THE USE OF FINE WATER SPRAYS TO SUPPRESS FUME EMISSIONS WHEN CASTING REFINED FERROMANGANESE

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ABSTRACT

During casting of refined ferromanganese alloys in sand beds at temperatures up to 1800^{o}C a considerable amount of very fine brown fume is generated by the active oxidation of the alloy. This fume is difficult to capture because of the large flux of fume generated. The fume flux is associated with the high evaporation rate of Mn at elevated temperatures, the large thermal plumes over the casting beds, the large surface area of the casting beds and the very fine nature of the fume. This paper describes how the use of fine water sprays along the edge of the roof covering the casting bed has led to a significant reduction in visible diffuse emissions. The flux of fume generation during casting is also markedly reduced when water sprays are used in the vicinity of the casting beds. Possible fume suppression mechanism investigated included the interaction of the moist air stream with the Mn vapor in the boundary layer over the liquid alloy and the resultant formation of a thin layer of Mn oxide on the metal surface that reduces the Mn evaporation flux. Video techniques are used to semi-quantify the flow patterns over the sand bed, to calculate the energy in the fume plumes and to provide input parameters for CFD modelling of air flows over the casting bed. These data are used to optimize the capture of the fume from sand beds both inside and outside the smelter building. The safe use of fine water sprays in the vicinity of liquid metal is considered and practical tips to avoid water / metal contact are presented. The use of fine water sprays represents a cost-effective way of reducing fume emissions.

1 INTRODUCTION

Eramet Manganese Sauda is constantly working to reduce diffuse emissions from the ferromanganese smelting operations. One of the primary sources of diffuse emissions had been from the refined ferromanganese casting beds. A project was initiated to evaluate increase in the existing fume hood size and capture efficiency but CFD modelling indicated that it would be difficult and expensive to capture all the emissions. This article describes how water sprays along the edge of the roof over the casting beds were developed as an effective and low cost alternative to conventional fume hoods. As well as capturing any fume escaping from under the existing casting bed hood and roof the water sprays also reduce the amount of fume being produced.

1.1 Eramet NorwaySauda

Eramet NorwaySauda, one of three Mn alloy smelting plants in Eramet Norway, operates two 40MW Submerged Arc Furnaces producing High Carbon Ferromanganese (HCFeMn) using ores from Gabon and South Africa. A large proportion of the HCFeMn is decarburized in the Manganese Oxygen Refining converter (MOR) unit to produce medium and low carbon ferromanganese.

1.2 Diffuse Emissions

Secondary fume emissions are generated at the furnace tap holes, metal transfers, oxygen refining as well as casting and pouring operations. Most of the existing fume capture systems over point sources around the smelter have good capture efficiency, but some fugitive emissions do occur during the pouring of refined ferromanganese into the casting beds because of the very high metal temperature (~1750^{o}C), the high vapour pressure of Mn and a large surface area of the cast metal to be evacuated. These fumes contain fine manganese oxides, particularly Mn_3O_4, which are easily inhaled due to their small particle size. Exposure to high levels of fine particles from metallurgical processes has been linked to cancer, pneumonia, chronic obstructive pulmonary disease (COPD) and other respiratory and cardiovascular syndromes [1,2,3,4,5]. Inhalation of certain manganese compounds has also been linked to inflammation and neuropsychological disturbances [6,7,8]. It is imperative that these fumes are removed from the local work place, urban communities and the environment at large by means of correctly designed and maintained fume extraction and capture systems [9].The location of the Sauda plant close to the city centre and major settlement areas enhances the need for complying with legislation as well as expectations from our neighbors.

2 PROCESS DESCRIPTION

2.1 Refining of High Carbon FerroManganese

HCFeMn containing approximately 78% Mn, 7% C and less than 0,50% Si is produced in the two 40 MW HCFeMn furnaces. Each furnace taps about 30 ton HCFeMn twelve times per day. A portion of this HCFeMn is cast in sand beds, cooled, crushed and sold. The remaining HCFeMn is decarburized by blowing with high pressure oxygen through a top lance in a converter similar to a steelmaking BOF converter. Final refined FeMn metal analysis is 0,5-1,5% C, ~81,5% Mn, ~16,5% Fe, and ~0,1% Si. The initial HCFeMn temperature is approximately 1350^{o}C, rising to 1750^{o}C at the end of the blow for a refined FeMn alloy containing 1,5% C or 1800^{o}C for an alloy containing 0,5% C. This high operating temperature creates severe operating challenges such as converter refractory wear, casting of super-heated refined alloy, and significant Mn losses as fume due to the high vapour pressure of Mn at these temperatures. Olsen reports the typical Mn recovery is approximately 90-92% to the metal, 0-3% to slag and 5-10% to fume, depending on the process variant and the desired end point % C [10].

2.2 Casting and Solidification

Two casting beds are available for solidifying the refined alloy. Each casting bed consists of a refractory lined runner to deliver the alloy from the converter to the first of 9 interconnected pockets formed in olivine sand. The refractory lined runner is positioned inside the furnace building in an enclosed pouring station connected to a bag filter plant equipped with micro-porous PTFE membrane – fibreglass filter bags. Extraction capacity is approximately 120,000 Nm^{3}/h. Fume capture efficiency is excellent with little diffuse emissions from this point source.

The casting beds themselves are located outside the furnace building but connected to the pouring station inside the building. The beds are covered with a roof but are open along their sides, as shown in Figure 1, for the front end loader machine access to remove the solidified alloy plates. The pouring-in runner is located at the left end of the casting bed and metal flows progressively from left to right as successive pockets are filled. A fume capture hood is located only over the first three casting pockets despite the fact that emissions are generated from all 9 pockets as metal flows from one to the next.

Figure 1: Casting beds showing fume escape from under extraction hood and roof.

The casting bed extraction system has a capacity of ~120,000 Nm^{3}/h. Because of the small extraction hood size the limited extraction fan capacity, the large surface area of exposed metal, the open sides of the casting beds and variable wind conditions, some fume escapes from the casting beds.

3 MONITORING DIFFUSE EMISSIONS

A variety of techniques are used to monitor emissions at the Sauda site:

3.1 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 identified, manually logged and their severity are compared to a set of standard images by the operators every shift. Results are presented on the key process parameters notice board in the control room, reported at daily production meeting and appropriate corrective actions are taken. The monitoring was implemented in 2007 and is a vital part of the efforts to increase awareness and create active involvement in our continuous improvement projects on diffuse emissions.

3.2 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.

3.3 Neighbour reporting

As the smelter is located close to the centre of the town and a popular ski centre, fume emissions may be a nuisance to plant neighbours. The neighbours are encouraged to telephone the control room and report diffuse emissions. Complaints, with details of the source and severity are registered and acted upon. The number and severity of complaints are used as a rough guide to emission improvement. The Eramet plants organise annual neighbour meetings, where results and plans are presented, and questions and comments from the neighbours are duly dealt with.

3.4 Dust Drop Out

Four dust drop-out measurement stations are located around the town to collect dust samples. Dust weight and analysis are reported on a monthly basis.

4 FUME FORMATION

4.1 Fume Characterisation

Table 1 shows the average XRF analysis of 10 fume samples taken from the discharge conveyor of the baghouse filter connected to the casting bed.

Table 1: Fume analysis

%Mn_3O_4	**%Fe_2O_3**	**%CaO**	**%MgO(%)**	**%SiO_2**	**%Al_2O_3**
97,1	2,4	<0,1	0,21	<0,1	0,36

Figure 2 shows the particle size distribution of the fume samples taken from the baghouse filter. 100% of the dust was <5 micron in particle diameter.

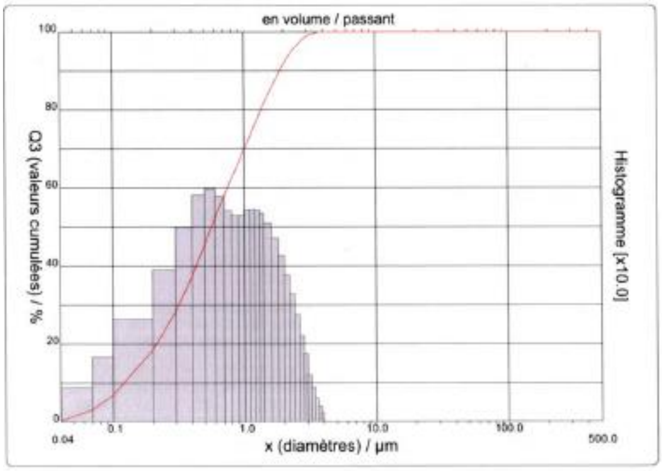


Figure 2: Fume particle size distribution

4.2 Mechanisms of Fume Generation

An understanding of the mechanisms of fume generation during refining and casting of refined ferromanganese is relevant to help decide on appropriate methods of fume capture and how fume production can be suppressed. Little information on fume emission generation mechanisms in the ferromanganse industry could be found but studies by Guezennec [11], Gonser and Hogan [12] and Huber [13] describe fume generation from EAF and BOF steelmaking furnaces. Mechanisms include:

- Volatilization of low boiling point metals; especially prominent in the hot spots under the arc or oxygen jet. Metals such as Zn. Cd. Pb and Mn will preferentially volatilize producing a very fine particle size fume rich in the volatile component. As the MOR converter filter dust and casting bed filter dust contain ~97% Mn_3O_4 and very little Fe_3O_4, this is considered to be the prominent mechanism during O_2 blowing in the MOR converter and during casting.
- Splash or emission of droplets at the impact zone of the arc or oxygen jet on the steel bath. These particles tend to be larger in size and contain slag components. The author has observed a significant amount of splash being ejected from the MOR converter, especially if the O_2 lance stand-off distance is incorrectly adjusted, however little or no splash occurs during casting.
- Projection of droplets by bursting of CO bubbles from the decarburisation reactions within the steel bath. These medium size fume particles are often present as hollow or half spheres and are of approximately the same composition as the steel bath.
- Bursting of the droplets as they come in contact with the oxidizing atmosphere within the furnace / converter. These small particles are also of the same composition as the steel bath.
- Carryover from the additions of solids to the furnace, such as lime, scrap, carbon. These coarse particles have the same composition as the addition materials.

Naess [14] found that the fume produced during the oxidative ladle refining of silicon primarily results from oxidation of the exposed metal surface, with oxygen transport from the surrounding atmosphere to the metal surface being the limiting factor.

Due to the high metal temperatures and the relatively low boiling point of Mn, evaporation followed by oxidation of the vapour directly to fine Mn_3O_4 is considered to be the most significant mechanism of fume generation during the casting of FeMn. Flow of metal from one casting pocket to the next is relatively calm with little or no splashing. Likewise there is no significant decarburization and subsequent bubble bursting / droplet ejections during casting. Fume formation by evaporation of Mn is supported by the fume analysis which is >97% very fine Mn_3O_4 particles. Had splash or bubble bursting from the liquid ferroalloy bath been a predominant mechanism, then the analysis of the fume would be closer to ferroalloy composition, specifically the fume would have contained more Fe_3O_4.

4.3 Kinetics of fume generation

A discussion of the kinetics of Mn_3O_4 fume generation over the casting beds will help understand the unexpectedly high energy measured in the fume plume rising over metal during casting. Normally, the filter and fan extraction capacity are partly based on the plume energy calculated from convection energy considerations only and do not take into account any oxidation reactions occurring between vaporized species and air. Any additional exothermic reactions will increase the fume plume energy and rise velocity, thus potentially overpowering the extraction capacity leading to diffuse emissions.

The maximum possible rate of vapourisation of a species occurs into a vacuum and is calculated using the Langmuir equation derived from the kinetic theory of gases, Dennis et al. [15].

$$E_A = p_A \left(\frac{M_A}{2\pi RT} \right)^{0.5} \tag{1}$$

Where E_A is the evaporation rate of A in kg/s.m^2, M_A is the molar mass of A in kg/gmol and R is the universal gas constant in J/gmol.K.

Turkdogan et al. [16] have shown that, at high oxygen partial pressures over the metal surface, metal evaporation rates can approach those in vacuum and thus can be predicted by the Langmuir equation. This effect is known as oxidation enhanced vapourisation and is caused by oxidation of the metal vapour above the liquid surface [17] forming a MnO mist, reducing the partial pressure of Mn in the boundary layer and promoting further evaporation of Mn into this sink. The possible rate limiting factors are the mass transfer of Mn in the melt to the interface, evaporation of Mn at the interface, Mnvapour transport away from the interface in the gas and transport of O_2 to the interface. Because of the high FeMn temperature (~1750°C) the evaporation of Mn is fast. Also the relative abundance of Mn in the FeMn (~80%) is not likely to cause depletion at the metal surface. Therefore, the rate of Mn loss /MnO fume formation is considered to be controlled by the counter-diffusion of Mn and O_2 in the boundary layer that exists above the metal surface. This is shown schematically in Figure 3 after Lee et al. [18].

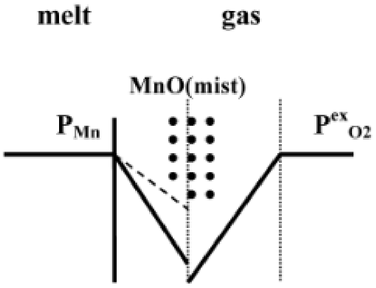


Figure 3: Boundary layers and concentration profiles for the oxidation enhanced vapourisation of manganese (18)

5 FUME CAPTURE

5.1 Fume Extraction System Characterisation

As the extraction system over the casting beds was under performing it was decided to create a CFD model of the system and design a fume extraction system capable of capturing 100% of the fume. Els et al. created an initial CFD model using FloEFD 11.3.0 proprietary software to quantify the heat transfer due to the convection energy from the FeMn cast plates and the radiation energy received by the back wall of the casting beds [19]. A combination of site data from the fume extraction duct testing (flow, temperature, pressure), FeMn temperature, plume velocity, plume energy and sand bed geometry were used to determine suitable CFD input parameters. Figure 4 shows a clip from a high speed video recording of the fume that was made to measure the plume rise velocity. Based on these measurements the energy in the fume was calculated and was found to be more than predicted from natural convection considerations typically used for fume extraction design. This supports the assumption that an additional energy source, namely the exothermic oxidation of Mn vapour and radiation from the particles in the plume, contributes to the plume rise velocity and growth.

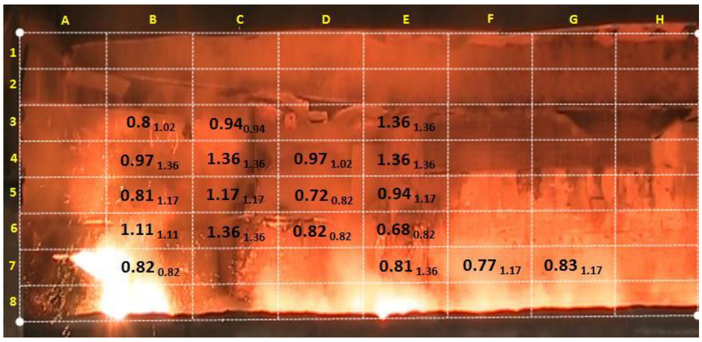


Figure 4: Fume velocity over sand beds [19]

5.2. CFD Model of Fume Capture Enclosure Over The Casting Bed

Figure 5 shows a possible arrangement of a large overhead hood with fixed end walls and a closure door along the front of the casting bed to limit ingress of air. The model was based on the existing extraction capacity of 120,000 Nm^3/hour.

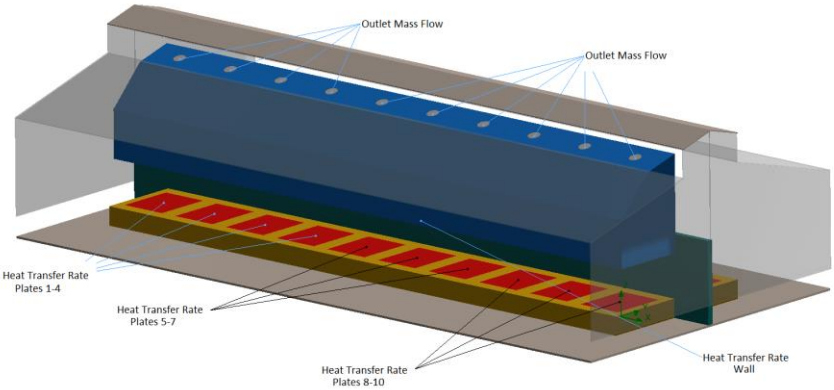
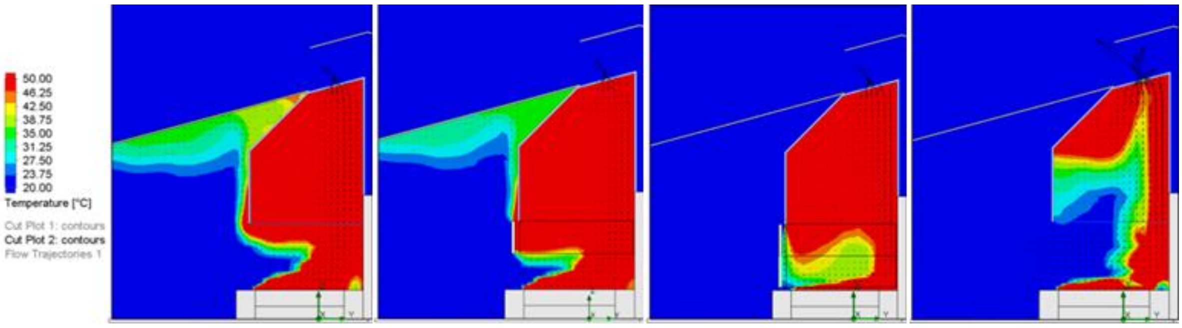


Figure 5: Schematic layout of casting beds

Figure 6 shows the model predictions for different degrees of opening of the front opening door.



2m Opening
94% Capture

1m Opening
96% Capture

0.1m Opening
100% Capture

Double Extraction
Volume
100% Capture

Figure 6: Comparison of temperature plot through cross-section of hood [19]. Temperatures over 20°C outside of the hood volume indicates fume leakage.

To achieve 100% fume capture either the casting beds need to be nearly totally enclosed by the hood, end walls and a door along the long, front side of the casting bed, or the current extraction capacity needs to be more than doubled. Such an enclosure would be expensive to construct and exposure to high thermal loads would probably lead to high maintenance costs, therefore it was decided to investigate the use of water sprays as used in the mining industry for dust suppression and in the oil industry to suppress fires.

5.3 Use of water sprays to capture fume.

Preliminary tests began using a hand-held high-pressure water spray directed at the escaping fume, as shown in Figure 7. A beneficial effect was visually apparent.

Figure 7: Test with a hand-held high-pressure water spray.

General purpose large angle, flat jet, K 1590 type nozzles manufactured by PNR were installed every 2m along the roof edge over the casting beds, as shown in Figure 8 [20]. Each nozzle delivered 15 l/min water at 15 bar pressure These nozzles work on a deflection principle where water is directed through the nozzle orifice onto a specifically designed engineered surface to produce a wide angle flat jet spray pattern with medium impact and medium sized droplets so as to maintain the spray coverage in windy conditions. The sprays point outwards to avoid water accumulating on the floor close to the casting bed. Fume that escapes from under the roof is “scrubbed” out by the water sprays. The ground in front of the casting beds slopes away from the bed to prevent water accumulation and icy conditions in winter. Excess dirty water is collected in the smelting plant sedimentation basin for cleaning before discharge. Water pipes and nozzles are heat-traced to prevent freezing in winter. Since the installation of these nozzles, the visible emissions from the casting beds have been very significantly reduced.

Figure 8: Permanently mounted water sprays along the casting bed roof. No fume is escaping from under the roof.

5.4 Theoretical framework for fume capture using water sprays

The following section is a draft theoretical method to calculate the secondary fume particle capture using a spray of water droplets. An CFD analysis will be able to verify the validity of the assumptions regarding flow.

Figure 9 is a simplified depiction of the expected flows around the casting bed. Due to the buoyancy of the hot gas and the work applied by the extraction system, the secondary fume initially moves upward. However, due to insufficient extraction capacity, build-up of the fume occurs beneath the roof of the casting bed. Subsequently, the fume spills out from below the roof and, upon rising, comes into contact with a spray of fine water droplets. Secondary fume particle capture is expected to occur in the region depicted on the figure. If the droplet spray is able to cool the gas to below the ambient temperature then the flow path of the gas is expected to roughly follow that of the droplet spray (green arrow). If, however, the gas remains relatively buoyant, then the scrubbed air will leave the particle capture region (in the direction approximated by the yellow arrow) and diffuse into the atmosphere.

Within the expected particle capture region, a cross-flow exists between the spray of droplets and the secondary fume. Calvert [21] developed an equation for particle penetration through a counter-current vertical spray chamber. Penetration is defined as the fraction of particles of a specified diameter that are **not** captured. The aforementioned equation can be modified to predict particle penetration in cross-flow chambers and can be used for this application to evaluate fume capture efficiency.

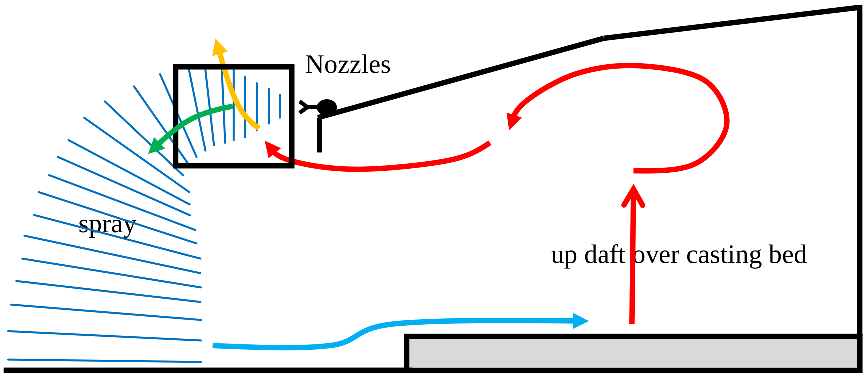


Figure 9: Expected flow across the casting bed

Due to the changing properties of the flowing streams, in particular the spray of droplets, it is suggested that the Calvert equations be used in conjunction with the principles of mass and energy conservation across *n* differential control volumes as depicted in Figure 10.

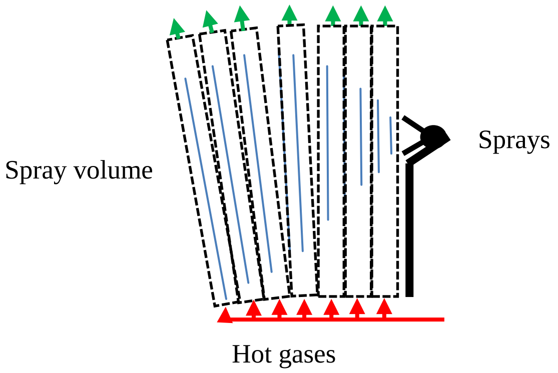


Figure 10: Flow of dirty gas through the spray volume

Figure 10 depicts the dust laden gas flowing through the spray volume into the control volume at the top. The net velocity of the gas out of the control volume can be approximated by accounting for changes in buoyancy with temperature and changes in horizontal movement due to shear forces applied by the droplets.

This method of simulation can take into account the following:

- The changing velocity vector of the droplets by calculating the acting net force resulting from gravitational and drag effects.
- The changing droplet size and fume temperature by applying the principles of mass and energy conservation across each control volume.
- The changing length of the scrubbing contact zone by considering the initial length of the contact zone at the start of the control volume and the velocity vector of the droplets.

The following may be assumed to simplify the calculations:

- The fume gas flow is split equally amongst the *n* control volumes.
- The water droplets and gas leave the control volume at the same temperature, and the gas is completely saturated.
- The spray droplets within each control volume are of uniform size, i.e., even though the hot fume gas comes into contact with the bottom-most spray first, the energy transfer can be assumed to be divided amongst all the droplets within the control volume.
- The gas flow into each control volume is perpendicular to the velocity vector of the droplets moving through the control volume. This corresponds to a tilting of the control volumes as depicted in the Figure above.

With regard to whether the spray of droplets will completely evaporate before reaching the ground, energy balances must be completed across control volumes along the entire flow path of the spray. A method to estimate the ingress of ambient air into the control volumes will be important along the spray path following the particle capture region in order to allow for continued mass transfer of water from the droplets.

6 FUME SUPPRESSION

As well as capturing the escaping fume, it was noticed that the amount of fume being produced during the casting operation was visibly reduced. For the water sprays to suppress the fume generation rate, the spray must have an effect on the flow rate of oxygen/air to the metal surface, on the flow pattern of the air directly over the metal surface, or the enhanced formation of a very thin oxide protection film on the metal surface.

Figure 11 shows that the updraft from the casting beds draws in moisture saturated air over the flowing liquid metal. When water droplets evaporate in a high temperature zone, the latent heat of evaporation will have significant cooling effect on the rising plume. When water evaporates to form steam, the steam will occupy a volume ~1700 times greater than liquid water, and thus the steam formed will dilute the O_2 in the air over the casting beds. The necessary partial pressure of water in air to render the air inert is about 30% [21]. This is achieved at an air temperature of ~70°C.

Figure 11: Moisture saturated air being drawn in over the casting beds.

7 CONCLUSIONS AND FUTURE WORK

Water sprays have been shown to be effective in capturing diffuse emissions and suppressing fume generation during casting. Fume suppression mechanisms are unclear but may include dilution of the O_2 in the atmosphere over the cast metal

The paper is very much “work in progress”, therefore the following actions will be carried out to more fully understand the beneficial use of water sprays:

- Laboratory scale: Melt FeMn in a laboratory scale induction furnace and introduce gas through a lance positioned above the liquid metal surface. The dust produced will be captured and characterised with respect to generation flux (amount of dust per time and area units), phase and chemical composition, particle shape, particle size and particle and agglomerate size distribution. The variables to be investigated include metal temperature, gas flow rate, and gas composition - primarily with respect to oxygen and water vapour content.
- Industrial scale: Determine the optimum droplet size for fume capture and fume suppression.
- Industrial scale: Place dust samplers over the casting bed to measure the fume generated during casting. Make tests with and without water sprays to give an indication of fume generation rate.
- Industrial scale: Make tests with fog nozzles (water + compressed air) instead of water sprays in order to reduce the amount of water used so as to maintain a dry floor in the furnace building in areas where molten metal is being transported. According to Wighus [21], fog nozzles use 1/5 to 1/10 for the water volume compared to sprinkler systems for the same cooling and inertisation effect.

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