DESIGN OF A COOLED FOULING PROBE TO INVESTIGATE SCALING MECHANISMS FROM THE ALUMINIUM PRODUCTION OFF-GAS

D.P. Clos[1], Heiko Gaertner[1,3], Petter Nekså[2], Sverre Gullikstad Johnsen[3], Ragnhild Elizabeth Aune[1]

[1] Department of Materials Science and Engineering, Norwegian University of Science and Technology (NTNU), Trondheim, Norway (daniel.p.clos@ntnu.no):
[2] SINTEF Energy Research, Trondheim, Norway
[3] SINTEF Materials and Chemistry, Trondheim, Norway

ABSTRACT

The Norwegian aluminium industry needs to invest a large amount of time and resources in cleaning procedures due to scale formation in the off gas channels/ducts and gas treatment facilities. Future efficient heat recovery from the off-gas is highly desirable, but at present it is rather limited due to fouling issues. Currently, only a qualitative understanding of the mechanisms behind scaling has been established. Deeper insight into the scale formation fundamentals is therefore required for further development of mitigation techniques.

In the present study, details from the design of a cold-finger fouling probe are presented together with the plans and objectives for an upcoming experimental campaign at a Norwegian aluminium production plant. Existing knowledge in regards to the off-gas and deposit composition and chemistry is reviewed, and a selection of proposed theories on reaction mechanisms are discussed. The complex nature of the problem at hand, which involves transport and deposition of polydisperse particles of various chemical compositions in a corrosive environment featuring turbulent flow and thermal gradients, requires a multi-disciplinary approach to convey reliable results. In view of this, relevant models for particle deposition onto surfaces in the frame of Computational Fluid Dynamics (CFD) are also outlined.

INTRODUCTION

Production of aluminium by the Hall-Héroult process is an energy intensive process where a significant amount of heat is generated inside the electrochemical cells. It has been established by (Grjotheim and Kvande 1993) that up to 40% of this heat is lost in the off-gas, which is heavily loaded with solid particulates and corrosive gases due to the following processes:

1. Alumina dust fines are sucked into the off-gas channel/duct by the air draft during feeding of alumina.
2. Bath fumes vaporize mainly in the form of $NaAlF_4$ (g).
3. The electrolyte (mainly cryolite: Na_3AlF_6) is entrained by the vapour.
4. The reaction between bath fume components and the moisture generates corrosive HF.

Recovering heat from such a heavily contaminated gas is a challenging task due to issues related to fouling. A special feature in the fouling process in the aluminium off-gas is the presence of scaling reactions, which form hard layers that are strongly adhered to the wall and thus, difficult to remove. Currently, there is only a qualitative understanding of the mechanisms behind the formation of the so-called “Hard Grey Scale” (HGS). Reactions between the quenched vapour fumes ($NaAlF_4$), the entrained electrolyte species, and the moisture present in the system seem to be key factors in the formation of scale as suggested by the following reactions (Cochran, Sleppy et al. 1970) and (Karen Sende Ösen, Thor Anders Aarhaug et al. 2011):

$$5\ NaAlF_4\ (s) \rightarrow Na_5AlF_{14}\ (s) + 2\ AlF_3\ (s) \qquad (1)$$

$$3\ NaAlF_4\ (s) + 3\ H_2O\ (g) \rightarrow 6\ HF\ (g) + Na_3AlF_6\ (s) + Al_2O_3\ (s) \qquad (2)$$

$$2\ NaAlF_4\ (s) + Na_3AlF_6\ (s) \rightarrow Na_5Al_3F_{14}\ (s) \qquad (3)$$

$$5\ Na_3AlF_6\ (s) + 3\ AlF_3\ (s) \rightarrow 3\ Na_5AlF_{14}\ (s) \qquad (4)$$

A comparison between the chemical composition and crystalline structure of scale samples and free particles retrieved from the off-gas channel/duct has been performed by (Dando and Lindsay 2008). Their findings showed that significant amounts of cryolite (Na_3AlF_6) were present in the free particles collected but not in the scale samples, suggesting that reactions involving consumption of cryolite (reactions 3, 4) might be of importance. Consumption of cryolite in scale samples has also been observed by (Gaertner, Ratvik *et al.* 2013), who reported a lower degree of crystallinity in the case of scale samples than free particles. The particle size distribution was also analysed by (Gaertner, Ratvik *et al.* 2013). The obtained results showed a two-peak distribution of particles with mean sizes of 0.5 and 6.2 µm. Particles smaller than 10 µm made up 60-80% of the total mass with an increasing concentration in trace elements (Ni, Fe, P, V, Co) and alumina content in the coarser fractions. The fractions in the sub-micron range proved to contain considerable amounts of sulphur potassium and lead. This result is similar to a study performed by (Næss, Slungaard *et al.* 2006), who reported a mass fraction of 90% of particles below the 10 µm range.

In order to further investigate the scaling formation mechanisms, a fouling probe, or “cold-finger”, is in the process of being designed and built for industrial measurements by the present authors. A fouling probe can be used to expose a surface, with a given geometry and controlled surface temperature, to a fouling stream. The circulation of a coolant inside the probe is intended to regulate the wall temperature.

A classification of existing types of fouling probes, based on the objectives of the measurements in which the probe is to be used, has been suggested by (Marner and Henslee 1984). The first category of probes, *i.e.* heat flux meters, analyses the effect of deposits on heat transfer by monitoring the heat flux through the probe walls over time (Næss, Slungaard *et al.* 2006),(A. K. Temu, E. Næss *et al.* 2002). Thus, by estimating the thermal resistance of the deposits, the deposition rates can be calculated. The second category, *i.e.* mass accumulation devices, aims at quantifying the amount of deposits over a period of time, thus obtaining a direct measure of the deposition rates (A. K. Temu, E. Næss *et al.* 2002). The third category, *i.e.* optical devices, makes use of optical cameras or laser techniques to have a direct observation of the deposition phenomenon (Adaramola and Næss 2012). The fourth category, *i.e.* deposition devices, corresponds to those probes where the main objective is the deposit collection for further analysis (Fleer 2010). Finally, the fifth and last category, *i.e.* acid condensation devices, aims at measuring acid dew points to map temperature intervals where acids can condensate on the walls and cause corrosion problems.

In the present case where the designed cold-finger is to be inserted in an off-gas channel/duct under in-situ industrial conditions; direct quantification of the deposits will not be possible. The reason for this is that loosely-attached deposits tend to accumulate on the downstream side of the probe, where the wake generates a low velocity/pressure region (Næss, Slungaard *et al.* 2006). It is therefore believed that, the loose part of the deposit might be lost during probe extraction. Hence, a heat flux meter type probe is presently being designed by placing sensors, *i.e.* thermocouples and heat flux meters, on different zones on the probe surface. The probe will also have an outer shell, which can be removed and replaced to allow for reproducible experiments, sensors protection from fouling gas and further destructive sample analysis.

COLD-FINGER DESIGN

The main layout of the cold finger presently being designed can be seen in Fig. 1. The system consists of three concentric tubes built in a tube-in-tube configuration. For simplicity, the inner, intermediate and outer tubes will henceforth be referred as tubes 1, 2 and 3 respectively. The working fluid is pressurized air, and it will be referred to as the *coolant*, whereas the dust laden process gases circulating outside the probe will henceforth be referred to as the *off-gas*. The cold-finger is planned to be introduced perpendicularly into the off-gas channel/duct through an opening flange. Thus, the off-gas will flow in a perpendicular direction against the probe (cross-flow configuration). The upstream side where the off-gas impinges the probe is denoted as the *front side*, whereas the downstream side will be referred as the *rear side*. The coolant flow is controlled by a flow regulation valve (V1) and led through a heater (H1) before it enters the inner tube (1). Once the air reaches the right end of the inner tube, it is transferred to the inter-tube space between tubes 1 and 2 before it flows back (to the left), *i.e.* to the coolant outlet.

It is planned to place a heater before the inlet to regulate the inlet temperature of the coolant. Pressure and temperature sensors are placed both at inlet and outlet positions to regulate the coolant conditions, and to monitor the overall heat flux absorbed by the probe. The coolant will be cooled before reaching the backpressure valve, which is placed at the outlet to control the coolant pressure inside the probe. Downstream from the backpressure valve the air coolant will be released to the atmosphere.

A circumferential rod will be welded to the outer surface of tube 1. This circumferential rod guides the coolant into a "spiral flow" along the outer surface of the inner tube (1). This will allow for a significant reduction of the hydraulic diameter of the "inter-tube" flow area, thus contributing to a higher coolant Reynolds number which will improve the heat transfer in the inter-tube region compared to the off-gas side.

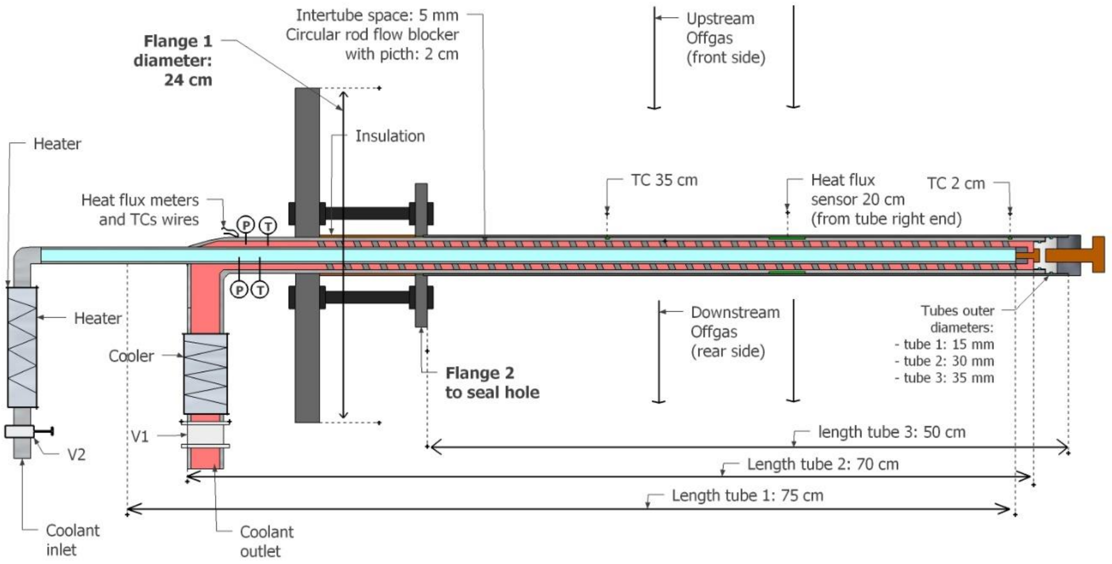

Fig. 1: Schematic drawing showing the main details of the cold-finger design

Thus, eventual variations in the coolant conditions should have little impact on the overall heat transfer monitored since the main heat resistance will be located at the off-gas side. Moreover, the flow guidance provokes the desired turbulent flow with a low mass flow of coolant. This low coolant mass flow is necessary to obtain a significant/measurable change in coolant temperature, which again is necessary for accurate monitoring of the heat transfer over time. Preliminary calculations have been performed in order to estimate a suitable probe geometry and coolant flow conditions to satisfy the above-mentioned constraints. A simplified model for the coolant circulation within the probe was developed by using a heat transfer correlation from (Gnielinski 1976) and a correlation for the coolant pressure drop from (Incropera 2007). The constraints were set as to obtain a coolant temperature increase between 4-15°C and to have a heat transfer coefficient on the coolant side in a range of at least 3 times that at the off-gas side. A correlation from (Churchill and Bernstein 1977) for heat convection from fluid in cross-flow with a cylinder was used to estimate the heat transfer coefficient on the off-gas side (78 W/m^2 K). That was calculated considering the reported off-gas temperature of 100°C and velocity of 15m/s. Three cases with different coolant inlet temperatures were calculated by minimizing the coolant-side pressure drop with results displayed in Table 1. Those cases were chosen in order to study the effect of thermophoresis on fouling. An inter-tube spacing between tubes 1 and 2 of 5mm was found suitable to meet the constraints for the different cases. Those numbers are just an indication of what operational range can be expected and will of course need to be adapted to the final real conditions.

As can be seen in Fig. ***1***, two thermocouples and two heat flux sensors are placed in the surface of Tube 2, which has grooves to accommodate the sensors and their lead wires. The heat flux sensor also contains a thermocouple. Therefore three point measurements will allow assessing the temperature profile along the probe axis on the front side, which might vary due to possible off-gas and coolant temperature gradients along this axis. The two heat flux sensors are placed at the front and rear sides of the probe's centre. These will provide local heat flux information and a direct correlation with the thickness of the fouling layers building up in these areas.

Tube 3 acts as a sheath fastened to Flange 2. This removable tube is the substrate for scale growth. A small gap between tubes 2 and 3 is provided to avoid stacking of the tubes due to thermal expansion during the experiments, and the space is filled with thermal grease in order to obtain a good thermal contact between both tubes. Tube 3 (Outer shell) can be removed easily and replaced with new tubes. This sheath design allows for running different experiments with reproducible initial conditions. Cross-sections of the outer tube can be cut to prepared samples for different type of analysis in a cost efficient manner because the same sensor system and controlling components are re-used. Moreover, different types of materials and surface quality can be used to study the onset and growth of depositions. Initial experiments will use carbon steel for tube 3.

Table 1: Calculated coolant flow conditions in the annulus region of the cold-finger.

Inlet coolant temperature (°C)	**20**	**60**	**80**
Volume flow (l/min)	47	51	53
Mean velocity in annulus (m/s)	7.8	8.5	8.8
Pressure drop coolant (mbar)	5.9	6.4	6.6
Heat transfer coefficient coolant side (W/(m^{2}C))	250	250	250
Temperature loop coolant (°C)	15	8	4
Average Reynolds number for coolant flow in annulus	3E+04	2E+04	2E+04
Overall heat flux (kW/m^2)	2.0	1.0	0.5

The probe is fastened to a main flange (Flange 1) which is to be attached to the duct flange in the experimental site. Flange 2 is fastened to Flange 1 by three rigid bars with screws and its function is to seal the inner hole of the flange and to accommodate Tube 3. The three tubes are fitted on their right ends to cylindrical pieces with O-rings. The O-rings allow tubes 2 and 3 to glide on them upon thermal expansion and to seal the probe to avoid coolant leakages. The cylindrical pieces are joined together by screw pieces, which facilitate their assembly and disassembly. Finally, two dummy tubes with the same length than the cold-finger can be inserted through flange 2 and fastened to flange 1. This will allow studying of the screening effects present in real heat exchangers on the fouling characteristics.

CONCLUSIONS AND FUTURE WORK

A detailed description of the design of a fouling probe for industrial measurements from the off-gas generated in the electrochemical cells used during aluminium production has been presented. The cold-finger offers the possibility to monitor continuously the fouling phenomenon by analysing its effect on heat transfer. Moreover, the replaceable outer tube can be cut down to perform chemical and physical analysis of the deposits. This allows measuring the thickness of the deposited layers and studying the change in chemical structure and composition that leads to the formation of hard scale from the initially soft and porous deposits. This design also allows for cheap (no machining required) replacement of the outer tube by new ones. This enables good experimental reproducibility with same initial surface conditions and testing of different tube materials and surface properties. This is an important feature since the formation of scale is likely to occur due to different processes that might influence each other. Thus, having the possibility to have multiple screenshots of the deposits evolution under controlled conditions should provide with the missing data that can allow determining and quantifying which factors contribute to the scale formation. Moreover, the possibility of adding two dummy tubes enables studying of the impact of screening effects that are present in real heat exchangers on the fouling behaviour. Future work could also involve inserting the cold-finger in a test section, which can better mimic real conditions inside heat exchangers and where off-gas can be extracted and circulated under different volume flows.

The first experimental measuring campaign in a Norwegian aluminium plant is planned for the fall of 2017. The main objectives of the first campaign will be to run several experiments with same probe wall temperature and tube material to investigate the reproducibility of the fouling results. The deposits will be analysed in order to determine their chemical composition (EPMA, ICP-MS), morphology and deposit thickness (SEM) and crystal phases (XRD, IR). Finally, the probe will be left for a longer period, in the range of months, to investigate the evolution of the initial deposits. Moreover, an Eulerian/Eulerian-based model of a 2-dimensional flow around a cylinder will be developed with the objective of calculating deposition rates as function of flow conditions and particle size. This approach has been successfully used in the past to describe particle deposition rates and to account for the large results scattering in experimental studies (Johansen 1990, Johnsen and Johansen 2009). Measurements of the turbulence intensity field and off-gas composition will also be carried out to have suitable boundary conditions for the planned modelling activities. In conclusion, we expect the cold-finger to be a robust and reliable tool for investigating scale formation from its onset and provide with answers regarding time-scales, mechanisms, possible triggers for scale formation and differences and similarities between scales formed at various locations.

REFERENCES

A. K. Temu, E. Næss and O. K. Sønju (2002). "Development and testing of a probe to monitor gas-side in cross flow." Heat transfer engineering **23**(3): 50-59.

Adaramola, M. S. and E. Næss (2012). Study of particulate fouling and resuspension. Department of Energy and Process Engineering. Trondheim, NTNU.

Churchill, S. W. and M. Bernstein (1977). "Correlating Equation for Forced-Convection from Gases and Liquids to a Circular-Cylinder in Cross-Flow." Journal of Heat Transfer-Transactions of the Asme **99**(2): 300-306.

Cochran, C. N., W. C. Sleppy and W. B. Frank (1970). "Fumes in Aluminum Smelting - Chemistry of Evolution and Recovery." Journal of Metals **22**(9): 54-&.

Dando, N. and S. J. Lindsay (2008). Hard grey scale. Light Metals 2008, TMS (The Minerals, Metals & Materials Society).

Fleer, M. (2010). Heat Recovery from the Exhaust Gas of Aluminum Reduction Cells. Master, Reykjavík University.

Gaertner, H., A. P. Ratvik and T. A. AArhaug (2013). Trace element concentration in particulates from pot exhaust and depositions in fume treatment centers. Light metals 2013. M. M. S. TMS (The Minerals.

Gnielinski, V. (1976). "New Equations for Heat and Mass Transfer in Turbulent Pipe and Channel Flow." Int. Chemical Engineering, **16** 359–368.

Grjotheim, K. and H. Kvande (1993). Introduction to aluminium electrolysis : Understanding the Hall-Hérloult process. Düsseldorf, Aluminium-Verlag.

Incropera, F. P. e. a. (2007). Fundamentals of Heat and Mass Transfer.

Johansen, S. T. (1990). "The deposition of particles on vertical walls." Int. Y. Multiphase Flow **17**(3): 335-376.

Johnsen, S. G. and S. T. Johansen (2009). Deposition modelling from multi-phase dispersed flow. A boundary layer wall function approach. Heat Exchanger Fouling and Cleaning. Schladming, Austria.

Karen Sende Ösen, Thor Anders Aarhaug, Asbjørn Solheim, Egil Skybakmoen and C. Sommerseth (2011). HF measurments inside an aluminium electrolysis cell. Light Metals 2011. S. J. Lindsay, TMS (The Minerals, Metals & Materials Society).

Marner, W. J. and S. P. Henslee (1984). A Survey of Gas-Side Fouling Measuring Devices. U. S. D. o. Energy. Pasadena, California, USA, California Institute of Technology.

Næss, E., T. Slungaard, B. Moxnes and O. Sønju (2006). Experimental investigation of particulate fouling in waste heat recovery from the aluminium industry. 13th International Heat Transfer Conference. Sidney, Australia.