ON-LINE CLEANLINESS MONITORING WITH LIBS-BASED SENSOR

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ABSTRACT

To meet galvanised steel customers' high-quality requirements and in partnership with industrial lines Tata Steel SEGAL and ArcelorMittal EUROGAL, a new on-line equipment has been developed by CRM Group and Sarclad Ltd. Based on the Laser-Induced Breakdown Spectroscopy technique, this system measures the strip cleanliness at the exit of the cleaning section of galvanising lines. One of its main benefits is its ability to differentiate between iron fines and surface carbon pollutions, even for low levels. With the data sent to the plant, several process parameters can then be optimised to increase the surface quality of the product, to reduce the energy consumption and maintenance operations in the furnace and the bath: electrolysis current level, degreasing bath concentration, brushes pressure, …

In the first part of this paper, measurements obtained on galvanising lines to validate the industrial demonstration unit will be presented. The second part will focus on the achieved work to transform this unit into a fully industrialised and commercial solution.

KEYWORDS

On-line cleanliness, LIBS characterisation, galvanisation, iron fines, carbon pollution.

1. INTRODUCTION

Galvanisers have long been looking for a way to measure the residual contamination of the substrate surface accurately and reliably at the exit of their cleaning section. This is indeed a key parameter for the quality of coated steel, especially in the automotive sector where there should be no aspect defect.

The contamination sources are various, but two main pollutants are generally mentioned: surface carbon from mill oil and iron fines. In the long term, carbon will turn into soot in the furnace, reducing its efficiency, and will eventually fall onto the rolls and the strip. Iron fines can create pick-up defects on the rolls and increase the dross content in the zinc bath by combining itself with zinc and aluminium, leading to a drift in the bath composition. In addition, all these problems can result in aspect defects on the final product.

If residual contaminations are continuously monitored on-line, corrective actions can be planned before being forced to downgrade a whole production due to aspect defects. In addition, if the contamination source can be differentiated from the others, its cause can be quickly identified and eliminated by making targeted corrections to the cleaning section.

CRM Group has therefore developed a new on-line equipment able to differentiate between iron fines and surface carbon pollutions. This equipment uses a Laser-Induced Breakdown Spectroscopy (LIBS) method developed and patented by CRM Group [1]. It can be placed at the exit of a cleaning

section in galvanising lines to measure the residual contamination levels. This paper describes the carried-out work to achieve this on-line monitoring with a non-contact LIBS-based sensor.

2. MONITORING CLEANLINESS WITH LIBS

The Laser-Induced Breakdown Spectroscopy is a non-contact spectral analysis technique. It has many applications in geology, metallurgy, and other physical sciences. Over the years, it has been implemented in several industrial environments provided a robust design as well as adequate protective equipment against the harsh external conditions (temperature, humidity, dirt, …).

In galvanising lines, two major contamination sources to be monitored are the surface carbon coming from the mill's oil and the iron fines. Being able to differentiate both sources is highly valuable to galvanisers, as the causes of an increase in pollution levels are not the same for surface carbon or iron fines.

2.1. Laser-Induced Breakdown Spectroscopy quick-start guide

A short-pulsed laser beam with a very high energy density is delivered to the surface being analysed through a focusing lens. That energy is sufficient to ionise matter and create a high-temperature plasma around the laser impact. Inside the plasma, electronic transitions occur continuously, powered by the laser beam energy. When dropping from an energised state back to a lower layer, an electron emits a photon at a specific wavelength given by the *Planck-Einstein relation*:

$$E = h\nu = hc / \lambda \tag{1}$$

Where E is the photon's energy in Joules (J), h is the Planck constant in J·s, ν is the photon's frequency in s^{-1}, c is the speed of light in m/s and λ is the photon's wavelength in m. In an electronic transition, E is simply the energy difference between the energised state and the layer where the electron stops. The set of wavelengths emitted by a chemical element is called its emission spectrum and uniquely identifies it. The electromagnetic range covered by the lines in such a spectrum can extend from UV to visible and infrared.

Molecular vibrations and rotations can also occur in the plasma, due to thermal agitation. In this case, photons are emitted in molecular bands i.e., groups of lines so closely spaced to each other that they all appear as a single band.

All these wavelengths come out of the plasma in all directions with the intensity being maximal at an angle perpendicular to the surface where the plasma was created. In the Laser-Induced Breakdown Spectroscopy, this emitted light is then collected and directed by an appropriate combination of lenses and mirrors to an optical fibre. The fibre transmits the light to a spectrometer and all the information it carries about the elements present in the plasma can be analysed.

2.2. Differentiating surface carbon from iron fines pollution

Since selecting lines in the UV range of the spectrum would impose higher constraints on the choice of optical elements, the chosen lines must lie in the visible range. In a LIBS spectrum, iron emits a lot of lines while most carbon lines are found in the UV range. The remaining visible lines for carbon are either not sensitive enough or squeezed between two large iron lines.

To tackle this problem, the solution was to create a 100% nitrogen atmosphere around the plasma. The carbon and nitrogen thus recombine into cyanide radicals CN. These radicals emit a line in the visible range around 388 nm which is sensitive enough and isolated from other lines. To make up for the random intensity variations between spectra related to plasma behaviour but not to pollution variations, the surface carbon is monitored via the ratio of the CN line and one of the nitrogen lines.

Likewise, the monitoring of iron fines contamination is achieved with a ratio of two iron lines. They were selected by a laboratory procedure developed by CRM Group and described in [1]. The chosen iron lines gave the best correlation with the iron fines levels on reference samples.

2.3. Overview of the demonstration unit

CRM Group and Sarclad Ltd. developed and built an industrial demonstration sensor shown in Fig. 1 and based on the LIBS technique described above. The objective of this equipment is to measure the residual contamination levels on the strip at the exit of the cleaning section in galvanising lines. Both surface carbon and iron fines contaminations are considered.

It features a Nd:YAG Q-Switched laser with a pulse energy of 70 mJ at 1064 nm. The repetition rate is 20 Hz for a typical pulse duration of less than 7 ns. At the other end of the system, a high-resolution spectrometer with a 4096-pixel CMOS detector is used. It spans a wavelength range starting from ~330 nm to ~590 nm.

The laser beam is focused through a set of diverging-converging lenses. Thanks to the combination of a very precise translation stage and a distance sensor, the focal point is always maintained at the surface of the strip, even if its thickness changes.

The casing of the sensor head has been designed to be water- and dust-tight. The whole system is kept at room temperature with a chilling unit. The flow of nitrogen can be controlled with some electro-valves. Safety equipment like ultrasonic sensors have also been added.

A spectra acquisition and analysis software has been developed by CRM Group. It outputs two monitoring signals: one for the surface carbon and one for the iron fines. It also controls the different components of the sensor head and continuously checks if all the conditions to safely operate the unit are met.
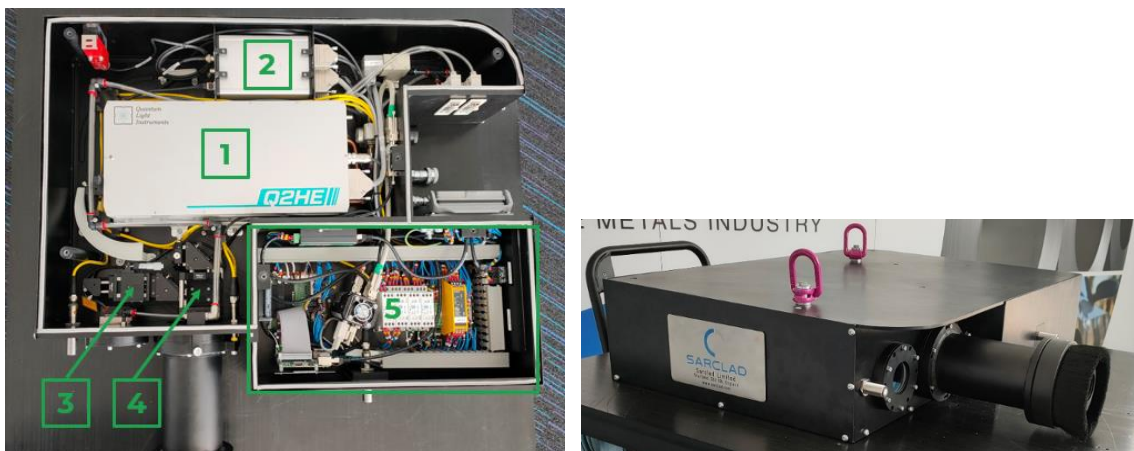

Fig. 1. LIBS demonstration unit with (1) the laser (2) the laser controller and the spectrometer (below) (3) the laser beam focusing unit (4) the light collecting unit and (5) the electronics box

3. CORRELATING LIBS WITH POLLUTION LEVELS

The LIBS demonstration unit does not provide a direct measurement of the contamination levels on the strip. Previous works [1], [2] showed however a significant linear correlation between the LIBS values and both the iron fines and surface carbon contents in the range of interest for galvanising lines. Once it has been established by the procedure described below, applying such a correlation to the LIBS unit's output signals yields the residual pollution levels on the strip at the exit of the cleaning section.

3.1. Procedure for turning LIBS measurements into actual contamination levels

In this procedure, measurements from the LIBS unit are compared against reference measurements for different levels of contamination. A linear fit is then computed using the Least-Squares method, along with the coefficient of determination r^2. To achieve the best correlation, a reliable and field-proven reference method must therefore be chosen.

The swabbing test, or any other known variants of the 'scotch-tape' method, is nowadays one of the most widespread among galvanisers. It is a very simple technique to quickly assess the cleanliness of a strip. First, a moistened tissue with isopropyl alcohol or a clear tape is rubbed onto the strip surface. Second, the pollution can be measured in laboratory in the former case or, in the latter case, visually compared to other contaminated tapes which act as baseline 'standards'. The first step is usually performed when the line is idle but there exist handheld devices which can apply the tissue onto the scrolling strip.

While being fast and easy, the 'scotch-tape' test lacks repeatability, is heavily dependent on the operator performing the action of rubbing or the visual comparison with the baseline 'standards', is most of the time an 'all-or-nothing' measurement, cannot differentiate between iron fines and surface carbon, is highly discontinuous and only gives at best an averaged value of the pollution level over a relatively large surface of the strip with a very large standard deviation. Moreover, when analysed in laboratory, some methods can be sensitive to the chemical composition of the fabric itself. In other words, the only purpose of this test is to have a quick and very rough estimation of the strip contamination, but it cannot be used as a reliable reference method.

Transferring the pollution from the strip to another substrate inevitably induces loss of information in the process, causing a bias in the measurement. A better approach is thus to measure the contamination directly on the steel substrate or to reduce the loss of information to a minimum during the transfer. This must be done in a laboratory, with a controlled environment, on metallic samples picked from the strip. The samples must be properly packaged and handled with care to avoid external contamination. It takes therefore more time than the 'scotch-tape' test, but the results are more reliable.

For the surface carbon, it can be done with a combustion-based method. Four 1 x 10 cm² samples are placed in an oven and heated until all the surface carbon has been burnt off. The measured value is the Total Organic Carbon (TOC) i.e., the quantity of surface carbon present on *both* sides of the samples.

For the iron fines, the technique is called Inductively Coupled Plasma (ICP) spectrometry. A 5 x 5 cm² surface on *one* side of the sample is covered with a resin which is then carefully ripped off, dragging the iron fines with it. This mix of resin and iron fines is dissolved into a HCl solution and is fed to a plasma torch. The light coming out of the torch is analysed by a spectrometer, giving the quantity of iron fines that was present on the steel substrate.

Several metallic samples were therefore collected. Most of them were cut from coils that had been processed through CRM Group's Continuous Advanced Surface Treatment pilot line with different cleaning conditions. As a result, they all had various levels of surface carbon and iron fines. Three samples were also picked up on the strip in Tata Steel SEGAL plant at different location: before, in the middle and after the cleaning section.

When possible, each laboratory and LIBS measurement was performed several times. All three methods being obviously destructive, each sample was therefore cut into smaller pieces which were analysed separately. Moreover, in the case of the LIBS unit, one repetition corresponds to the average spectrum of fifty non-overlapping laser shots. This is to account for the various random phenomena taking place inside the plasma and the non-uniformity of the surface contaminations. A laser impact on the surface of the sample being a circle with a diameter of around 2 mm, the total analysed surface for the LIBS per repetition is roughly 1.60 cm².

3.2. Correlation results for surface carbon pollution

Table 1 gives the surface carbon contamination measured on 12 metallic samples with the LIBS demonstration unit and the combustion-based method mentioned earlier, along with the average value µ and the corresponding coefficient of variation (CV). Missing values in the table simply indicate that there was not enough material to replicate the measurement.

Samples A1 and A2 and C1 to C7 are two sets of samples from CRM Group's pilot line, while S1 to S3 were obtained from Tata Steel SEGAL, as explained in section 3.1.

Table 1. Laboratory and LIBS measurements on metallic samples for surface carbon pollution

| Sample | LIBS measurements (-) | | | | | Laboratory measurements (mg/m²) | | | | |
	1	2	3	µ	CV (%)	1	2	3	µ	CV (%)
A1	0.39	0.38	0.38	0.38	1.07	7.53	7.14	-	7.33	2.66
A2	0.45	0.48	0.47	0.46	2.16	14.80	17.04	-	15.92	7.03
C1	1.68	1.70	1.70	1.69	0.40	76.73	87.25	-	81.99	6.41
C2	1.85	1.82	1.82	1.83	0.88	88.48	77.40	88.45	84.78	6.15
C3	2.36	2.40	2.38	2.38	0.66	120.38	122.58	-	121.48	0.90
C4	2.78	2.76	2.89	2.81	1.95	96.80	91.15	89.23	92.39	3.48
C5	2.32	2.21	2.23	2.25	2.14	79.95	82.58	-	81.26	1.62
C6	1.67	1.72	1.68	1.69	1.24	66.15	58.38	58.08	60.87	6.14
C7	1.32	1.32	1.31	1.32	0.18	40.70	39.03	40.10	39.94	1.73
S1	2.81	2.79	2.93	2.84	2.11	94.00	91.80	94.80	93.53	1.36
S2	0.37	0.37	0.39	0.38	3.38	18.30	13.60	12.70	14.87	16.52
S3	0.42	0.51	0.41	0.45	10.36	13.00	11.30	12.50	12.27	5.81

When inspecting the values in Table 1, it can be observed that the average pollution levels range from as low as 7.33 mg/m² up to 121.48 mg/m². The coefficients of variation for the laboratory measurements are below 10.00 %, suggesting some scattering in the data, whereas they are almost all below 5.00 % for the LIBS measurements.
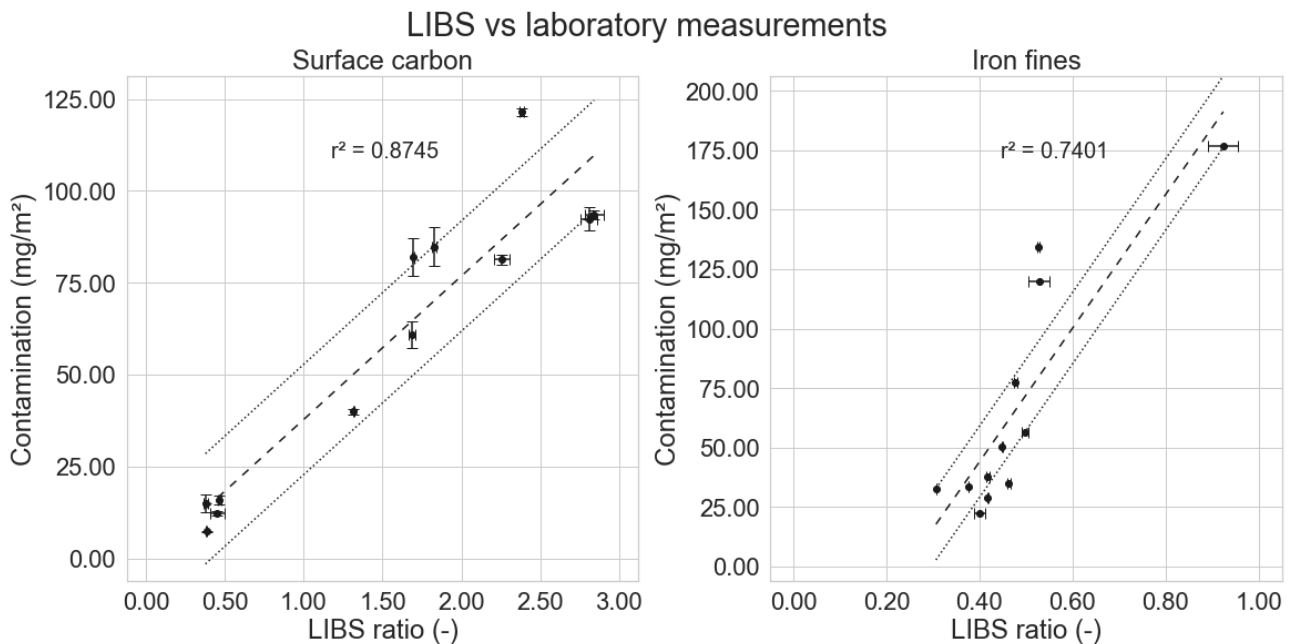

Fig. 2. Correlations between LIBS and laboratory measurements

The coefficient of determination for the correlation shown in Fig. 2 (left) is 87.45 %. The dashed line is the correlation curve while the two dotted lines are respectively offset by -15.00 and +15.00 mg/m². Despite a higher scattering on the laboratory measurements, the linear fit gives a very consistent relationship between the surface carbon pollution on the metallic samples and the LIBS ratio measured with the demonstration unit.

3.3. Correlation results for iron fines pollution

Like previous table, Table 2 gives the iron fines contamination measured on 12 metallic samples with the LIBS demonstration unit and the ICP method. Only one laboratory measurement could be achieved on the samples.

Table 2. Laboratory and LIBS measurements on metallic samples for iron fines pollution

Sample	LIBS measurements (-)					Laboratory measurements (mg/m²)
	1	2	3	μ	CV (%)	1
A2	0.38	0.38	0.37	0.38	0.23	33.52
A3	0.31	0.31	0.31	0.31	0.12	32.80
C1	0.47	0.48	0.48	0.48	0.70	77.58
C6	0.49	0.50	0.50	0.50	1.25	56.23
C7	0.42	0.42	0.41	0.42	1.02	37.79
C8	0.39	0.40	0.42	0.40	3.05	22.17
C9	0.45	0.45	0.45	0.45	0.14	50.12
C10	0.42	0.42	0.42	0.42	0.27	28.89
C11	0.46	0.46	0.47	0.46	0.77	34.77
S1	0.92	0.89	0.96	0.92	3.48	176.85
S2	0.53	0.53	0.53	0.53	0.42	134.17
S3	0.56	0.51	0.52	0.53	4.19	119.87

In this case, the pollution levels range from 22.17 mg/m² to 176.85 mg/m². All LIBS measurements have a CV below 5.00 %, and most of them are even below 1.50 %.

The coefficient of determination for the correlation shown in Fig. 2 (right) is 74.01 %. Again, the dashed line is the correlation curve while the two dotted lines are respectively offset by -15.00 and +15.00 mg/m². The lack of replicates in laboratory measurements clearly weighed down the correlation. But the linear fit still gives a good indication of the relationship between the LIBS ratio and the iron fines pollution measured on the samples.

4. VALIDATING THE DEMONSTRATION UNIT ON TWO INDUSTRIAL GALVANISING LINES

The demonstration unit has been successfully fitted to two galvanising lines, namely ArcelorMittal EUROGAL and Tata Steel SEGAL. Acquisitions have been done in real line conditions at the exit of their respective cleaning section. The laser impacts did not hamper the defect-free galvanisation process. In SEGAL, some parameters of the cleaning section were modified to study the impact on the cleanliness of the strip.

4.1. Industrial measurement campaigns at ArcelorMittal – EUROGAL

The graph on Fig. 3 shows the differentiated monitoring of the surface carbon and the iron fines with the LIBS demonstration unit during one trial at EUROGAL. The leftmost axis gives the

contamination level through the measured LIBS signal while the left and right axes are the converted LIBS signal using the correlations obtained in section 3 for surface carbon and iron fines respectively.

For this trial, the cleaning section was running as usual and acquisitions with the demonstration unit were made to have an idea of the overall pollution level on the strip.
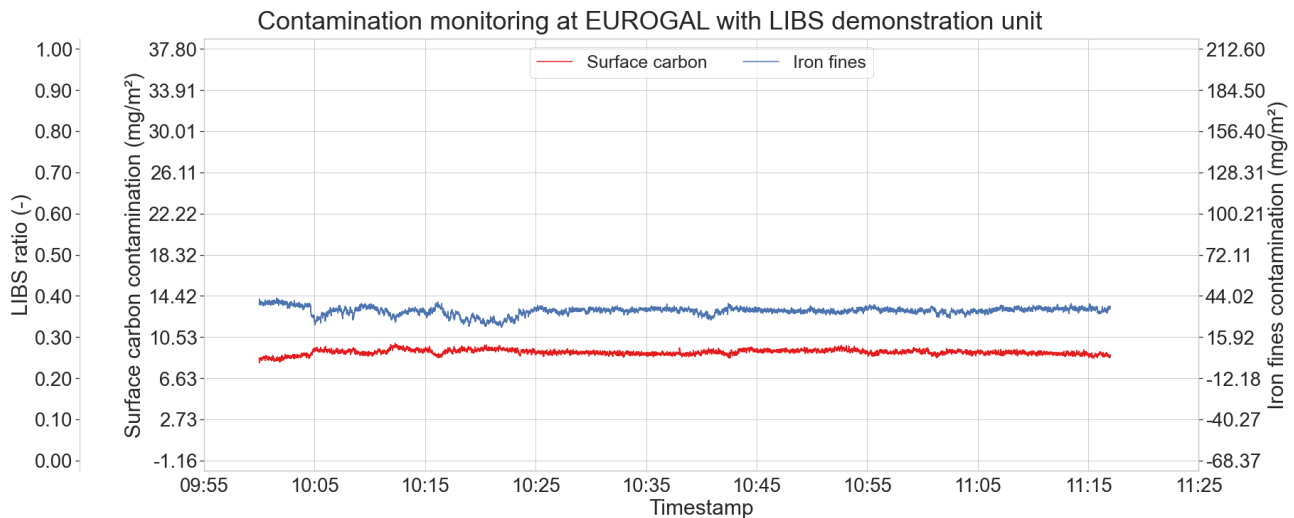

Fig. 3. Results of contamination monitoring trial at EUROGAL

The iron fines contamination is higher than the surface carbon's contamination, but both remain rather stable. The surface carbon content is very low (< 10 mg/m²) but is still picked up by the LIBS demonstration unit. The iron fines pollution is around 40 mg/m².

4.2. Industrial measurement campaigns at Tata Steel – SEGAL

The graphs on Fig. 4 show the differentiated monitoring of the surface carbon and the iron fines with the LIBS demonstration unit during one trial at SEGAL. The leftmost axis gives the contamination level through the measured LIBS signal while the left axis is the converted LIBS signal using the correlations obtained in section 3. The right axes refer to two of the process parameters that have been identified as having the biggest influence on the LIBS signal, namely the line speed in the cleaning section and the electrolysis current.

For this trial, four coils from the same order were processed and four cleaning conditions were tested: starting first with normal operation, the cleaning section was then completely shut off. Spraying was put back on after about 20 minutes. Later, half of the brushes were reengaged while the electrolysis degreasing bath was running at 50% current capacity.

Since the demonstration unit was located after the cleaning section, the effect on the LIBS signal of a change in the cleaning parameters is shifted in time. For example, the two spikes in the surface carbon signal after 12:40 are most probably a consequence of the two-step inversion of the current flow just before 12:40.

Even though all phenomena are not completely understood yet, it is clear that spraying has a huge impact on the cleanliness of the strip. While the surface carbon signal is rising as anyone would expect, the iron fines surprisingly appear to drop when spraying is not activated. Knowing that spraying is the first cleaning step, one possible explanation has been put forward: the degreasing solution that is fed to the sprays is heavily loaded with iron fines, since it flows in the opposite direction to the strip, cascading from downstream of the cleaning section. In other words, the degreasing solution starts as 'fresh' at the end of the cleaning section but accumulates iron fines as it flows back to the entry of the section. In this scenario, surface carbon should increase while iron fines on the strip may decrease when spraying is idle.
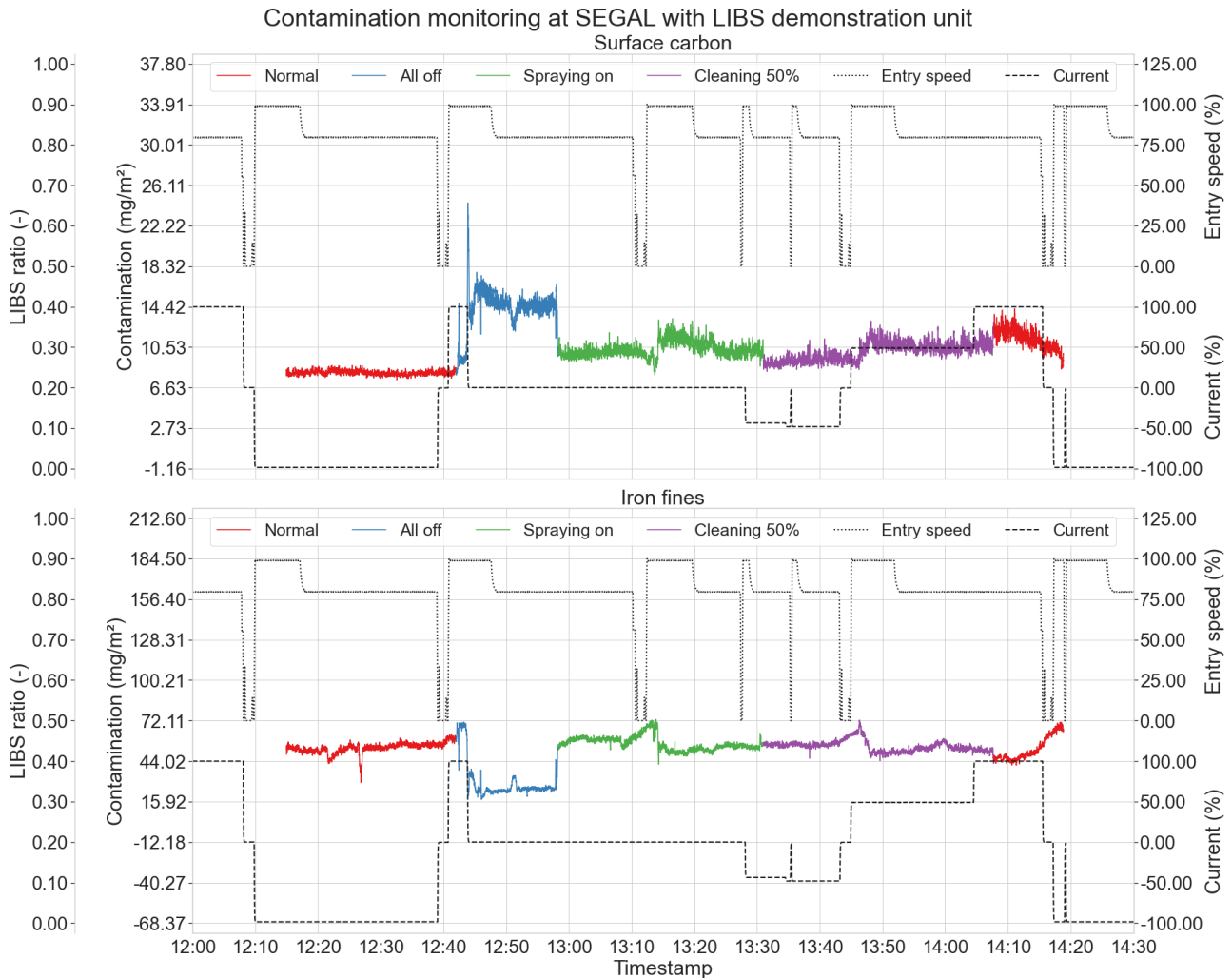
Fig. 4. Results of contamination monitoring trial at SEGAL

Entry line speed also appears to influence the cleanliness, even if to a lesser extent than spraying. After welding the new coil, the entry line speed is higher to catch up with the line speed of the central section. This means the strip spends a bit less time in the cleaning section, which results in slightly higher contamination levels for a few minutes. This can be observed especially for the surface carbon in Fig. 4 between around 12:45 and 12:50, around 13:15 and 13:20 as well as between around 13:50 and 13:55. Likewise, when the strip is stopped for welding while sprays are on, it looks like iron fines are building up on the strip, further supporting the hypothesis explained in the previous paragraph.

Finally, the sequential inversion of the electrolysis current is believed to produce the 'steps' in the LIBS signal that can be observed, for example, at around 13:15, 13:30 and 13:45. Inversion of the current is needed to avoid premature wear of the electrodes. In the electrolysis bath, the strip acts as the cathode (reduction) when the current is 'negative' and as the anode (oxidation) when the current is 'positive'. When the latter happens, it is believed that a very thin oxide layer begins to grow on the strip surface. This layer tends to increase the overall signal picked up by the demonstration unit, as LIBS is very sensitive to oxides.

5. DEVELOPING THE INDUSTRIAL AND COMMERCIAL SOLUTION

Having established reliable data acquisition and demonstrated the suitability of the technology in the industrial environment, work has been undertaken at Sarclad (Rotherham, UK) to develop a robust commercial design for permanent installation at any typical cleaning line. The design review has

incorporated principles of design for manufacture, maintenance and use and will consider the operating environment and intent of the steel producer. The resultant product will adhere to all relevant standards and attain CE marking. The core areas of improvement are covered below.
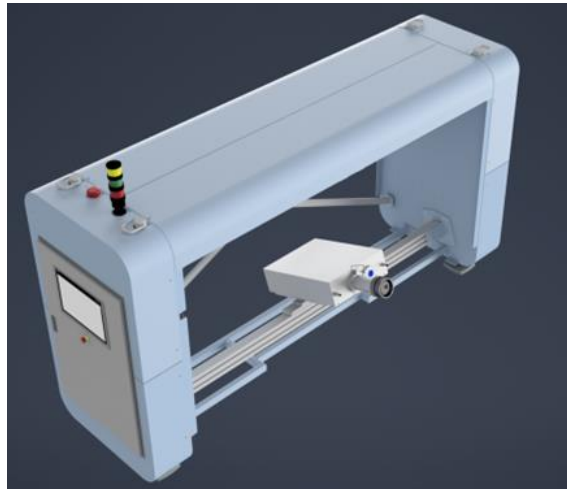

Fig. 5. Overview of the designed commercial solution

5.1. Automated line traverse

A clear requirement for production use is the ability to provide measurements at any point across the width of the strip. To facilitate this the unit will be mounted on a motorised traverse rail which is controlled by an industrial PLC capable of integration with the line process control to move to set points according to strip width and desired point of measurement.

5.2. Operator interface, data analytics and integration to production systems

A configurable user interface will be developed to allow real time access to the data by operators and control of core commands. Via these developments, integration of the system to the production line process control can be facilitated, allowing display of key metrics in real time, storage of data for subsequent analysis, and system operational set up according to product mix/line operation.

5.3. Simplified design for robust operation and maintenance

The demonstration unit used in this study had certain design features that allowed flexibility of operation to optimise the technology in a research context. Elements of these flexibilities are not required in a permanent production unit. The principles of design for build and maintenance have been employed to arrive at a more robust design for the industrial environment.

5.4. Laser safety and system security in the operational environment

The installations in this study have fully complied with laser safety requirements by utilising a combination of robust systems interlocks, shielding and exclusion zones. This will be improved going forward by designing in key shielding arrangements to the housing and site-specific working practices. Further, the integrated design will facilitate armouring to protect the measuring head in the event of a strip break etc. with only the sacrificial beam shroud being exposed. The equipment will be rated to IP53 to protect from dust and water, with the innovative beam shroud protecting the external optic. Site specific measures will be incorporated to mitigate the effects of extreme temperatures, humidity, and vibration.

6. CONCLUSION

A new on-line equipment has been developed by CRM Group and Sarclad Ltd to measure the residual contamination levels on the strip after the cleaning section of galvanising lines. It can differentiate between iron fines and surface carbon pollutions thanks to a method based on the LIBS technique and established by CRM Group [1].

While it does not provide a direct measurement of the contamination levels on the strip, linear correlations between the LIBS values and the contamination levels could be obtained in laboratory on samples coming partially from SEGAL plant and from coils processed on CRM Group's pilot line. The laboratory techniques used were a combustion-based method for the surface carbon and ICP for the iron fines, as the widespread 'scotch-tape' test was shown to be not reliable.

The correlation for the surface carbon reaches a r^2-value of more than 87% and gives a very consistent relationship between the LIBS and the surface carbon contamination. For the iron fines, the r^2-value is 74%, and despite being lower than for the surface carbon, the linear fit still gives a good indication of the relationship between the LIBS and the iron fines pollution. More replicates in laboratory measurements could clearly help to improve the correlation.

The demonstration unit has then been successfully fitted to two industrial galvanising lines, namely ArcelorMittal EUROGAL and Tata Steel SEGAL. Acquisitions have been performed in real line conditions. Even though all phenomena are not understood yet, these trials outlined the influence of the sprays, the entry line speed and the electrolysis current as the main process parameters on the cleanliness of the strip and on the LIBS signal. The demonstration unit was able to pick up contamination levels as low as < 10 mg/m² for surface carbon and 16 mg/m² for iron fines.

Having established reliable data acquisition and demonstrated the suitability of the technology in the industrial environment, work has been undertaken at Sarclad (Rotherham, UK) to develop a robust commercial design for permanent installation at any typical cleaning line. Core features of this solution include automated line traverse, operator interface and analytics, integration to existing production systems, simplified design for robust operation and maintenance, laser safety, system security and CE marking.

More industrial trials are being carried out to further study the effects of process parameters. The correlations obtained in laboratory will be improved via additional laboratory tests and statistical significance tests to account for the inherent sampling and analysis variability.

REFERENCES

[1] T. Gossuin and G. Moreas, 'Cleanliness measurement by innovative LIBS method' in *Proc. 12th Int. Conf. Zinc & Zinc Alloy Coated Steel Sheet (Galvatech 2021)*, Vienna, Austria, Jun. 21-23, 2021, pp. 906–912.
[2] T. Gossuin, G. Moreas, C. Pelletier, J. van Eenennaam, M. Roiseux, M. Ferte, N. Labbe and J. Di Girolamo, 'On-line characterisation of the cleanliness of coils to be galvanised for exposed automotive parts (CleanEx)', CRM Group (BE), Tata Steel IJmuiden (NE), SEGAL (BE), ArcelorMittal Maizières Research (FR), EUROGAL (BE), RFCS GA 847318, Periodic Report 2, Apr. 2022.
[3] U. S. Inan and M. Gołkowski, *Principles of Plasma Physics for Engineers and Scientists*. Cambridge, U.K.: Cambridge Univ. Press, 2011.