent application of speckle correlometry is within biomedical imaging, e.g. of blood flow in tissues. Of direct interest to the present project, [22] used the dynamic speckle pattern (which changes in time due to minute changes of the illuminated object) to analyze imbibition in paper. Other authors have used the far field speckle patterns at multiple wavelengths to reconstruct the three-dimensional surface of a scattering object, [23].

6.5 White-light microscopic imaging

To examine the processes and their timescales, that influence the EIS measurement, we set up a simple light microscope measurement of paper floating on a fluid. Here we examine the area of full penetration over time, that has a large effect on the resistance in the EIS measurement. A first set of imbibition experiments was performed on three types of paper: regular photocopy A4 sheets, and samples of 80 gr and 120 gr Red Label paper.

The infiltrating fluid considered here was a mixture of cranberry juice and water, in 50/50 proportion. The cranberry juice was chosen for its bright red color, but it contains sugary and viscous fruit syrup, preservatives etc., which alter its fluiddynamic properties, especially within microscopic rough channel networks. Scissors cut paper samples were set to float on the mixture and imaged from above with a visible light microscope, at around 420x magnification. Figure 15 shows four snapshots of the imbibition process. The video framerate is 15 fps. The dataset is taken from the red video channel and averaged over a two-frame time window to remove a flickering artifact. From what we can observe, the imbibition dynamics of diluted cranberry juice (and, we suspect, of water-based inks) in paper are highly discontinuous, and the observable
fluid opacity roughens in a possibly self-similar fashion (statistics of the interface being invariant under scale changes). However this cannot be a mathematical fractal due to the finite smallest length-scale of this process, the minimum pore size. This type of measurement, however, is just a scattering-limited projection of the internal distribution of fluid. The initial part of the dataset acquired by this technique (direct imaging) is biased by the ink being barely visible from the top face of the sheet (or, alternatively, the fibers being highly scattering in the visible range).

![Image standard deviation σ(t) (thinner line), and its least-squares power-law fit.](image)

**Figure 16.** Image standard deviation $\sigma(t)$ (thinner line), and its least-squares power-law fit.

One of the aims of the present work is to characterize the morphology of the imbibition front of water in paper. In the case of visible-light microscopic imaging, the backreflected light intensity that is obtained from top-face imaging is clearly limited in depth by fibre scattering. We consider the evolution in time of the spatial statistics of this signal as a proximate value for the imbibition front roughening in the depth direction, with the caveats discussed above. In figure 16 we plot the image standard deviation versus time, and observe a different exponent than the one predicted by the Lucas-Washburn equation (0.64 instead of 0.5). This discrepancy can have a number of explanations: the data is less reliable at the beginning of the experiment, as discussed above, and due to the absence of an appropriate sample stage, it was not possible to record the exact starting time of the imbibition process. The aspect ratio and roughness characteristics of the paper pores also influence the porous wettabibility (however previous literature [26] found a smaller exponent to explain anomalous front broadening in elongated-pore media). We cannot rule out other effects such as interaction of the fluid with the ‘filling’ chemicals and fibril adsorption, in determining the overall imbibition behaviour.

**7. Conclusions**

This work explored the possibility of applying Electrical Impedance Spectroscopy (EIS) to characterize liquid imbibition in paper. We developed lumped-parameter models of the wetting process and compared them with experimental data. In addition, we considered a number of alternative non-destructive imaging and characterization techniques to possibly complement EIS while satisfying acquisition speed and spatial resolution requirements, however at present we are not able to present a technique that systematically outperforms all the others. Two-electrode, single-frequency EIS is simple to implement and realtime but does not provide spatially-resolved information. The current model extends the insight of the measurement, but still has limitations.
Like others [13], we conclude that a combination of EIS with at least one other measurement method would allow to adjust the model to understand the process better.

None of the other investigated measurement techniques is a superior alternative to EIS, but some are of interest as additions. To this point it is unclear if EIS, with a multielectrode setup, would give more than the modulus. The influence of the surrounding electrodes is also to be determined. The need to switch off most electrodes for each measurement results in a trade-off between spatial and time resolution. We need to evaluate if the modulus of the multielectrode measurement is a step function or continuous. In case the modulus is a step function, optical measurement is preferable, for lateral and time resolution.

Gamma-ray intensity attenuation, in the selected setup, does not give further information about the system. Without the pinhole, this gives the same information as a simple measurement of water uptake, with less precision. With the pinhole, only steady state samples can be evaluated, due to the required measurement time.

Optical microscopy measurements have a high spatial and time resolution, but only give insight to one surface. The permeability of paper is different in all directions, which has to be accounted for. Confocal laser scanning microscopy would add information in the third direction, but introduces time constraints again.

While the non-instantaneous measurement techniques give a good spatial resolution, they do not allow a full understanding of the process, which is the goal here. Combining EIS with confocal microscopy and an accurate water uptake measurement will give further insight into understanding the water uptake in paper, while allowing the addition of further components in the future. To improve and better control future measurements, an altered EIS setup was proposed.

8. References


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1. Abstract
The increasing role of peptides in biosensors for biological applications like personalized medicine development warrants the need for their stability, functionality and reproducibility. Pamchip® microarrays involve use of immobilized peptides for such an application. Quality control of the PamGene chips using fluorescent dye reveal occasional large deviations in intensity, causing the batch of chips to be rejected. These deviations could be emanating from aggregation of certain peptides, concentration issues, sample rejection criteria or insufficient quality control checks. In our report, we attempt to verify and suggest approaches to circumvent the aforementioned issues.

2. Company profile
PamGene was founded in December 2000 and is a company engaged in the research, development, manufacturing and commercialization of life science applications based on its proprietary micro array technology. The PamChip® microarrays and PamStation® instruments form a platform for testing biological and clinical samples.

PamGene is a Translational Research & Biomarker Service Company that helps clients
- during drug discovery to generate drug candidates;
- during drug development to establish biomarker profiles to optimize response prediction;
- with biomarker profiling in the clinical setting;
- with co-development of innovative research diagnostics in clinical setting. Additionally we are focusing on opening up new opportunities for the development of Personalized Medicine (pharmaceutical discovery, translational and clinical). Most of PamGene’s projects are in oncology and many of these involve medicines that inhibit or modulate cellular kinases and kinase pathways as well as nuclear receptors and their signaling mechanisms. Our collaborators apply our technologies for biomarker research and to support
drug discovery in areas including tumor tissue and compound profiling in diseases concerning kinases in Oncology and also in several other diseases and fields of expertise such as the Central Nervous System, Immunology and Obesity.

3. Problem description

3.1 Company problem description

Currently several different PamChip® microarrays are being produced in a clean-room manufacturing plant and using semi-automated manufacturing process. These microarrays are made of a highly porous ceramic membrane (the solid support) on which typically up to 144 different peptides are immobilized.

The production of PamChip® microarrays includes several processes starting at the incoming inspection of raw material, chemical treatment of the solid support (i.e. the porous product carrier), immobilization of the biological materials (peptides) onto the porous solid support and assembly to produce the final microarray products. The production of microarrays may suffer from quality issues which yield to out-of-spec products - thus rejection. In particular, the signal intensities of the immobilized peptides may vary both intra- and inter-batch. Moreover the signal intensity of individual peptides which showed acceptable results at a certain batch may show out-of-spec signal intensities (either too low or too high) at the next batch. Several hypotheses have been drafted to understand this phenomenon but up to now neither the theoretical background nor the practical solutions have been found to resolve this issue.

The hypotheses related to varying signal intensities include i.e.:
- The effect of chemo-physical properties of the peptides (peptide sequences, pH, isoelectric point, lyofilisation etc.) on the solubility of the peptides.
- The effect of preparation of the peptide solutions which include accurately dissolving 144 different peptides in 2 ml tubes each as a first step, followed by further dilution of peptide solutions in small volumes of typically 15μl into a concentration of 1 mM per peptide in a 384 well plate.
- The way to mix small volumes optimally (e.g. 15 μl in a well 384 well plate) of precious, vulnerable, biological materials to obtain a homogenous solution.
- Storage effects before further processing e.g. aggregation of the peptides due to, for example, thawing, de-protection, centrifuging and vortexing.
- Dispensing of the 300pl peptide droplets onto the substrate, which process is particularly affected by humidity and temperature.

So a high number of chemo-physical conditions will affect the end product’s quality. The conditions of several processes are being controlled e.g. dispensing accuracy, but others are not. The aggregation of peptides in a solution due to e.g. lack of solubility is a particular example for which (chemo-) physical disciplines are relevant to resolve the problem, as well as the problem of mixing solutions.

The workshop should focus on 1) the design of a device which could detect the presence of aggregation and 2) the design of a model which can predict the effect of process and material conditions on the solubility of peptides. In other words, we appreciate to get an answer on:
- How to detect the presence of small aggregates in small volumes (say 150 volumes in a 384 well plate of 15 μl at a concentration of 1 mM each).
- The process and material conditions which have an effect on the solubility of peptides laid down in a predictive model.
3.2 Rephrasing the company problem
The entire production process is schematically depicted in Figure 1. It is unknown where the major cause for the irreproducible results lies or where in the process it occurs. We do know that according to PamGene, if an outlier is found in one microarray it is found in all the arrays produced within that batch. In other words all microarrays produced from the same spotplate show the same irregularity. This isolates the problem to an unpredictable factor that occurred before this point (Point 6).

4. Problem solving strategy
The problem of PamGene is irreproducibility in the production process of their PamChip® microarrays. To tackle the problem we distinguish four main strategies A: Finding out what causes it by performing quality control test. B: Finding out what is causing the effect by searching for a correlation between the physical properties of the peptides and their liability to give deviant results. C: Controlling the problem by in-line quality control that detects the deviations in an early stage of production and thus allows corrections. D: Working around the problem, by providing a reference to the customer that allows correction of their measurements. In the following sections these three solution directions are explained a bit more.

4.1 Strategy A: Tracking down the problem by data mining and step by step quality control
Within this strategy the aim is to have a workable number of tests that can be done to find out where in the process the deviation occurs. This is probably the first thing that has to be performed before a investing in the lateral approaches such as in-line quality control.

4.2 Strategy B: Tracking down the problem by data mining the Sypro ruby tests
Following this process we assume that the problem is caused by some (combination) of physical or chemical properties of the peptide. The Sypro Ruby tests that PamGene performs as an end quality control on 10 out of 960 microarrays, can be used to study the variation for each peptide and within each array. By correlating these variations with properties such as
solubility or peptide chain length it might be possible to find the fundamental properties that cause the observed irreproducible results.

4.3 Strategy C: In-line feedback control of the problem

The rationale behind this strategy is that if you cannot solve a problem you can at least try to detect it at an early stage and take corrective actions. We propose to perform checks on the aggregation and concentration of all the peptide solutions within the production process. The results of these checks can be used as a feedback to for instance spot an extra droplet or replace a certain peptide solution on the spotplate before spotting all the arrays. If this methods is successfully implemented it is prevented that a complete batch of produces arrays has to be discarded.

4.4 Strategy D: The work around

The thus far described strategies are aimed at solving the problem in such a way that no out of spec microarrays are produced. If this is for some reason not feasible it can still be feasible to correct the results by using knowledge obtained by the end product quality control: the Sypro Ruby test.

5. Strategy A: Tracking down the problem by data mining

From every batch PamGene takes several chips, and performs a SYPRO Ruby test on them, to assess the quality of the batch. The test entails adding a dye to the chips, which will bind to the peptides. The amount of dye which has been bound can be measured, and is an indicator of the peptide concentrations on the chip.

This section is divided in two. In the first section we analyzed average data from each batch, and compared batches. In the second section we further analyzed variations within one batch.

5.1 Batch to Batch analysis

We obtained average SYPRO Ruby data from PamGene from 86 batches. The first thing that we notice is that there is quite a substantial variation from batch to batch in the individual peptide intensity as seen in Figure 2. This variation is highly correlated from peptide to peptide, hence to correct for this, the peptide intensities are scaled with the median intensity of all the peptides in its measurement.

After this normalization has been done, we look at the remaining variation of each peptide as function of batch number. Our goal is to give a score which captures the likelihood that a peptide will be the one that causes the batch to be rejected (i.e., that it deviates significantly from the expected value), and correlate that score to physical parameters of the peptide. This may provide information about the cause of the problems.
Proceedings Physics with Industry 2013

Figure 2: Two arbitrary peptides v.s. batch number, compared to the median of the 144 peptides as a function of batch number.

We looked at two different ways of scoring:

1. We define a "goodness" as the number of measurements for which the intensity $I$ is within 30% of the average intensity $\langle I \rangle$.

2. We define a "badness" as the Mean Square Error (MSE) divided by the average energy squared, i.e.:

$$Badness = \frac{1}{\langle I \rangle^2} \sum_i (I_i - \langle I \rangle)^2$$

where $I_i$ is the intensity of a certain peptide in batch $i$.

Both scores anti-correlate reasonably well with one another as can be seen in Figure 3, however it should be clear that the "badness" score is more sensitive to extreme outliers. It is interesting to see however, that the two worst scoring peptides coincide on both scales, and that these are also the peptides that were most often the cause of batch rejection. These two peptides have sequences: PVIENPQYFGITN (worst score), and ASAASFETYILDP.
Next, we correlated three physical parameters of the peptides (hydropathy index, total charge, and solubility) to the goodness score. As can be seen in Figure 4, it turns out that none of these parameters show a correlation to the goodness score. It has to be mentioned that these are rather simple parameters that can be calculated by looking at the individual amino acids. In other words, the detailed structure of the peptide has no influence on any of these variables.

![Correlation of goodness with physic-chemical parameters.](image)

Finally, we did observe that the peptides which have the worst score also seem to have very low average SYPRO Ruby test scores (Figure 5). The two worst scoring peptides (which, as we pointed out earlier, also cause the most batch rejections) both have average SYPRO Ruby test scores well below the median of the experiment.
5.2 Analysis within one batch

When one peptide in the test set fails to be within the desired limits, this can cause a whole batch to be discarded. We think however that it should be possible to not discard this batch, rather to provide a baseline that the user has to take into account. The baseline can be taken from a representative sample of chips from within the batch. This does however require the variations to be from batch to batch, and not within the batch, i.e., it should be possible to take a representative sample.

In order to check the feasibility of this suggestion, we looked at the goodness of 26 chips coming from one batch (batch 129). As can be seen in Figure 6, within one batch, certain peptides have a relatively low goodness. The fact that they vary substantially within the batch makes it harder to extract a baseline from these peptides. On top of this, one should be cautious with drawing conclusions about the entire batch just by looking at a subset of chips in that batch.
6. Strategy B: Tracking down the problem by data mining and step by step quality control

Based on definition of the goodness, we looked more in depth to understand the possible correlation between aggregation propensities of peptides and secondary structures by using online available software “http://tango.crg.es/protected/academic/calculation2.jsp”. However at the current position we have not found very specific correlation between “good” peptides and “problematic” peptides. However this observation maybe valid but it is not conclusive, due to small number of sampling and available data with not specific initial and processing characteristic and conditions. The results are summarized in Figure 7.

![Image](http://example.com/image.png)

**Figure 7:** Selective characteristics of problematic and good peptides calculated by Tango.

To develop a model to predict the possibility of peptide aggregation one needs more systematically collected data as well as considering physical properties of the protein such as solubility, hydropathy, charges, solvent specifications, processing condition and even considering the properties of the substrate (porous material) and their interactions with the peptide.

At current state we believe the issue is an integrated problem of processing, possible peptide aggregation and solubility sensibility with limited systematically available data. So we propose to first detect the problematic sites in the process and get a statistically valid estimate of how the process can be improved considering minimum cost and change to the production line and finally satisfying the quality of final products.

By the following scheme (Figure 8), we analyzed the process step by step and suggest Quality Control (QC) measures which have been missed and also can be used to identify the lack of solubility, presence of aggregation and possible interactions between surfaces.
Problems we thought of tackling are:

- Processing which are less of concern right now
  - Nozzle-peptide interactions: the problem can be confirmed by estimating the concentration of peptide before entering the nozzle and after passing through the nozzle. If there are major loss, it can be improved by enhancing the solubility of the specific peptide
  - Waiting time in the process which may result in aggregations: if the problematic peptides are sensitive to environmental parameters, extra care should be taken in sequence of spotting or conditions of the clean room
  - To reduce the probability of aggregation in carrier plates use, siliconized plates
- Detect the aggregation, solubility issue and interactions between peptide and surface of nozzle (plate) during the process by sampling and monitoring concentration and aggregation (molecular weight and hydrodynamic diameter) in each step. We suggest to sample before and after each production step, especially on problematic peptides, and run an offline size exclusion chromatography and dynamic light scattering tests. The suggested tests will help to determine the spots prone to aggregation in the processing and solubility-sensitivity of the each peptide. We also recommend the GPC/SEC-light scattering with a concentration detector and a light scattering detector.
7. Strategy C: In-line feedback control of the problem

Early detection of aggregates before spotting: Quality Control 1

Introduction:
The problem of non-reproducible protein intensities from PamChips® at a later product could be very well a result of aggregation of peptides during the fabrication process. In order to account for this, we propose a method to detect presence of aggregates after peptides are loaded into a spot-plate. Quality control at this stage is pertinent with respect to protein aggregation and the concentration of the protein themselves.

Dynamic Light Scattering (DLS):
DLS is a very versatile technique to measure particle size distributions and has been often used to measure protein aggregation. The use of DLS has been recently combined with ThioflavinT (ThT) assay to monitor aggregation of polypeptides1. The authors here created a home-built DLS setup, the schematic of which is shown below and measured aggregation as a function of time. A schematic layout of the DLS instrument and simultaneous measurement of protein aggregation is shown below.

Adapted from Quake et al. (2013) “Simultaneous Measurement of Amyloid Fibril Formation by Dynamic Light Scattering and Fluorescence Reveals Complex Aggregation Kinetics”.

Construction:
A 633 nm laser is focused down to a 50 μm waist by a 25 mm focal length plano-convex achromatic lens. A 10X, 10 mm focal length objective (OBJ) below the flow cell collects light scattered from the sample defining a scattering vector 60 degrees to incidence. Scattered laser light was directed through a 550 nm cutoff dichroic mirror (DCBS) and then through a long-pass (LP) 600 nm cutoff filter in order to protect the detector from the fluorescence excitation field and to select light scattered from the incident beam. The filtered scattered light was coupled into a single mode fiber (SMF) via an NA matched fiber coupler lens. In the same
setup, fluorescence from ThT was measured as a marker of protein aggregation. ThT is a dye which does not bind to peptides as such but gives a very strong fluorescence upon binding to peptide aggregates containing a specific structure\(^2\). At this point, we do not know if the aggregates formed from the peptides have cross beta sheet or not.

Commercial DLS setups are also available which also perform the same task. [http://www.wyatt.eu/index.php?id=dynapro-plate-reader](http://www.wyatt.eu/index.php?id=dynapro-plate-reader). The specifications include a sample volume of 4 µl with concentrations as low as 10 mg/ml. The measurement time is estimated to be around 100 seconds per well.

This setup can be separate and not integrated in the current assembly line. Upon validation by DLS on one spot-plate, the rest of the spot plates can be used for further fabrication. The existing 384 spot-plates will have to be replaced with a 384 plastic spot plate with flat bottom for DLS measurements.

Another way to detect aggregation would be to use ThT which upon excitation at 446nm gives a strong fluorescence at 484 nm if aggregates are present. If no aggregates are present, there is a very weak signal. ThT can be used in a peptide: ThT ratio of 5:1 for a fairly stable measurement. 100 μM of peptides and 20 μM of ThT in a final volume of 50 µl should be enough for a typical absorbance measurement\(^2\). A disadvantage of this technique is that this dye is very specific for cross beta sheets in protein aggregates and thus can detect only such aggregates.

**Estimation of protein concentration: Quality Control 2**

After verification by DLS that no aggregates are present, the next addition to the assembly line would be verification of peptide concentrations. This is to account for any dispensing issues in the nozzle or settling/adsorption in the tubes. To measure protein concentrations, we propose two methods:

1. **Biuret method**

   **Principle:** This is a standard method of estimation of protein and peptide concentrations. It is based on the ability of Cu (II) ions to form a violet-coloured chelate complex with peptide bonds (-CONH-groups) in alkaline conditions. The lone pairs of electrons from 4 nitrogen atoms in a peptide bond coordinate a copper (II) ion. A chelate complex is immediately formed which absorbs 540 nm light and appears violet. Thus a color change indicates presence of proteins. Thus concentration of peptide bonds would be in linear correlation with the color intensity. If the concentration of peptide bonds is less, as when short-chain peptides are present, the change in color would be from blue to pink. Thus by simple absorption spectroscopy, concentration of peptides can be estimated.

   **Protocol:**
   a. Biuret reagents are available commercially and the test is linear up to concentrations of 5 mg/ml.
   b. The peptide aliquots in the spot-plates are already at very high concentrations (~660 mg/ml) and thus will have to diluted appropriately.
   c. Equal volumes of biuret reagent and peptide solution should be mixed and incubated for 5 minutes and mixed well.
   d. After 5 minutes an intense pink/violet color should appear, the intensity of which should be linearly correlated to protein concentration,
e. A standard curve must be prepared so as to extrapolate values of intensity obtained at 540nm to get protein concentrations.

Troubleshooting

If upon measurement, the concentrations are same, it means that the deposition of peptides is correct. If not, the following could be the reasons:

1. Adsorption of peptides to walls of spot-plates.
2. Settling down of peptides in spot-plates due to prolonged waiting times.
3. Aggregation of certain peptides.

2. Fourier Transform InfraRed (FTIR) spectroscopy method:

**Principle:** IR spectroscopy exploits the fact that molecules absorb infrared radiation at specific frequencies that is characteristic of their structure. Usually, IR spectrophotometer measure amide bonds in protein chains and can accurately quantify protein concentrations without relying on amino acid composition or dye binding capabilities.

**Protocol:**

The methodology is very simple as it requires very low volumes (typically 1-3 µl) of peptides. Upon spotting of the samples, the instrument dries the sample and measures each spot with an infrared beam with varying frequencies generating spectra. By fitting this spectrum, peptide concentrations can be determined. A typical infrared spectrometer is currently available from a number of manufacturers including Millipore (Direct Detect®), Anadis Intruments BV and Metler Toledo.

<table>
<thead>
<tr>
<th></th>
<th>Colorimetric Assay</th>
<th>FTIR based assay</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Efficiency</strong></td>
<td>Depends on complex formation of copper.</td>
<td>Relies on absorption of IR by peptide bonds.</td>
</tr>
<tr>
<td><strong>Cost criteria</strong></td>
<td>Cheap (4000 € for homebuilt setup). Commercial setups expensive.</td>
<td>up to 20000€</td>
</tr>
<tr>
<td><strong>Sample volume</strong></td>
<td>5-50µl</td>
<td>5-50µl</td>
</tr>
<tr>
<td><strong>Concentration required</strong></td>
<td>50µM</td>
<td>50 µM</td>
</tr>
</tbody>
</table>

**Changes required in current assembly line:**

In the current production setup, a separate area must be designated for measuring protein concentration. This area should have a flat-bottom plastic plate (384 well standard plates) on a movable stage. A nozzle should now accurately pipette corresponding peptide aliquots from spot-plates into these wells.

A proposed fiber based spectrophotometer can be integrated below the movable stage holding the 384 well plate. This would emit 540nm wavelength light to measure absorbance from the 144 wells. This is a fairly quick process. An algorithm can be written to measure the concentrations from the absorbance values. If all the values are within a given range, the nozzle can move ahead to deposit on the carrier plates. The measurement can take around
15-20 minutes and thus one proposed suggestion here would be not to allow the peptides in the spot plates to settle down. Hence slow periodic shaking would be optimal. This is just to be sure that settling is never an issue.

8. **Strategy D: The workaround.**
   - One of the problems that occur time to time in the production line is the outliers. It can still be possible to correct the results by using knowledge obtained by the end product quality control, the Sypro Ruby test.
   - This assumption can be checked by testing the microassay from the batch that does not have outlier with the microarray that has outliers but was normalized. By applying the Protein Tyrosine Kinase assay with cell or tissue lysates on both chips and comparing the results it is possible to see if there is a significant difference in the results or they are reliable. That hypothesis needs further investigation but it will show if it is possible to save the hall batch just by finding a proper normalization.
Note that for this method to work it is essential that intra-batch results are consistent. As was explained in 6.2 this is not always the case. Though the majority of peptides show low enough intra batch variation to be able to act as a predictor for itself, for some especially low signal peptides this is not the case. Maybe in the future batches that have been made and are out-of-spec can be stored and used to test the feasibility of this approach.

9. Conclusions and outlook

- There seems to be little correlation between the goodness factor and physico-chemical characteristics like charge, hydropathy index and solubility based on obtained data. This hints that probably other characteristics influence aggregation (if an issue) of peptides.
- Pilot experiments determining if the peptides are aggregation prone and/or sensitive to solvent should be performed. Simultaneously, DLS and SEC technique will confirm existence of aggregates in solutions.
- Optimizing the solvent and processing conditions of the “problematic” peptides for a better solubility which will result in less lateral aggregations
- Chemical modification of “difficult” peptides by addition of amino acid residues, thereby changing net charge, pI and solubility.
- The intra-batch reproducibility is low for a few peptides. This should be investigated further as it is possible that these peptides do not deliver reproducible results en the assay as well.

10. References

2. L.S. Wolfe et al., Protein-induced photophysical changes to the amyloid indicator dye thioflavin T, Proc Natl Acad Sci USA 107, 16863 (2010).
1. Abstract

Deviations from the desired zinc layer thickness in the process of steel coating cause appreciable losses for the steel industry. Vibration of the steel strip is considered to be an important reason behind the zinc layer inhomogeneity. This report discusses several solutions to the vibration problem, that to the best of our knowledge could be applied in the industrial environment. These solutions are active and passive damping, optimizing the gas wiper operation, and twisting the strip.

2. Company profile

Tata Steel is an Indian multi-national steel manufacturing company. With a turnover of US$25 billion, they are one of the world’s leading steel manufacturers. A steel manufacturing plant in IJmuiden, The Netherlands, was started in 1918 under the name Hoogovens. This plant was acquired in 2007 by Tata Steel. Tata Steel supplies for the automotive, construction, packaging, and domestic application markets. Among the various lines of Tata Steel in IJmuiden are three hot-dip galvanizing (HDG) lines.

3. Problem description

Galvanizing is the process of coating steel plates with a zinc coating, in order to protect from corrosion and improve the appearance of the plates. A common technique is continuous hot-dip galvanization (HDG). The hot-dip galvanizing process is sketched in figure 1. A strip of steel is passed through a bath of liquid zinc at a temperature of 450 °C. Typical dimensions of the steel strip are widths around 1-2 m and thicknesses around 0.5-2 mm. After leaving the zinc bath, the strip travels 40-50 m upwards in a cooling tower, where it cools down such that the zinc solidifies.
When the strip leaves the bath, a large quantity of zinc is dragged along with strip due to the strong adhesion (among other factors) of zinc to steel. The coating thickness increases with line speed. Because zinc is more expensive than steel, it is undesirable to have an excessive coating thickness. Therefore, gas wipers are used to blow off the excess zinc after the strip leaves the bath.

The efficiency of the gas wipers depends strongly on the distance between gas wiper and strip: the closer the wiper is to the strip, the less gas is required to bring down the coating to the required thickness. This also allows for higher line speeds. The typical current maximum line speed is 180 m/min; this is determined by the efficiency of the gas wipers mainly due to vibrations. It is therefore desirable to place the gas wiper as near to the strip as possible.

A known problem in these lines is vibration of the strip. If the strip vibrates, then the distance between gas wiper nozzle and strip changes continuously. Because of this, the resulting zinc layer thickness will not be constant along the length of the strip. Industrial requirements on zinc layer thickness variations are continuously tightening, putting serious requirements on the system. A further risk is that the strip might actually touch the nozzle if the strip vibrates too heavily or if the gas wiper nozzle is located too close to the strip. The molten zinc would then get deposited on the nozzle, which would necessitate nozzle cleaning, causing an interruption of the production line.

Three different vibration modes have been observed: a string mode, a twisting mode, and a flapping mode. (Note that the said measurements only included three sensors, thus limiting the number of different modes potentially observable to three.) The paths of the strip with regard to the rest position in each of these modes is illustrated in figure 2.

Various excitation mechanisms exist along the length of the strip: it can be excited by the sink rolls and the stabilizer rolls, by the roll on the top of the cooling tower, by the gas wipers, and
by the air cooling systems that are typically located inside the tower. These excitations may be
caused for example by worn-out bearings in the rolls, or by instabilities in the air flow around
the strip. It might also be the case that other vibration excitation mechanisms are important,
including the ones originating far from the gas wipers either before or after the galvanizing
area.

3.1 Solution strategies

Four different solution strategies have been identified during the meeting. A feasibility check
was performed for each solution, to determine which ones are the most promising. They are
described in the sections below. The possible solutions are:

- The possibility of passively damping the rolls by creating a spring-damping system was
  investigated. If the damping spring is well adjusted, the strip and damping form a
coupled resonant oscillator. This would greatly damp the vibrations.

- Potentially even more effective than passive damping is active damping, for example by
  hydraulic control of the rolls that touch the strip. Various possible setups have been
described.

- The structure of the air flow in the jet produced by the gas wiper was studied. A region
  has been found in the literature, in which the jet flow is almost independent of the
  distance between nozzle and strip. This is very desirable, because it means that strip
  vibrations will not result in coating inhomogeneity. A solution was proposed to attempt
to reach this “plateau” regime.

- The modes that travel along the strip have frequency which is dependent on the tension
  on the strip. Twisting the strip along its center will introduce a tension profile, which
  may break up these eigenmodes. A scale model of a twisted steel strip was built to test
  the feasibility of this solution.

4. Analysis and modeling of the deviation of the strip

Our working hypothesis is that the inhomogeneity of the zinc layer is caused by the vibration
of the steel strip in the direction perpendicular to the strip plane close to the gas wipers.
Therefore, measuring the distance between the gas wipers and the strip is the first step
towards understanding the problem. A dataset of the said measurements has been received
from Tata Steel, covering about 10 minutes at the sampling rate of 100 Hz (65545 points). Even
though this dataset only concerns a single steel coil, we will assume that it is representative of
the typical operating conditions in the plant.

One can clearly identify regions of stable operation and regions of sudden jumps (see Fig. 3).
In order to get some insight into the vibrations, we have chosen a set of 90 second windows of
stable operation and calculated a Fourier transform of these subsets. Subsequently, we
averaged the said data to obtain the power spectrum (Fig. 4 and table 1).

It is worthwhile to note that using only the two highest-power peaks one can accommodate
for the coordinate of the steel strip with an error that is smaller than 5% in the stable operation
mode. Assuming that there is a single unique cause for every excitation mode, this implies
that accommodating for these two sources of vibration would appreciably decrease the
vibration amplitude in the stable operation mode.

However, if one aims to solve the vibration problem, it is also crucial to have a prediction time
that is as long as possible and also predict the jumps. In order to do that we have turned to an
autoregressive model. The general idea behind the model can be understood in terms of a
simple formula

\[ X_t = a_1 X_{t-1} + a_2 X_{t-2} + a_3 X_{t-3} + \ldots + a_N X_{t-N}, \]  (1)
Figure 3. Time-series data of the inductive sensor readings. The horizontal axis shows time in the units of 10 milliseconds, whereas the vertical axis is in arbitrary units. It is assumed that the reading of the inductive sensor is linearly related to the distance between the steel strip and the gas wiper.

Figure 4. Average power spectrum of the vibrations of the strip in the stable regime (c.f. text for more details). The horizontal axis shows frequency in Hertz, whereas the vertical axis is in millimeters.

where $X_t$ is the coordinate of the strip at time $t$, and $\alpha_1, \ldots, \alpha_N$ are real numbers that are chosen such that the model predicts previous data correctly. One efficient way to find $\{\alpha_i\}$ is known as the Burg's method [1]. We have applied it to the problem at hand [2].

In what follows, we try to predict the highest-amplitude jump in the data that has been made available to us (the jump is around 5% of the average amplitude). To illustrate the potential and the shortcomings of this algorithm, we start the prediction at different points.

We see that in the stable operation regime the prediction is excellent and deviates from the experimental values by less 0.6% in 10 seconds. If the prediction starts in the middle of the jump, the error stays below 1.25% in 5 seconds. Finally, if the predictor has no knowledge of former jumps, the upcoming jump is obviously predicted very poorly, except for very short timescales ($< \text{1s}$).

However, it might be the case that the big jumps happen due to the actions of the operator (such as the change of the line speed or the tension). In that case, the prediction algorithm does not have to try to guess when the next big jump is going to happen. On the other hand, if it is impossible to relate the big jumps to the actions of the operator, it might still be possible to predict them if they are not completely random. In that case, a dataset spanning a large amount of big jumps is required in order to train the algorithm.

In conclusion, one can envision a continuously operating predictor, which can predict the position of the strip several seconds ahead of the time.

In conclusion, one can envision a continuously operating predictor, which can predict the position of the strip several seconds ahead of the time.
Table 1. Peaks identified from the average Fourier power spectrum (Fig. 4) of the vibrations.

<table>
<thead>
<tr>
<th>Frequency, Hz</th>
<th>Power, a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.31</td>
<td>3.42</td>
</tr>
<tr>
<td>0.56</td>
<td>9.64</td>
</tr>
<tr>
<td>0.61</td>
<td>14.8</td>
</tr>
<tr>
<td>1.2</td>
<td>11.8</td>
</tr>
<tr>
<td>2.4</td>
<td>148</td>
</tr>
<tr>
<td>4.9</td>
<td>13.4</td>
</tr>
<tr>
<td>5.3</td>
<td>269</td>
</tr>
<tr>
<td>5.6</td>
<td>65.8 (double peak at 5.58 and 5.60)</td>
</tr>
</tbody>
</table>

Figure 5. Comparison of the measurement and the prediction of the deviation of the strip starting the prediction at different times. The horizontal axis shows time in the units of 10 milliseconds, whereas the vertical axis is in arbitrary units. The black vertical line denotes the time when the prediction starts.

Figure 6. Absolute error of the prediction of the deviation of the strip starting the prediction at different times. The horizontal axis shows time in the units of 10 milliseconds, whereas the vertical axis is in arbitrary units. The black vertical line denotes the time when the prediction starts.

5. Passive damping

5.1 General Idea

The strip can be seen as a big mass on a spring system that oscillates at certain frequencies, but that is only slightly damped by for example the air or the liquid zinc. The general idea behind adding passive damping would be to turn one of the rollers into another mass on a spring system with an eigenfrequency matching the ones of the strip so that it will couple to the strip vibrations and energy will be transferred to it. Since we can now damp this roller we now provide a way for the energy of the strip to be efficiently dissipated. In this section we provide some theory on what design parameters to use for the coupled oscillator system (the rigid roller that is now turned into a damped oscillator) and how to calculate the energy dissipation.
rate of this coupled oscillator as function of frequency. We propose to use the stabilization roller as a damped oscillator and for a typical vibration amplitude vs frequency spectrum we propose what parameters for the spring and damping system one should use.

Figure 7. Schematic of the strip, which can be seen as a mass $M_s$ on a spring (with spring constant $k_s$) with only weak damping $\gamma_s$. The stabilization roller, with mass $m_{roll}$, which is otherwise rigid is now attached on a spring (spring constant $k_{roll}$) with a certain damping $\gamma_{roll}$ and thereby passively damps movement of the strip.

5.2 Theoretical background

The displacement $x(t)$ of a damped driven oscillator is described by the equation of motion:

$$m\ddot{x} + \gamma\dot{x} + kx = F\cos(\omega t),$$

where $m$ is the mass, $\gamma$ the viscous damping term, $k$ the spring constant, $F$ the amplitude of the force (units of Newton), $\omega = 2\pi f$ the angular frequency and $f$ the driving frequency of the vibration source. This is typically rewritten in text books as:

$$\ddot{x} + 2\beta\dot{x} + \omega_0^2x = A\cos(\omega t),$$

where $A = F/m$, $\beta = \gamma/(2m)$ and $\omega_0 = \sqrt{k/m}$. The response will be of the form:

$$x(t) = D\cos(\omega t - \delta),$$

where $\delta$ is the phase difference between the driving force and the resultant motion and $D$ is the amplitude of the resultant motion. $D$ is given by:

$$D = \frac{A}{\sqrt{(\omega_0^2 - \omega^2)^2 + 4\omega^2\beta^2}}$$

When an object moves with velocity $v = \dot{x}$ it dissipates an amount of energy per second $P_{diss}$ given by:

$$P_{diss} = \gamma v^2.$$
An oscillator \( x(t) = D \cos(\omega t - \delta) \) therefore dissipates in one period \( (1/f = 2\pi/\omega) \) an average amount of energy \( P_{\text{diss}} \):

\[
P_{\text{diss}} = \frac{1}{2\pi/\omega} \int_{0}^{2\pi/\omega} \gamma x(t)^2 \, dt = \frac{1}{2\pi/\omega} \int_{0}^{2\pi/\omega} \gamma [-D \omega \sin(\omega t - \delta)]^2 \, dt = \frac{1}{2\pi/\omega} \frac{\gamma D^2}{2\omega^2} \frac{2\pi}{\omega} = 0.5 \gamma D^2 \omega^2
\]

(7)

If the strip vibrations at a certain frequency with a certain amplitude \( B \), you can approximate the force \( F \) acting on the roller through \( F = Bk \). Then as function of \( m, k, \gamma \) you can calculate the displacement of the roller and the amount of energy it dissipates as function of frequency.

5.3 Putting in numbers

The stabilization roller has a mass \( m_{\text{roll}} \) of about 500 kg. Since we determined in one data set that the largest vibrations in the strip have frequencies of 2.5 Hz and 5.5 Hz, we use a spring constant of \( k_{\text{roll}} = 3 \times 10^5 \) N/m such that the eigenfrequency of the roll is \( f = \frac{1}{2\pi} \sqrt{k/m_{\text{roll}}} = 4 \) Hz. Such a spring constant corresponds to a compression of 0.3 mm when a force of 100 N is exerted, this seems reasonable. If we assume the roller is driven by vibrations with an amplitude of 1mm, we calculate the force exerted on the roller by \( F = k \times 1 \text{mm} \). When using the above mentioned formulas we can calculate the amplitude of the vibrations of the roller and the amount of energy being dissipated as function of frequency. We do this for light damping \( (\gamma = 3000 \text{Ns/m}) \), close to optimal damping \( (\gamma = 12000 \text{Ns/m}) \) and very heavy damping \( (\gamma = 60000 \text{Ns/m}) \). It can be seen that for light damping the roll likes to resonantly oscillate at its resonant frequency, but only efficiently dissipates energy in a narrow frequency band. When it is heavily damped it hardly oscillates and only dissipates energy at low frequencies. A more optimum amount of damping to use would be such that it dissipates energy in a broad frequency range, since the exact frequency spectrum of the vibrations of course varies. We then plot a typical noise spectrum that we deduced from a test set of data, and the noise energy dissipation as function of frequency. We used a damping optimum such that all resonances have some amount of damping. If one has a mode that is vibrating with an amplitude of \( x_{\text{max}} = 1 \text{mm} \), at a certain frequency \( f_{\text{strip}} = 5 \) Hz, and the mass of the strip is 500 kg, we estimate the amount of energy \( E \) in this mode through:

\[
E = 0.5kx_{\text{max}}^2 = 2\pi^2 f_{\text{strip}}^2 mx_{\text{max}}^2 = 0.25 \text{ J}
\]

If it is dissipated at a rate of minimal \( 0.1 - 1 \) W this seems like a more than reasonable amount of energy dissipation to damp the strip in a passive way.

![Figure 8. a) Calculated amplitude of the 'stabilization' roll when it is mounted on a spring and is driven by 1mm vibrations of the strip for various degrees of damping. b) Shows the energy dissipation.](image-url)
5.4 Further remarks

For the optimal parameters used the low frequency modes are not damped as well as the higher frequency modes. One could compensate for this further by either shifting to a lower central frequency (decrease \( k \)) or to make the dissipation spectrum broader by using a larger \( \gamma \).

When adding passive damping our first suggestion would be to use for this purpose the stabilization roller or the correction roller. Possibly, one could also use the sink roll in the zinc bath or the tower roll, but we think one should then be aware of new vibration modes that can be introduced whereby these rolls now swing in horizontal direction.

Finally, when one applies passive damping on multiple rolls one could also consider to optimize one roll for low frequencies and one roll for higher frequencies, but of course this complicates the implementation.

6. Active damping

Decreased vibrations directly result in a more uniform zinc layer. Besides that, if the vibrations are decreased, one can operate the gas wipers at a smaller distance from the steel sheet, and exploit the non-linear region of the zinc layer dependence on the distance-to-aperture ratio (c.f. section 7). However, one then has to worry about the contamination of the gas wipers by the splashes of zinc, even though that can be alleviated to a certain extent by decreasing the temperature of the zinc bath thus increasing the viscosity of liquid zinc (which should be further investigated).

One method to decrease the amplitude of the vibrations is active damping. In this particular system we have found three input points for the active damping (Fig. 10). Namely, the stabilization rolls in the zinc bath, the gas wipers and the roll at the top of the cooling tower. In what follows, we look at these three possibilities in more detail.

6.1 Rolls

In order to estimate if the cancellation of vibrations using rolls is feasible, we have to calculate the forces and velocities required. Before doing that, however, we note that displacement of a roll, required to move the steel sheet at the gas wipers by a certain amount is dependent on the distance between the roller and the gas wipers. Displacement at the stabilization roll results in approximately the same (difference of 2\%) displacement at the gas wipers. On the other hand, displacement of the top roll will result in only 1/25th of displacement at the gas wipers.
We now proceed to calculate the forces. Two forces are relevant in the system: tension and gravity. However, we are only interested in the horizontal forces, as we plan to move our rolls horizontally. Therefore, gravity does not play a role. When it comes to tension, we can calculate it using the following formula:

\[ F_T = EA \frac{\Delta L}{L}, \tag{8} \]

where \( E \approx 200\text{GPa} \) is the Young modulus of steel, \( A = 10^{-3}\text{m}^2 \) is the area of a steel sheet that is one meter wide and 1mm thick. In order to achieve a higher degree of accuracy, it is important to take the temperature dependence of the the Young modulus is into account, as at 320°C it is approximately 90% of the value at ambient temperature [3]. Finally, \( L \) is the length of the sheet that is being deformed and \( \Delta L \) is the change of length.

We start with the calculation of the force on the stabilization roll, in case it is used for the feedback. We assume that the fixed points of the steel sheet is the top roll and the roll at the bottom of the zinc bath. That is, we assume that the gas wipers exert negligible force on the steel sheet. If we assume that the distance between the stabilization roll and the top roll is 50m, whereas the distance between the stabilization roll and the fixed roll at the bottom of the zinc bath is 1m, we find that \( \Delta L \) is 1\( \mu \)m and 50\( \mu \)m, respectively, if the stabilization roll moves 1cm. In that case, the forces are 205N and 10kN, respectively. The horizontal projection of the sum of the forces is then 100N. This is the force that active control system has to be able to exert in order to move the steel sheet by 1cm.

In the case of moving the top roll, the force needed is calculated similarly. For a displacement of 25cm, the force then is 12N, in addition to the force compensating for the strip tension. Considering that we want to cancel vibrations of up to 5Hz, the velocities needed are 1.25m/s and 5cm/s in the case of the top and the stabilizing rolls, respectively.

Besides the concerns about forces, displacement amplitudes and velocities of the rolls, one should take into account the fact that transverse displacement travels at a finite speed due to finite rigidity of the sheet. We have estimated that the velocity of the said waves is 25m/s. Hence, in the case of moving the top roll, either a reliable prediction of the deviation after 2s, or a robust delayed feedback control is required.

A further concern is the introduction of scratches on the steel sheet, if the stabilizing rolls slip. This could happen if they are detached from the steel sheet for a sufficient period of time.
therefore introducing a difference of velocities between the stabilization rolls (that are not
driven) and the steel sheet. However, since the top translational speed of the stabilizing roll is
5cm/s, we believe that slippage would be negligible. Moreover, one can alleviate this problem
to a certain degree by increasing the diameter or the mass of the stabilization rolls thus
increasing the moment of inertia.

We have concluded that due to the reasons above moving the stabilizer roll is more practical
than moving the upper (top) roll.

6.2 Varying the dimensions of the nozzle of the gas wipers

One method to actively control the thickness of the zinc layer on the metal substrate is to
control the pressure of the air jet coming in contact with the molten zinc (see also Fig. 11).

![Figure 11. Schematic overview of the metal substrate with zinc coating (out of scale) in the
vicinity of the gas wipers. The center between gas wipers is set to y=0. L represents the
distance between metal substrate and gas wiper nozzle, while d represents the width of the
gas wiper nozzle.](image)

In normal circumstances, the molten zinc at the metal substrate is blown off (until ≈ 10 μm) by
high pressure coming from the air jets from the gas wipers. However, the variation in the zinc
thickness throughout the steel plate is too large due to the oscillations of the steel plate in this
state. By actively controlling the width of each of the nozzles, one could in principle reduce
the pressure at one side and increase the pressure at the other. The following section will
discuss what the orders of magnitude of the forces induced by the gas wipers are, and
whether that could resonate the entire system. We will also look at how far we would have to
change the widths of the nozzles and whether that is feasible. Normally, if the steel plate is
displaced to the right due to an oscillation, i.e. we have a displacement of Δy, the layer of zinc
reduces at the right side, and increases at the left side. One could also argue that this
corresponds to the change in zinc layer thickness due to the drop or increase of ratios Ld. To
counter this, one would like to keep the ratio Ld constant by an active feedback system to
regulate the nozzle width. This is also represented in Fig. 12. A sensor (e.g. a camera) records
the displacement of the steel strip to the right and left. This information is converted to a
voltage in an A/D converter. From here, the controller, with the empirically adjusted gains,
will put a voltage on the piezoelectric actuators to increase or decrease the nozzle width d.
So if there is displacement to the right of the metal substrate, L decreases, so the d should also decrease at the right side. On the left side, L increases, so the d should also increase. It is estimated that during the manufacturing process, the change in L can be 10%. Therefore, d should also be able to change 10%. This would imply that, given the width of the nozzle as being 1 mm, there should be a piezoelectric activator that can have a displacement of at least 0.1 mm. The reason to take piezoelectric actuators is due to the high accuracy and frequency with which they can be displaced, and the high forces they can withstand. After a quick search, it was found that there are piezoelectric actuators available for this kind of operation [4]. The maximum amount of force that is being exerted by the gas wiper on the plate is inversely proportional to nozzle width d, and was calculated to be in the order of 50 N. This is not negligible in comparison to the force required to displace the steel strip by 1 cm, which is in the order of 100 N. Therefore, a more refined calculation is required in order to determine the feasibility of this approach.

7. Air jet structure

The structure of an airjet is well known [5]. The exit velocity of the airjet ($u_0$) is conserved within the so-called potential core, see Fig. 13. Outside the potential core region, the velocity of the airjet ($u_m$) is decreasing as the distance from the nozzle is increasing. In Ref. [6] it is shown that if one stays within the potential core of the airjet, there is a plateau where the distance between the gas wiper and the strip does not influence the final thickness of the zinc coating as can be seen in Fig. 14. This suggests that if the strip is within the potential core of the gas wiper, the thickness of the coating is constant, even if the strip is vibrating. At present the distance between the gas wiper and the nozzle ($L$) is 10 mm and the nozzle width ($d$) is 1 mm, which means that we are outside the potential core. The easiest way to ensure that the strip is inside the potential core, would be to move the strip towards the gas wiper. However, this is not desired because the risk that the strip actually hits the gas wiper due to vibrations is too large. A collision between gas wiper and strip means a shutdown of the production line to clean the gas wiper and this of course is expensive. Therefore, the safe way to ensure that the strip is within the potential core, is to enlarge the potential core.

Figure 12. Schematic overview of the electronics that could be required for an active feedback system, where the nozzle width is controlled with piezoelectric motors.
[7] showed that the length of the potential core is only depending on the width of the nozzle (d) according to

\[ \frac{L}{d} = 8. \]  
\[ (9) \]

This means that if we want to keep the distance between the strip and gas wiper at \( L = 10 \) mm and at the same time be within the potential core -2 mm (in case of vibrations), the nozzle width should be adjusted to \( d = 1.6 \) mm. However, at the same time, the thickness of the coating should not change if we make the potential core larger. The thickness scales, in a rough first order approximation, with the velocity at which the air hits the strip \( (u_m) \).

Currently, the exit velocity of the gas wiper \( u_0 \) is 200 m/s. At a distance \( x \) from the gas wiper outside the potential core region the velocity of the airflow is given by

\[ u_m = u_0 0.866 \sqrt{\sigma} \sqrt{L/x} \]  
\[ (10) \]

with \( \sigma \) an empirical constant between 7.5 and 7.7 ([7]). This means that in the current situation, the velocity at which the airjet hits the strip is about 150 m/s. The centreline velocity of the potential-core is determined by the pressure of the gas wiper. Currently, this pressure is 600

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*Figure 13. Schematic drawing of a Jet. Region I corresponds to the potential core region.*

*Figure 14. Influence of the nozzle to strip distance. Squares: experimental data with error bars; triangle: simulations; circle: analytical model; dotted line: plateau. Figure taken from [6]*
mbar. A decrease of the centreline velocity by 25% means also a decrease in gas wiper pressure of 25% to 450 mbar in a first order approximation. A summary of the suggested changes can be found in table 2.

**Table 2.** Old and new parameters for gas wiper exit velocity ($u_0$), the velocity with which the gas wiper hits the strip ($u_{um}$), the width of the nozzle ($d$), the nozzle to strip distance ($L$) and the pressure in the nozzle ($p$). Note that the new parameters are very rough first order estimates.

<table>
<thead>
<tr>
<th></th>
<th>$u_0$ [m/s]</th>
<th>$u_{um}$ [m/s]</th>
<th>$d$ [mm]</th>
<th>$L$ [mm]</th>
<th>$p$ [mbar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Old</td>
<td>200</td>
<td>150</td>
<td>1</td>
<td>10</td>
<td>600</td>
</tr>
<tr>
<td>New</td>
<td>150</td>
<td>150</td>
<td>1.6</td>
<td>10</td>
<td>450</td>
</tr>
</tbody>
</table>

The above analysis gives a very rough first order approximation. Before any of these suggested changes are tested in a real production line, we would suggest to do a more sophisticated modeling. As a starting point for this modeling the following formula proposed by [6]

$$h_{opt} = \frac{T_{max} + \sqrt{T_{max}^2 + 4(1 + \nabla P_{max})}}{4(1 + \nabla P_{max})}$$

(11)

can be used. Here $h_{opt}$, $T_{max}$ and $\nabla P_{max}$ are the non-dimensionalized optimal coating thickness, maximum shear-stress and maximum pressure gradient, respectively. This analytical formula can be used with numerical simulated values of $T_{max}$ and $\nabla P_{max}$.

8. Twisting strip: experiment

Three types of vibration modes are distinguished in strip vibration at the gas wipers: string mode, twisting mode and flapping mode (illustrated in figure 2). The behavior of the strip is a combination of several eigenmodes. In order to change the vibration behavior and the amplitude at the gas wipers, the eigenmodes can be adjusted by increasing the stiffness and altering the shape of the strip. The eigenfrequencies are dependent on the tension on the strip. An increase in stiffness to change the amplitude of the vibrations at the gas wipers might be incorporated in the strip by twisting it along the vertical axis.

Twisting induces shear and tensile stress at the outermost edges of the strip. However, it is important that the vector combination of the shear and tensile stress due to twisting at these edges and the extra tensile stress on the strip do not exceed the yield strength of the material. This puts a limit on the maximum allowable twisting. For example: consider a strip with the dimensions 40m $\times$ 1m $\times$ 0.0001m. If this strip is twisted by 180°, the outside forms a helix, and its length is extended by 3.1 cm. The Young’s modulus of steel is approximately 200 GPa. Given this Young’s modulus, the strain induced by the elongation results in a stress of 100 MPa at the edge. This is something that should be considered before implementing a twisted strip in a production line, since it may be undesirable to subject a production strip to such stress. It may be considered to use a twisting angle of less than 180°.

In order to prove the concept of twisting the strip, a scaled down test model was built. It is shown in figure 15. A strip with the dimensions 2m $\times$ 0.04m $\times$ 0.0005m is put under tension. Except for the thickness of the strip, this is a scaling of 20 : 1 (the real strip has a thickness of 1 mm). The strip was excited by a single impact of a pendulum, which was then immediately removed.

In order to measure the vibration, a diode laser was used. This laser is pointed at a small mirror near the bottom of the strip. The laser beam is then reflected towards a gridded paper sheet, where the laser spot is recorded with a camera, operating at a recording frequency of 24 Hz. Results are shown in figure 16. The string mode causes a deflection of the laser spot in the vertical direction, and the twisting mode causes a deflection of the laser spot in the horizontal direction. The flapping mode is not measured by this technique.
Figure 15. Photograph of the scaled-down experiment.

Figure 16. Measured trajectories of the laser spot during the twist experiment. The strip vibration frequency exceeds the recording frequency, such that each frame shows a path rather than a spot. Left: typical screenshot of an untwisted strip. Right: typical screenshot of a strip that was twisted by 180°.

Analysis of the recorded amplitude as a function of time shows that increasing the twist of the strip up to 180° results in the decrease of the amplitude of the twisting mode in comparison with the amplitude of the string mode. The amplitude of the string mode is virtually unchanged by the twisting. In typical spectra, the relative importance of the string mode, as compared to the twisting mode, was greater for the twisted strip than it was for the untwisted strip. In other words, we have observed that the twisting mode almost disappeared in a twisted strip. Surprisingly, no significant differences between a 90° twist and a 0° twist were found. It was found that the fundamental of the string mode exists even if the strip is twisted 180°: the strip displacement rotates along with the strip.

The analysis reported here was carried out by simple visual inspection of recorded videos.
Spectrum analysis of a high-speed camera recording of the spot trajectory would give a more detailed insight in the actual physics at work, and this may be an interesting follow-up experiment.

9. Conclusions and outlook

Four possible solutions were proposed to mitigate the vibration of a steel strip during hot dip galvanization. The gas wiper nozzle shape might be altered by increasing the nozzle width; this could bring the galvanization process in a regime where vibration of the strip does not affect the resulting zinc thickness as strongly. The rolls might be passively damped. The optimal damping on the stabilization roll of 500 kg was calculated to occur when using a spring with $k = 300$ N/mm, with a viscous damping of $12000$ N s/m. Some actively controlled feedback systems were also described. These could also work as feasible damping mechanisms, though this requires care, especially because the system must work continuously without failure in a quite hostile environment. Finally, the possibility of twisting the strip around its axis was considered. We have estimated that for a 2 m wide (or narrower) strip, the tension induced by a rotation of 180° or less does not exceed the yield strength of the steel. Experimentally, twisting the strip was found to reduce the twisting mode of vibration and slightly increase the damping of the initial vibrations of a scaled-down model consisting of a steel strip that was struck by a pendulum. However, the “string mode” vibrations still exist. In general, great care should be taken before implementing any of these ideas on a production line, due to the large financial interests in continuous high-quality production. Nevertheless, this work should provide several interesting opportunities to further optimize the hot dip galvanization process.

10. References


[2] Our code is based on https://gist.github.com/tobin/2843661, see Appendix A for our code.


Appendix A: Matlab code for strip coordinate prediction

clear all;

N = 3300; % Order of LPC auto-regressive model
P = 4300; % Number of samples in the extrapolated time series
M = 3300; % Point at which to start predicting

t = 1:P;

over=load('over9000.csv');
over2=load('fullset.csv');
x = over2(1:39001:43300);

a = arburg(x, N);

y = zeros(1, P);
y(1:M) = x(1:M);

 [~, zf] = filter([-0 a(2:end)], 1, x(1:M));

y((M+1):P) = filter([0 0], -a, zeros(1, P-M), zf);

h1=figure;
plot(t, x, ... % signal
t, y, ... % extrapolation
t, x - y); % difference
l = line(M*[1 1], get(gca, 'ylim'));
set(l, 'color', [0,0,0]);
grid on;
legend('actual signal', 'extrapolated signal', 'error','start of extrapolation');
axis([1000 4300 35 45]);
print(h1,'-depsc2','3300-up.eps')

h2=figure;
plot(t, x, ... % signal
t, y, ... % extrapolation
t, x - y); % difference
l = line(M*[1 1], get(gca, 'ylim'));
set(l, 'color', [0,0,0]);
grid on;
legend('actual signal', 'extrapolated signal', 'error','start of extrapolation');
axis([1000 4300 -5 5]);
print(h2,'-depsc2','3300-down.eps')
RGS Development

Advanced solid state materials for thermoelectric power generation

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1. Abstract

In this report, review of current state-of-the-art has been performed for the optimization of the thermoelectric properties of HMS (Higher Mangenese Silicide) MnSi₁₋₃ material class. Following the phonon-glass electron-crystal theory, different types of dopants are discussed for increasing the electrical conductivity of the material. Furthermore, band structure calculated by first principles gives not only good predictions in electrical conductivity, but also important information on n- and p-type semiconductor transition induced by doping. Most importantly, we point out that crystal structure can influence thermal conductivity significantly. By cooperation of nano particles with the mold, significant reduction in thermal conductivity of the crystal can be expected. This is due to the formation of smaller sized crystals in the sample which increases the phonon scattering. Taking these aspects into account, HMS shows many promising prospects as a new type of thermoelectric material in the coming future.

2. Company profile

RGS Development BV operates a cutting edge silicon tape casting technology that allows the lowest cost manufacturing of silicon and silicon composite sheet materials. The company develops custom silicon solutions in order to harvest the excellent properties of silicon in high tech energy materials. RGS Development BV offers application development programs, technology transfer, technology services and initial production capacity in various fields of applications. RGS Development BV is active in: Energy Storage, Thermo Electrics, Membrane Technologies, Solar Photovoltaics and Structural Silicon Composites. RGS Development BV was founded in 2000 as technology start-up from the Energy Research Centre of the Netherlands-ECN.
3. Problem description

Thermoelectricity is a promising source of electric power, thanks to its ability to locally scavenge energy by converting a heat flow in electricity, when placing a thermoelectric device in a persistent thermal gradient. However, the major barriers to mass commercialization of this technology are the poor performance and the high costs of the materials used today. A good thermoelectric material must have a high Seebeck coefficient (high conversion of heat to electricity) to produce the required voltage, a high electrical conductivity to reduce current transport losses, and a low thermal conductivity to reduce thermal losses. Nano-structured semiconductor materials are believed to provide the necessary breakthrough in material properties that will enable the large scale use of thermoelectric power generation. The challenge is to tune materials in a way that they behave as electronic crystals (high electrical conductivity) in combination with a phonon glass (low thermal conductivity). RGS Development BV is producing materials based upon a metallurgical process growing eutectic structures from the liquid state. In these ‘two phase’ materials, a metal-silicide phase is mixed within a silicon phase with phase dimensions in the nm to um scale. The phase boundaries between the two materials impact phonon and electron transport properties and can thus be used to tune the material appropriately. The challenge is to provide more insight in the behavior of these phase boundaries on electronic and phonon characteristics in a material. For this purpose a very promising thermoelectric material is chosen (manganese-silicide / silicon), which has been produced by RGS Development BV and characterized by the Fraunhofer Institute for Physical Measurement Techniques in Germany with very promising results. Based upon literature research on the materials involved and analytical models that have been developed to describe semiconductor and interface properties the basis for a qualitative understanding of the material will be laid. This work will be supported by experienced scientist in the field of electronic properties of semiconductors as well as phonon properties. The objective of the week will be to achieve a deeper understanding of the properties of mixed semiconductor nanomaterials using the technically very relevant MnSi_{1.73+x} Si material class as example.

Input

RGS Development BV will provide a detailed introduction to the problem and an incomplete literature overview. In co-operation with academia presentations on the state-of-the-art know how on electronic and phonon properties of nano-structured semiconductors will be given. Based upon the know-how presented in the introduction, the literature know-how base will be
deepened by literature research. This know-how will then be applied on the MnSi-Si system e.g. by developing modeling software or executing analytical calculations with the objective to gain a qualitative understanding of the material for further improvement. Scientist from RGS Development BV will be present during the week to provide a direct feedback to questions and discussion of results.

4. Basic theory

The thermoelectric effect is the direct conversion of temperature differences to electric voltage and vice versa. A thermoelectric device creates voltage when there is a different temperature on each side. Conversely, when a voltage is applied to it, it creates a temperature difference. At the atomic scale, an applied temperature gradient causes charge carriers in the material to diffuse from the hot side to the cold side. For n and p type semiconductors, charge carriers are electrons and holes respectively. And so on arranging the p and n type semiconductor as shown in the Fig. 2, one can generate e.m.f. in the circuit.

Figure 1. Thermoelectric device for exhaust gas applications.

Figure 2. Thermoelectric generator
The figure of merit of such a system is given in equation 1.

\[ ZT = \frac{\sigma S^2}{\kappa} T \]  

where \( \sigma \) is electrical conductivity, \( \kappa \) is thermal conductivity, \( T \) is temperature (in K) and \( S \) is Seebeck coefficient. The Seebeck coefficient is reported in equation 2 and is given by the parabolic band, energy-independent scattering approximation:

\[ S = \frac{8\pi^2 k_B^2}{3\hbar^2} m^* T \left( \frac{\pi}{3n} \right)^{2/3} \]  

The electrical conductivity (in classical Drude’s model) can be written as:

\[ \sigma = ne\mu \]  

and the thermal conductivity can be divided in electronic and phononic parts

\[ \kappa = \kappa_e + \kappa_{ph} \]  

The Wiedemann-Franz law express the ratio of the electronic contribution to the thermal conductivity to the electrical conductivity of a metal (5).

\[ \kappa_e = L_0 \sigma T \]  

where \( L_0 = \) Lorentz factor \( 2.4 \times 10^{-8} \) J\(^2\) K\(^{-2}\) C\(^{-2}\) for free electrons, \( m^* \) is the effective mass of our system, \( \mu \) is the mobility of electrons and \( n \) is electronic charge density. However, this does not fully apply for our system made of alloy of doped semiconductors.

### 4.1 Key Parameters

The key parameters that one can play with to improve the figure of merit of the system are electrical conductivity(\( \sigma \)), thermal conductivity by phonons(\( \kappa_{ph} \)), effective mass(\( m^* \)) and charge carrier density(\( n \)). The electrical conductivity is governed by charge carrier density(\( n \)) and electron mobility(\( \mu \)).

### 4.2 RGS measurement results

The MnSi\(_{1.73+x}\) sample prepared by RGS(Ribbon-Growth on Substrate) technology is measured for resistance and Seebeck coefficient values and is found to be in the range of currently present thermoelectric materials as shown in Fig. 3. These values also indicates that there is still room for improvement by playing with the key parameters mentioned above. Fig. 4 shows the crystal growth struture of the MnSi\(_{1.73+x}\) sample near the nucleation points on the substrate. One can see that near the nucleation spots (where the heat transfer from the sample to the substrate takes place), the crystals structures are smaller in size (around 1 \( \mu m \)) and it grows bigger as it moves away from the nucleation points.

### 5. Problem solving strategy

The main figure of merit for thermoelectric generators is defined as equation 1. For increasing the figure of merit of our system we have to play with both electrical and thermal transport properties of the system. So, based on this we divide our focus is these two directions and look for solutions for the MnSi(2-x) class.
5.1 Doping and crystal structure

Material structure

The MnSi$_6$ is grown from a melt. By changing the ratio of Mn and Si atoms in the melt one can influence which phases will crystallize and in which form and ratio they will grow. The material which is desired is MnSi$_{1.7}$ but this cannot be grown purely because this is restricted by form of the phase diagram. One option is to grow from the eutectic point and precipitate MnSi$_{1.7}$ and Si simultaneously. The other possibility is to increase the Mn concentration to the 1-1.7 ratio, but this will case the MnSi phase to appear. Both scenarios have potential advantages and disadvantages. The MnSi is a very good electrical conductor but also a good thermal conductor. It’s presence however can be helpful when it forms nano domains [6]. Also, the eutectic growth mechanism can create an intricate grain boundary network which can scatter phonons. Other contaminants such as C in the melt may precipitate at the grain boundaries in combination with Si.

It is possible to replace some atoms in the crystal lattice with another element to enhance the...
### Table 1. possible dopants for MnSi$_{1.7}$

<table>
<thead>
<tr>
<th>Dopant</th>
<th>optimal concentration (atomic)</th>
<th>best ZT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.0015</td>
<td>0.65 @ 800K</td>
</tr>
<tr>
<td>Ge</td>
<td>0.01</td>
<td>0.7 @ 800K</td>
</tr>
<tr>
<td>Cr</td>
<td>0.03</td>
<td>0.65 @ 800K</td>
</tr>
<tr>
<td>Fe</td>
<td>0.1-0.3</td>
<td>lower ZT but n-type</td>
</tr>
</tbody>
</table>

properties of the material. For this purpose it is usually most favorable to chose an element from the same column of the periodic table if you want to keep the electronic properties the same, or from a column to the left or right of the original element to accept or donate an electron respectively. The substitution on a lattice site can also influence phonon scattering or the phase diagram. For example, addition of Ge to the melt will suppress the formation of the MnSi [1] phase making it possible to make a pure MnSi$_{1.7}$ crystal, albeit doped with Ge. Adding Fe to the melt in high concentrations can cause the resulting material to have a Seebeck coefficient with opposite sign, signifying the change of p-type to n-type material [3]. This is significant because for a thermoelectric device it is favorable to have both types of material. When adding a dopant it is necessary to re-optimise the relevant parameters for the material. The new optimum can be better in terms of the than the undoped case. A complete list of all possible dopants and corresponding references is given in the handbook of thermoelectrics chapter 31 and is summarized in Tab. 1 with values for the optimal dopant concentration.

### Material properties

It is very important to accurately know and understand the properties of the materials which can be made. The addition of dopant materials to the melt and the different crystal phases which are available to us will all have different electronic and thermal properties. Understanding the Seebeck coefficient, charge mobility, carrier concentration, effective mass and phonon thermal conductivity and how they depend on one another and on temperature is necessary to find the optimal configuration and optimal operating temperature. At the moment these curves are not known to us. However, we do know that our material does not follow the ideal curve shown in section 1 so that changes have to be made. For example, the expression given for the Seebeck coefficient is not valid in the whole range of carrier densities and does not even give rise to a maximum in $ZT$. Ref. [10] gives a more elaborate description and may be able to describe the material properties more accurately.

One of the material properties which is important and which has been seen to deviate from the ideal value is the charge mobility [5]. A hypotheses for this deviation is the presence of cracks or voids in the material which may have been formed by mechanical stress between the crystal phases which has occurred during the cooling stage because of a difference in the coefficient for thermal expansion. Features like this may have been seen in microscope images although they have not yet been positively identified. The literature confirms that defected materials exhibit a much lower mobility than ideal systems [8]. Since a decrease in the mobility directly translates into a lower conductivity, this is an important problem. An idea which has been proposed during the week is to apply an annealing stage after production. This stage must be long enough to heal cracks and transport dislocations, but must be not influence the general phase structure of the material since this is one of the mechanisms to scatter phonons. In short, the annealing step must increase the charge conductivity whilst keeping the thermal conductivity suppressed. We believe that there is an intermediate annealing step which meets these criteria.
5.2 Hindering the thermal conductivity

Thermal conductivity in crystalline solid materials can be described by separating electron $k_e$ and phonon contributions $k_{ph}$.

$$ k = k_e + k_{ph} \quad (6) $$

To improve the figure of merit of our material we need to lower the thermal conductivity while keeping the electrical conductivity almost unaltered. For this reason we have to focus on the phononic contribution only. Low thermal conductivities are characteristic of glassy materials. In such materials phonon scattering is maximized by the anisotropic and disordered aspect of the atoms arrangement. Unfortunately, the transition to a glass phase has a dramatic effect in reducing also the electrical conductivity. Different approaches have been reported in literature to target this goal at different lengthscales: atom substitution, nanostructuring and grain boundary maximization. [7, 4, 13] In particular, the possibility to realize nanostructures that maximize phonon scattering at particular energies (phonon glass) attracted new research interest in the field of thermoelectric materials [7]. This approach has been successfully applied with many materials to improve the figure of merit lowering the thermal conductivity while leaving the electrical conductivity unaltered [16]. Fig. 5 shows the examples of nanostructured Si and Si-Ge.

![Figure 5. (color online) Thermal conductivity of nanostructure Si and with Ge doped nanostructure Si. From ref. [16]](image)

Thermal conductivity is connected with the phonon lifetimes time according to the Matthiessen’s rule [14].

$$ \frac{1}{\tau} = \frac{1}{\tau_{e-ph}} + \frac{1}{\tau_b} + \frac{1}{\tau_m} + \frac{1}{\tau_u} \quad (7) $$

where $\tau_{e-ph}$, $\tau_b$, $\tau_m$, $\tau_u$ represent the phonon lifetimes in respect to the different scattering processes that are reported in Fig. 6.

Phonon lifetimes depends also on the phonon energy. This is because phonons with different wave-lengths are scattered optimally at particular length scales. Defined the temperature there will be an optimal compromise of the material meso and nanostructure to have the best effect in phonon scattering. This can be seen in Fig. 7 that shows how different phonons contribute to the final thermal conductivity. To improve the phonon scattering we have thus to think how to structure our material at different length scales: micrometric, nanometric and atomic scale.
In this terms we decided to focus the material structure optimization on the following aspects:
- boundaries
- unit-cell periodicity mixing
- changes in crystal orientation
- change in material density

Umklapp processes are the main responsible for the reduction in the thermal conductivity at temperatures higher than the Debye temperature of the material. Improving the umklapp scattering cross section can thus have a strong effect on the thermal conductivity. Umklapp type scattering can for example be favored by sudden changes in unit cell inside the material. In this regard \( \text{MnSi}_{1.7} \) is a very good material due to the large unit cell periodicity variations induced by slight changes in the local Si-Mn ratios (see Fig. 8). Scattering from boundaries depends instead on the grain size of the crystals and from the inter-phase mixing. At the same
time differences in density inside the material can give the mass-effect for phonon back-reflection.

Figure 8. (color online) unit cell periodicity variations between slight changes in the local Si-Mn ratios

RGS MnSi is grown in a Eutectic regime where multiple phases are intermixed in precise ratios. This effect is important to improve the thermoelectric characteristics of this material by favoring density and unit-cells fluctuations together with a large number of boundaries that can act as phonon scattering centers. What can we improve more?

Looking at the cross section of a MnSi – Si sample Fig. 9 we noticed that the phase separation during the growth generate features with characteristic micrometric sizes. We do not have experimental informations about the atomic scale disorder and unit-cell periodicities present. However, it is clear that the structuring at the nanometric scale can still be improved.

Figure 9. (color online) SEM image of MnSi_{1.7} cross-section.

Our solution involves the use nanoparticles during the growth of the material in order to modify the final material structure. Dispersing nanoparticle in the Si and Mn liquid melt we
expect to achieve different final advantages:
- scattering centers for the phonons at the nanometric scale: 20 nm nanoparticles
- favor the nucleation of new grains and reduce the size of the Eutectic features
- promote the formation of fractal structures to have multi-scale scattering centers
- renucleation may lead also to an improved unit-cell mixing and material stability

5.3 Tuning the growth

We use the well-known ribbon growth on substrates (RGS) process to produce MnSi$_{1.7}$. The principle of the process is explained as follows (Fig. 10): The relatively cold substrate extracts the crystallization heat from the liquid silicon in the casting frame. This causes the growth of the silicon ribbon on the substrate in the vertical direction (Vc) perpendicular to the material transport direction (Vp). By transporting the substrate (Vp) from the casting zone into the cooling down section, crystal growth stops, the wafer can be removed and the substrate can be re-used. This process has the ability to do fast solidification of metal silicide and metal silicide-silicon composite eutectic structures. The solidification velocity in conventional batch casting processes (Bridgman, CZ) is limited by thermal conduction of the solidification heat through the already solidified material. In such processes solidification is relatively close to thermodynamic equilibrium. In this process, larger deviations from thermodynamical equilibrium can be achieved by faster solidification (in the order of 1 mm/sec) and nucleation effects, where heat transfer and nucleation are controlled by the substrates material properties on which is casted. The thermal material properties of the substrate and the quality of the thermal contact, together with the melt composition define the growth speed of the solid sheet and the microstructure.

![Figure 10. (color online) The schematic principle of the growth process.](image)

MnSi$_{1.7}$ crystal features from the cooling side are visible from Fig. 4. As can be seen from the figure, there are very fine structures with typical size less than 1 $\mu m^2$ close to the nucleation area. However, as the solidification progresses, large dendritic structures start to appear. At the same time, needle-like Si structures with size of 5x100 $\mu m^2$ are observed as well due to the slow crystal growth. All these microstructures will be beneficial with respect to reducing the thermal conductivity by increasing phonon scattering. However, phonon scattering by microstructures are not sufficient to greatly reduce the thermal conductivity [2]. Referring to Fig. 7, nanostructure and atomic structure can also scatter phonons with different wavelengths (mean free paths) [17]. Here, in this session, we will focus on how to introduce nanostructures into our MnSi$_{1.7}$ films by tuning the solidification process.

Solidification starts at the contact point between the liquid bath and substrate [17]. Initially, a thin layer of fine grains will be formed. Among these fine grains in this thin layer, only a few grains will grow as stable columnar dentrites due to competitive growth between them. The direction of these columnar dentrites will depend on the heat flow in our process. As the
solidification progresses, equiaxed grains formed ahead of the columnar front. The equiaxed grains are randomly oriented, leading to a greater tip undercooling than the existing columnar dentrites. Eventually, the more and more equiaxed grains start to grow in front of the columnar dentrites. When the equiaxed grain growth fully block the growth of columnar dentrites, the solidification process changes from columnar to equiaxed growth. The whole process is shown in Fig. 11. The grain size during the solidification process can be influenced by the competing process between columnar and equiaxed growth. Adding particles into the liquid bath will both increases the density of nuclei and reduces the activation energy. As a result, the transition from columnar to equiaxed growth will happen at extreme low growth rate. In such manner, the grain size can be significantly reduced.

Figure 11. (color online) Simulation of columnar to equiaxed transition in solidification process [17].

5.4 Nanoparticle selection

Not all nanoparticle can be used to achieve our goal. We need to satisfy precise requirements:
- temperature stability (melting point 1500 °C)
- good dispersion inside liquid Si and Mn
- do not react with Si and Mn
- has the right size and shape
- improves the nucleation probability by lowering the undercooling temperature of at least one of the possible phases
- low cost and available materials

First of all we excluded the metallic nanoparticles due to the high reactivity and the probable dissolution or compound formation in the Si – Mn4 liquid at elevated temperatures. Between the commercially available compounds in table 2 are summarized possible candidates to satisfy our requirements.

<table>
<thead>
<tr>
<th>material</th>
<th>melting p. (°C)</th>
<th>reactivity</th>
<th>Egap (eV)</th>
<th>density (g cm⁻³)</th>
<th>size range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>2050</td>
<td>low</td>
<td>&gt; 6</td>
<td>4.0</td>
<td>5nm – 2μm</td>
</tr>
<tr>
<td>Si₃N₄</td>
<td>1900</td>
<td>low</td>
<td>&gt; 5</td>
<td>3.1</td>
<td>20nm – 5μm</td>
</tr>
<tr>
<td>BN</td>
<td>2970</td>
<td>-</td>
<td>&gt; 6</td>
<td>2.1 – 3.4</td>
<td>100nm – 4μm</td>
</tr>
<tr>
<td>C</td>
<td>&gt; 2000</td>
<td>SiC</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2. Nanoparticles evaluation to add to the melt of liquid Si.
The most promising are the top 3. In particular $A_2O_3$ is a particularly inert compound that has affinity with Si and it should disperse without problems in the melt. $Si_3N_4$ particles are also interesting but it might be difficult to disperse. Boron nitride BN can be also an interesting alternative. From the reactivity point of view we could only exclude $TiO_2$ due to the explosive reaction with $Mn$ at elevated temperatures, while for other compounds we could not find information regarding their affinity with $Mn$. Carbon compounds are not so promising due to the high carbon solubility in $Si$ and the formation of $SiC$. If this decomposition problem could find a solution all organic-metallic molecular compounds could give an easy access to structure tuning at the low nanometer range (0.5 – 5) nm due to the possible precise engineering of molecular geometries.

6. DFT calculations

6.1 Band structure of $Mn_{3.75}Fe(Cr)_{0.25}Si_7$ and $Mn_{4}Si_{6.75}C_{0.25}$

As discussed in Chapter 5, doping can have a significant effect on the band gap, therefore, influencing both the carrier mobility and Seebeck coefficient. Using first principles, electronic structures such as band gap can be calculated.[15] Based on band structure calculated from DFT(density functional theory) and combining Boltzmann transport equations, predictions can be made on the conductivity and Seebeck coefficient after doping. We performed DFT calculations on $C$, $Fe$, and $Cr$ substituted $Mn_{4}Si_{7}$ to investigate the doping effect. The choice of doping is due to the following considerations. First of all, carbon is one of the impurities included in the growth process, since it is used as crucible. Therefore, a small doping of carbon is desirable in the calculation. Secondly, $Fe$ and $Cr$ are two transition metal elements located next to $Mn$ on the periodic table. Experimental studies show that doping $Fe$ and $Cr$ can alter the conductivity of $Mn_{4}Si_{7}$.[11] Especially for $Fe$, doping can result in change from P type to N type semiconductor.[9] Therefore, they are highly interesting for fine tuning the electrical property of manganese silicide.

The band structures of $Mn_{4}Si_{6.75}C_{0.25}$, $Mn_{3.75}Fe_{0.25}Si_{7}$, and $Mn_{3.75}Cr_{0.25}Si_{7}$ alongside the undoped $Mn_{4}Si_{7}$ is calculated using DFT in Fig. 12. Comparing to the band structure of $Mn_{4}Si_{7}$, $Mn_{4}Si_{6.75}C_{0.25}$ shows no significant change in band gap. However, both $Mn_{3.75}Fe_{0.25}Si_{7}$ and $Mn_{3.75}Cr_{0.25}Si_{7}$ have a narrower band gap, which explains the change in conductivity.[9, 12] Apart from the narrowed band gap we see in Fig. 12(c) and 12(d), doping $Fe$ and $Cr$ has an opposite effect on the carrier density. While doping $Cr$ reduces the band gap by 0.1 eV, the conduction band remains above the Fermi level. On the other hand, the conduction band of $Mn_{3.75}Fe_{0.25}Si_{7}$ drops below the Fermi level, making it a n-type TE. As result, doping $Fe$ in this amount will decrease the hole density in the p-type $Mn_{4}Si_{7}$.

From the calculations we see that the impurity caused by carbon tends to have a minimum effect on the electrical properties of $MnSi_{1.74}$. On the other hand, doping of transition metals, such as $Fe$ and $Cr$, can have a profound influence on the carrier density. We do notice that there are several discrepancies between the experimentally determined band gap data and the one calculated from DFT.[12] But, we also recognise the effectiveness of theoretical calculation in predicting the trends in carrier density change and conductivity. Even under very limited computational time, DFT provides useful information on the TE property. We expect that combining with Boltzmann transport calculations, optimisation of ZT can be achieved cost-effectively.

7. Conclusions and outlook

From the work done during the Physics with Industry week a number of results are achieved that are helpful to give direction to the further optimisation of the $MnSi_{1.74}$ material that is
Figure 12. Band structures of \( \text{MnSi}_{1.74} \) (a), \( \text{Mn}_{4}\text{Si}_{6.75}\text{C}_{0.25} \) (b), \( \text{Mn}_{3.75}\text{Fe}_{0.25}\text{Si}_{7} \) (c) and \( \text{Mn}_{3.75}\text{Cr}_{0.25}\text{Si}_{7} \) (d). Zero energy is set to the Fermi level. The corresponding band gaps are: (a) 0.8 eV, (b) 0.8 eV, (c) 0.5 eV, (d) 0.6 eV.

produced by RGS Development in the field of thermoelectric applications. It is clear that after the first initial measurement results, the material has to be improved to become competitive. In general the first step in optimisation is the change in carrier concentration using the addition of dopant materials. It could be shown both from literature as also from theoretical bandgap calculations, that the atoms in neighbouring groups to Mn and Si are the potential candidates for this optimisation process. It could also be demonstrated that with the addition of Fe as dopant material, the conductivity can be changed from the p-type of the pure \( \text{MnSi}_{1.74} \) towards an n-type material. This is important for thermoelectric systems as they typically use a combination of n-type and p-type legs of the same material to avoid differences in thermal behaviour and stress formation. In addition it could be shown that carbon, which is one of the main contaminants in the RGS process is not harmful with respect to changes in the electrical properties of the material. With respect to phonon scattering, it is assumed that there are already two different scattering mechanism available in the \( \text{MnSi}_{1.74} \) material, one on a small scale due to impurities and the unit cell structure of the material itself. On the long range micrometer scale, the growth of the silicon and \( \text{MnSi}_{1.74} \) phases could possibly cause phonon scattering by boundary scattering effects. What might be missing is an intermediate scale scattering mechanism on 10 - 100 nm geometric scale. Therefore the material growth process was analysed and a possible concept to initiate crystal growth in the melt before the main crystallisation front was proposed. Such a process could be triggered by seed-particles of a material that is not reacting with the liquid melt. Based upon the results, there are a number of steps possible to improve the material further. As a recommendation to RGS Development a
2-step optimisation process is proposed based upon implementation risk and expected results. The first phase should be to optimise an addition of a dopant to maximise the electrical parameters conductivity and Seebeck coefficient. In a second step phonon scattering should be optimised by adding scatter centres in the missing orders of magnitude between 10 - 100 nm. Whether the proposed concept to add nucleation centres to the melt might work has to be tested in actual experiments. First materials were proposed that could be helpful to start this experimental work. Other interesting fields for improvements, such as crystal quality improvement by annealing, possible crack formation prevention, changes in the silicon-manganese ratio, or addition of non-doping elements such as Ge were noted in the literature or during discussion with RGS Development, however missing material analysis data or less clear conceptual understanding beyond the literature results prevented further insight development during the week. Nevertheless the literature overview on what has been tested and the expectation that future analysis work on the material produced will produce new insights, yield the conclusion that also in these fields, major improvement can be expected. In discussion with RGS Development it was confirmed that the results obtained in this project are very helpful to focus the development activities on $\text{MnSi}_{1.74}$ that are foreseen within the company and thus contribute to a shorter time to market for a competitive thermoelectric material in the important mid-temperature application range.

8. References


Proceedings Physics with Industry 2013


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