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A summary of the industrial use of water sprays to suppress fume emissions during the production of FeMn alloys

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Abstract – Tapping, slag raking and casting of ferromanganese generates significant amounts of secondary fume. Eramet Norway, Sauda (ENS) and Eramet Research Trondheim have worked extensively with water sprays over the last 10 years to suppress emissions during the casting of medium-carbon ferromanganese (MCFeMn) and high-carbon ferromanganese (HCFeMn) and from the roof ventilator openings of the furnace building over the furnaces. Initial test work to understand the emission suppression mechanisms involved was made by Eramet followed by laboratory test work at the Norwegian University of Science and Technology (NTNU) to characterise the industrial fume. Fume suppression mechanisms are suggested to include the formation of an inert layer over the metal surface, enhanced oxidation and cooling of the metal surface, agglomeration of the fume particles, and capture of the agglomerated fume by the water spray droplets.

ENS has carried out practical spray test work using overhead water sprays mounted along the edge of the roof line over the casting beds as well as horizontal sprays mounted low over the beds. With overhead sprays, specific air flow patterns have been observed which result in water saturated air coming in close proximity to the metal surface. A rebuild of certain casting areas reinforced the importance of understanding the nozzle positioning and air flow patterns. Both dual-media (air/water) and water-only nozzles at various pressures have been utilised. ENS also installed water sprays in the roof monitor area of the furnace building to capture fugitive fumes from tapping, slag raking and casting operations. This article presents findings of laboratory scale test work to identify possible fume emission suppression mechanisms as well comments on the various spray applications, with photos and comments on effectiveness and further work required.

Keywords: Secondary fume, manganese, casting, water sprays

INTRODUCTION

Eramet is constantly working to reduce diffuse emissions from the ferromanganese smelting operations. Some of the primary sources of diffuse emissions at Eramet Norway Sauda (ENS) have been from the furnace roof, slag tapping, and casting of both High Carbon Ferromanganese (HCFeMn) and Medium Carbon Ferromanganese (MCFeMn).

Good environmental performance is a major part of the plant's continuous improvement work towards a long-term sustainable operation. The location of the Sauda plant close to the city centre and local residents further enhances the need for meeting environmental expectations from the neighbours and complying with legislation. It is anticipated that the authorities will continue to tighten regulations on emissions over time, and expectations both from the companies own employees and the community will also continue to increase. Many improvements have been made by Eramet personnel to mitigate diffuse emissions, and this paper will focus on the use of fine water sprays over the metal casting beds and the furnace building roof ventilation openings as an effective and low-cost alternative to conventional fume hoods and filters. Possible mechanisms for the beneficial effects of water sprays on fume generation are discussed. This paper is a continuation of the work presented previously by Cowx *et al.* (2015).

THEORETICAL BACKGROUND

Fume formation mechanism

Little information on the fume generation mechanisms in the ferromanganese industry could be found, but studies from steelmaking suggest that CO bubble bursting and droplet ejection, droplets created by turbulence from O_2 blowing, and volatilization are the main mechanisms Guézennec *et al. (*2004); Huber *et al. (*2000). Considering that there is no turbulence due to O_2 blowing and little turbulence during casting, the high vapour of Mn at the elevated casting temperatures, and the fume is nearly pure Mn_3O_4, evaporation and subsequent oxidation of Mn is considered to be the primary mechanism.

Rate controlling mechanisms

Turkdogan *et al.* (1963) defined the phrase "enhanced oxygen vaporisation" as the phenomena when the metal evaporation rates at high oxygen partial pressures approached those in a vacuum because the metal vapour is immediately oxidised close to the metal surface, thereby lowering the effective vapour pressure of the metal over the melt. It is, however, rare that the oxygen diffusion rate, and therefore the oxygen partial pressure, exceeds the evaporation rate of a metal with a high vapour pressure such as Mn at high temperatures. Therefore, it is generally accepted that fume formation occurs as the two-step reaction Lee and Kolbeinsen (2005) explained. First, the Mn evaporates and oxidises to MnO in the oxygen-deprived gaseous boundary layer. Thereafter the MnO enters the atmosphere with more abundant oxygen to oxidise exothermically to Mn_3O_4. Thermodynamic models made by Olsen *et al.* (2007) confirm that MnO vapour would form at lower O_2 concentrations. Lee and Kolbeinsen (2005) also conducted a study of the high carbon ferromanganese (HCFeMn) system to determine that Mn will evaporate but not oxidise when the oxygen partial pressure is below 17 kPa. It is therefore suggested that the rate limiting mechanism for FeMn fuming at temperatures above 1600°C is not the Mn vaporization rate in itself, but rather the diffusion of the oxide mist through the gaseous boundary layer.

Formation of an inert boundary layer

Gates *et al.* (2015) suggested that the increasing water concentration (humidity) in the air passing over the casting beds causes steam formation and a reduction of oxygen partial pressure over the metal surface, thereby reducing MnO vapour formation. It was also suggested that the increased water concentration could cause a mechanism shift to lead to passive oxidation of the metal surface. Either one of these occurrences would cause the rate of oxygen enhanced vaporisation explained by Turkdogan *et al.* (1963) to decrease.

From visual observation, InfraRed pyrometer readings and Thermal Infrared (TRI) photographs taken by ENS and Gates *et al*. (in press), shown in Figure 1, it is feasible that the moist air cools the alloy surface and forms a thin layer of solidified alloy or oxide that hinders fuming. Very little fume can be seen over the large quiescent surface of the alloy plate, whilst fume is apparent over the connection channels between the plates where a new alloy surface is continuously exposed to the atmosphere.

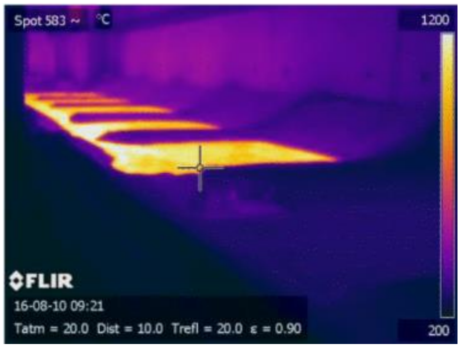

Figure 1: IR photograph of the casting beds Gates et al (in press)

Fume capture by impaction with spray water droplets

Gates *et al.* (2015) conducted a detailed study to determine the cause of the fume reduction witnessed at Eramet Sauda. The paper was mainly focused on the influence of the water as a heat sink to enhance convectional air flow effects and the physical mass transfer of industrial dust particles into the water droplets. One of the paper's conclusions was that there was a small percentage of fume particles captured by the water droplets, but it was not enough to explain the significant fume reduction seen on-site. However, only the impaction model explained by de Nevers (2010) was considered in this study. Later the model was re-evaluated to include impaction, diffusion, and interception into the capture efficiency. Yet again Gates *et al.* (2016) only confirmed that the expected mean droplet and fume particle sizes would not cause a significant reduction in the fume concentration.

From the red-brown colouration of the run-off water from the sprays, it was apparent that the water droplets were capturing some of the fume particles. A series of water catch pots were therefore set up at different positions around the casting beds (shown in Figure 1), the collected water was filtered, and the particles examined under an optical microscope Cowx *et al.* (2015). Although not quantified, these observations suggested that fume capture by impaction with the water droplets was greater than suggested by Gates *et al.* (2015) and that there are others factors that enhance fume capture, for example agglomeration of the fume particles.

Figure 2: Catch pots set up around the casting beds to capture water samples Cowx *et al.* (2015)

Fume particle agglomeration

In an attempt to understand the fume reduction mechanism when water vapour is introduced above a HCFeMn alloy, Gates *et al.* (2017) conducted laboratory scale experiments where an impinging jet of wet air was blown over HCFeMn and the fume cooled before it was captured. They showed that the captured relative mass fluxes of fume decrease as the water concentration increased. When a high water partial pressure (about 20 kPa) was introduced into the experiment the relative mass flux was approximately 79 % lower compared to the dry air experiment mass flux. The paper also included x-ray diffraction (XRD) analysis of the captured fume. The concentration of MnO decreased as the water partial increased. It was also suggested that the morphology and particle size distribution changes with a water presence. The possibility of agglomeration has been mentioned by Grey (1980) and Dingsøyr *et al* (1992) who classified "primary" agglomerates as being particles where the initial or protoparticles are held together by material bridges and sintering, whereas secondary agglomerates are primary agglomerates attached to each other by weak van der Waals forces.

Gates *et al.* (in press) completed an industrial measurement campaign at ENS. In the campaign, they captured dust at two different locations at the casting beds with sprayer on or off. They presented Scanning Electron Microscope (SEM) images, particle size distribution (PSD) results, Electron Dispersive Spectroscopy (EDS) results, and TRI image results.

With the SEM images, they showed four different groupings of particle sizes. With particles of about 5 μm, it could be seen that the particles which were captured while the sprayer system was inactive had smooth surfaces as though the particles were sintered bodies. The particles captured while the sprayers were active had rugged surfaces with smaller particles fused into the larger particles. When the particle size decreased, it was noted that the particles which were captured while the sprayer system was inactive was smaller in comparison to the active sprayer system case. This was mainly due to more agglomeration of the particles. (Gates *et al.*, in press)

Gates *et al.* (in press) further determined a particle size distribution (PSD) from the SEM images. The PSD confirmed that much more particles (about 78 %) are within the smaller ranges if the water sprays are inactive while the PSD shifts to the higher particle size region when the water sprayers were active.

Improved fume extraction hood efficiency

The cooling effect that the sprayers have on the environment and the melt shown by ENS pyrometer measurements and Gates *et al.* (in press) may have a two-fold influence in the fume extraction capability. The first is that the fuming rate is dependent on the melt temperature. At higher temperatures more Mn evaporates causing oxidation and more fuming. The spray capability to cool the melt surface reduces the fume formation. The second influence the sprays might have is cooling the air above plates, thereby reducing the buoyancy of the particulate plume over the metal. Reduced buoyancy would lead to decreased plume velocity, less entrained air and a smaller plume volumetric flow, which should theoretically reduce the required hood extraction volume required to achieve 100 % capture efficiency.

PRACTICAL APPLICATION OF WATER SPRAYS AND AFFECT ON DIFFUSE EMISSIONS

Plant description

Eramet Norway Sauda, (ENS) operates two closed 40 MW Submerged Arc Furnaces producing HCFeMn and a Manganese Oxygen Refining converter (MOR) to produce medium and low carbon ferromanganese. Both the HCFeMn and MC/LCFeMn are cast in sand beds.

Emissions from the furnace building ventilation openings

Secondary fume emissions are generated at the furnace tap holes, slag raking, metal transfers, oxygen refining as well as metal and slag casting and pouring operations. Most of the point sources around the smelter have dedicated fume capture hoods with good capture efficiency, but some fugitive emissions can occur during furnace pressure spikes, over-tapping, and metal and slag pouring operations. These fugitive emissions eventually find their way out of the roof ventilation openings as shown in Figure 3a.

ENS personnel mounted a series of air atomized water sprays over the roof openings and continuously monitor the diffuse emissions using a laser instrument, together with air velocity and temperature measurements. When the emissions exceed approximately 8 mg/Nm^3 air the water sprays are triggered and these continue until the emissions fall below the limit. If the emissions exceed 25 mg/Nm^3 air a second row of nozzles is triggered. The emissions are continuously presented on displays at strategic points around the plant and in the central control room so that immediate action can be taken. The active sprays are shown in Figure 3b. The excess spray water containing the collected fume runs down the building roof, collects in the gutters and drains, and is sent to the sedimentation basin that handles the surface run-off water from the plant. No water enters the furnace building. Work is on-going with "fog nozles" that produce finer droplets and use less water.

Whilst the sprays are very effective at reducing emissions, they have not totally eliminated roof emissions from uncontrolled events such as overtapping or a charge cave-in.

Figure 3a: Overview of furnace building ventilation openings. b: Water sprays over ventilation openings

Medium Carbon FerroManganese casting beds:

The majority of the HCFeMn (7 %C) produced at the plant is refined in the Manganese Oxygen Refining converter (MOR) to produce MCFeMn (1.5 %C) and LCFeMn (0.5 %C).

The refined FeMn is poured into one of two linear sand beds located outside the furnace building beds under a roof. Each bed has 9 interconnected pockets, roughly 2 m × 2 m × 0.1 m thick, formed in olivine sand. Considerable fugitive emissions occurred from the casting beds because of the very high metal casting temperature, the high vapour pressure of Mn, the large surface area of exposed metal, fume capture hoods were only installed over the first three pockets, the extraction capacity was limited (~120,000 Nm^3/h), and the open building sides that allow high volumes of air to infiltrate.

Extraction volume measurements and video filming techniques were used to semi-quantify the flow patterns over the sand bed and calculate the energy in the rising fume plumes over the beds to provide input parameters for CFD modelling Els *et al.* (2013). It was found that to achieve near 100 % fume capture, either the casting beds had to be totally enclosed, or the extraction capacity had to be more than doubled, requiring considerable investment in the bag filter and fans.

Because of the high cost of increasing the extraction capacity or enclosing the casting beds, old research was resurrected and preliminary tests were conducted using a series of hand-held high-pressure water sprays directed just over the metal surface as the metal was poured. The water sprays visibly reduced fume emissions.

Tests were then conducted with a modified “snow cannon” where water droplets were blown over the metal surface by the built-in fan. Unfortunately the powerful fan created a lot of turbulence and disturbed the capture of the fume.

To test the water spray concept further, general purpose 120° flat jet nozzles were installed at intervals along the roof edge over the casting beds, as shown in Figure 4. Each nozzle delivered about 20 l/min water at a pressure of 7 bar. These nozzles produce medium sized droplets so as to maintain the spray coverage even in windy conditions. The sprays pointed slightly downward from the horizontal rather than vertically downward to avoid water accumulating on the floor close to the casting bed.

Figure 4: MCFeMn casting bed showing fume emissions over the roof without (left) and with water sprays (right)

Moisture saturated air is drawn in over the cast metal by the thermal updraft generated by the hot metal. Any fume that does escape from the metal surface / under the roof over the casting beds is scrubbed out by the water sprays.

After modifications to increase casting capacity, the centre dividing wall was built up to the roof with no opening as before, the roof angle was “flatter” than previously and the water nozzles were mounted more "horizontally". This caused a recirculation effect under the roof and the escape of a small amount of fume. This illustrates the importance of understanding the flow patterns when placing the sprays. Figure 5 shows the flow pattern observed at ENS.

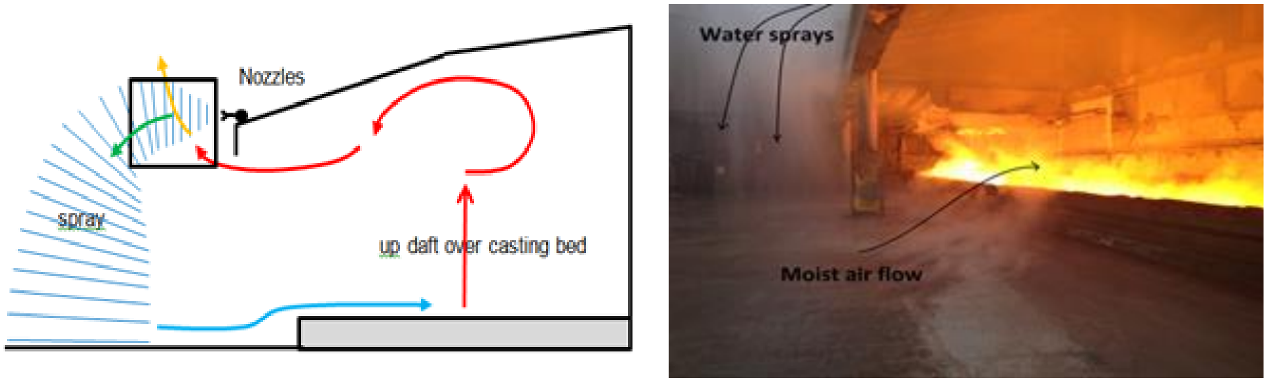

Figure 5: Flow pattern of moist air over casting beds

High carbon ferromanganese casting beds

The portion of HCFeMn that is not refined is cast out in a sand bed for cooling, crushing and sale. This sand bed is located inside the furnace building and consists of a fixed runner to deliver the alloy to the first of 8 interconnected pockets formed in olivine sand. There are only fume capture hoods over the first two casting pockets and the bed is open along one side for loader machine access to remove the solidified alloy plates. Diffuse emissions occurred from this casting bed, especially if the doors to the furnace building were open and disturbed the air flow around the bed.

The flat jet water sprays as used on the external MCFeMn sand beds cannot be used inside the furnace building because there would be too much standing water on the floor in areas where molten metal is being transferred by a crane. An alternative solution was to use air atomizing 120° fan jet nozzles with compressed air to generate a "fog" of fine water droplets (~50 µm). These nozzles add moisture to the atmosphere without wetting critical surfaces because the small drops evaporate quickly. Figure 6 shows the casting process with and without the fog nozzles.

Figure 6: HCFeMn casting bed without (left) and with fog nozzles in operation (right)

To avoid the thermal plume carrying away the very fine water droplets, the nozzles were mounted in the back wall of the sand bed low over the alloy surface. A flexible test rig was constructed to find the most effective nozzle type, the optimum number of fog nozzles (1-3 per pocket), nozzle angle (+30°—30° from the horizontal), and height above the metal surface (20-50 cm). The optimum combination was found to be 1 nozzle per pocket, slightly downward nozzle inclination angle and 20 cm above the alloy surface. The tips of the nozzles are set slightly behind the face of the steel plate to prevent damage from the front loader machine and also to prevent any water drips falling into the sand beds. There is no water spray scrubbing effect as the water droplets evaporate very quickly.

To prevent any water falling into the sand beds the nozzles were individually remotely activated by the crane driver as metal began to flow into each sand pocket. At the end of each casting, the water was stopped but the compressed air left on for 2 minutes to purge the lines of water to prevent dripping.

MONITORING DIFFUSE EMISSIONS

Continuous video camera surveillance

Diffuse emissions are continuously monitored in the smelter control room using 5 video cameras located around the periphery of the plant and 4 cameras scanning the internal plant operations. Emission incidents are manually logged and their source and severity are compared to a set of standard images by the operators every shift. Results are reported at the daily production meeting and appropriate corrective actions are taken. The monitoring is a vital part of the efforts to increase awareness and create active involvement in the continuous improvement projects on diffuse emissions. Figure 7 illustrates the improvement in the emission index since the water sprays were introduced on the MOR sand beds in 2011.

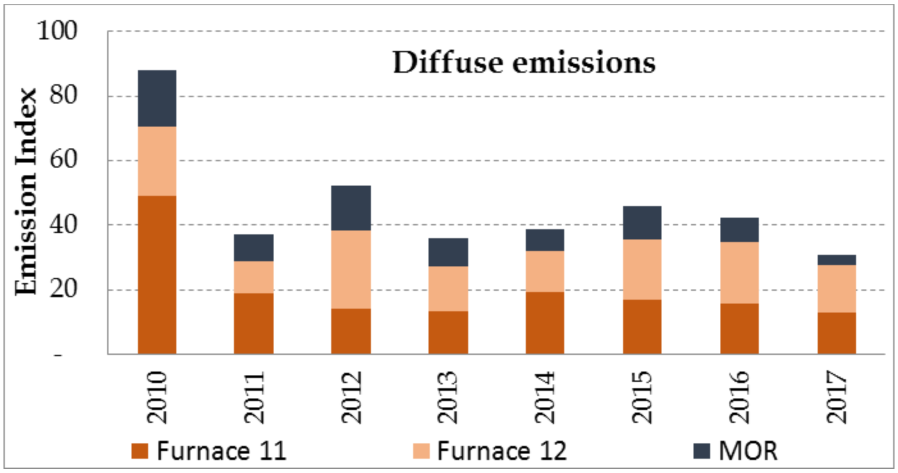

Figure 7: Visual estimates of emissions from the furnace building over the different units

Laser measurements

Diffuse emissions from the smelter building roof are measured by laser based instruments mounted across ventilator openings above the furnaces. Both Norsk Electro Optiks (NEO) and SICK systems have been tested. Emission readings are continuously shown on a display screen in control room and on screens at strategic points around the plant so that the operators can take rapid corrective action in the event of a discharge.

Dust drop out in the community

Four dust drop-out measurement stations are located around the town to collect dust samples. Figure 8 illustrates the general improvement in Mn in the drop out dust over time, despite the increase in production from the smelter. The gradual improvement in dust emissions has been a result of many improvement incentives in addition to the implementation of water sprays.

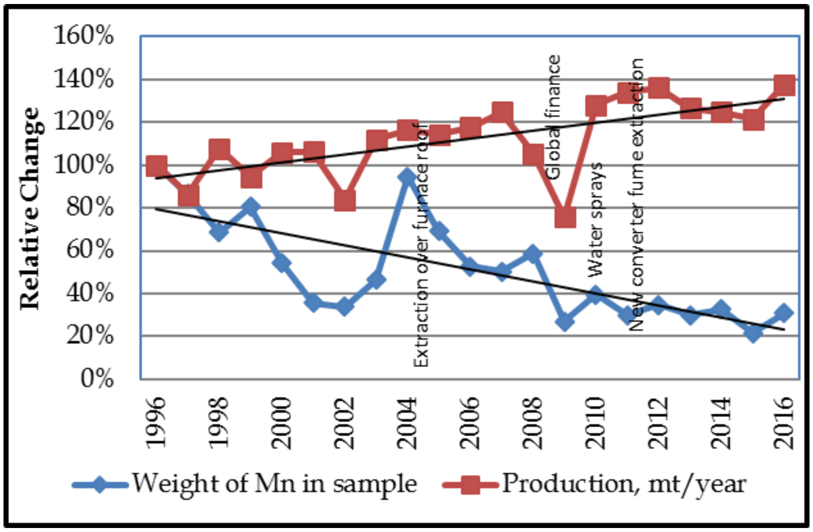

Figure 8: Relative change in weight of Mn in drop out dust collected at sampling stations around the city, and the relative change in production volume

Neighbour reporting

As the smelter is located close to the centre of the town and a popular ski centre, the plant continuously monitors emissions using video surveillance and laser instruments mounted at the furnace roof openings. These data alert the control room operators to an emission incident so that immediate action can be taken. Additionally, the plant neighbours are encouraged to telephone the control room and report diffuse emissions, which are registered and corrective actions reported back to the neighbour within 24 hours. The plant organises annual neighbour meetings where results and plans are presented, and questions and comments duly dealt with.

SAFETY ASSOCIATED WITH USING WATER SPRAYS IN A MOLTEN METAL AREA

The use of water sprays in the vicinity of liquid metal was rightly of concern and a detailed safety evaluation and HAZOP studies were carried out before the sprays were used. As a result of these studies the following design features were incorporated to mitigate contact between the metal and water.

- The MC/LCFeMn casting bed roof extends out 3 m from the edge of the sand bed to hold the water spray away from the sand bed.
- The nozzles chosen generate medium sized water droplets to avoid the spray being disturbed too much by ambient wind.
- The sprays are angled slightly downwards from the horizontal rather than vertically downwards to avoid water accumulating on the floor close to the casting bed.
- The ground in front of the casting beds slopes away from the bed to prevent water accumulation.

- Sprays are only used if the beds are hot so that any stray water droplets evaporate.
- No personnel are allowed in the area during casting.

CONCLUSIONS

The use of water sprays has been demonstrated to reduce diffuse emissions from the smelter. It appears that several mechanisms are involved:

Fume reduction mechanisms:

- Moisture saturated air is drawn in over the cast metal by the thermal updraft generated by the hot metal. The moisture may evaporate, generating a volume of steam which partially excludes air from the liquid metal surface and hinders the "forced evaporation of Mn" to form fume.
- Cooling of the metal surface and associated lower Mn vapour pressure.
- Moisture satured air may oxidise and cool the surface of the metal, forming a very thin layer of solidified metal or Mn_xO_y slag that hinders the evaporation of Mn.

Fume capture enhancement mechanisms include:

- The moist air changes the morphology and agglomerates the fine dust particles and enhances the capture of the dust particles by the water spray droplet impaction.
- The water sprays cool and saturate the air over the sand beds, reducing the plume rise velocity and turbulence, thereby increasing the effective extraction effect of the hoods over the sand beds.

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BSc in extractive metallurgy in 1972 and a PhD in 1987 on the plasma smelting of chromites and steel plant dusts from the University of Aston in Birmingham Peter started his industrial career with British Steel working on different BOF steelmaking plants in the UK. He then worked as R&D director for Tetronics R&D, UK, developing plasma and DC arc furnace applications before moving to Elkem Technology as senior specialist working on process development. In 1998 he moved to Eramet Norway Sauda Ferromanganese smelter as senior specialist on the Manganese Oxygen Refining, process manager, and finally strategic development officer before retiring in late 2015. He is now working as a consultant in the smelting industry specialising in process development and plant optimisation studies