VISUALISING THE SOURCES OF POTROOM DUST IN ALUMINIUM SMELTERS

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Abstract

'Potroom dust' comprises one of the major sources of particulate emissions from a smelter to the environment. With regulatory emission limits for particulates continually tightening, there is a need for smelters to understand the sources and pathways by which dust is generated in a potroom. Only armed with this understanding can smelters develop targeted strategies to counter these emissions. Methodologies to sample and analyse the composition of potroom dust (both settled on surfaces and airborne) have been applied in four smelters. By taking samples across a range of potroom locations and elevations, an overall compositional picture of dust can be built and visualised for any potroom. In general, settled dust is dominated by cover material and alumina - the role of each, however, is influenced by the granulometry of cover and how alumina is delivered to the pot. In contrast, airborne dust in a potroom is typically dominated by bath-related compounds.

Introduction

Potroom dust' can be defined as the air-suspended particulate in the potrooms of aluminium smelters. This particulate is typically process-related material that has escaped confinement. Typical components of dust include: alumina, bath-based compounds (crushed bath, bath droplets and fume), anode cover material, carbon dust, sulfur and metal impurities [1-3]. Such particulates can range in size from the nanometer-scale up to 100 μ m and beyond [2]. Particulates not specifically related to the smelting process (rust, silicates, marine salts) can also be found in potroom dust, albeit at more minor levels [4].

Smelters today face an important challenge to manage and reduce their emissions of potroom dust. Globally, regulated emission limits for smelters are becoming more stringent. In Europe, OSPAR-recommended emission limits have dropped from 1.0 to 0.6 kg/t Al for total fluorides and from 2.0 to 1.0 kg/t Al for total particulates, from the year 2007 to 2010, respectively [5]. These limits are particularly relevant to potroom dust as it contributes significantly to both types of emission. Firstly, any fugitive dust that escapes the potroom directly contributes to the total particulate emitted from a site. Secondly, potroom dust can contain 30-55% of fluorides and can contribute up to one-third of a smelter's emissions of total fluorides [2, 6]. The air quality of a potroom can also be regarded as an indicator of operational performance. Poor air quality can be linked to unstable pots (requiring frequent operator intervention), poor work practices on pots or excessive fines in raw materials (e.g. alumina and anode cover material) [7]. The effect of dust on the working environment of a potroom is another consideration for smelters, but was not an aspect covered by the study reported here.

To date, studies on potroom dust have provided only a limited level of understanding on the composition and sources of dust. Many of these studies (both in open literature and in industrial reports) have been highly focused and targeted at only specific fractions of dust [8]. For instance, studies on fluoride emissions are targeted at particulate fluorides; similarly, occupational hygiene studies are focused on fine, respirable dust particles (<10 μ m or <2.5 μ m in size) [3, 4]. The specificity of these studies makes compiling of results difficult – often the sampling and characterisation methods employed are incompatible. Many of the findings on the role and contribution of different sources of dust are therefore highly variable [8].

A further gap in knowledge is whether the composition of dust is uniform or whether it varies as a function of position or elevation in the potroom. The majority of past studies are based only on localised areas in the potroom, e.g. environmental studies focus on dust at the roof level (regarded as the point of emission), whereas occupational hygiene studies focus on dust at the operating floor level. There is also limited understanding on whether dust varies across different smelters and reduction technologies. It is clear, therefore, that a broad, 'big-picture' understanding of dust generation in a potroom has yet to be established.

Despite the variable methodologies and objectives of previous studies, when combined together, they do provide evidence that the likely major sources of potroom dust are alumina, pot fume and bath-related compounds [1, 2, 4]. Firstly, alumina is present as both the feedstock to the process and a component of anode cover material. The fine fractions (< 45 μ m) of feed alumina are often implicated by smelters as one of the most significant contributors to potroom dust [9-11]; however evidence to this link has thus far been circumstantial [2]. Pot fume, or particulates entrained in the hot cell gases of a pot, becomes a source of dust when it escapes the confines of gas collection systems. Pot fume is typically bath-rich (in the form of aerated bath-fines, bath droplets and condensed bath vapour or fume) and may also contain entrained alumina and carbon soot [1-3, 12]. Anode cover material, being typically a mixture of crushed bath and alumina, is a third likely source of dust. It acts as a barrier to both anode air burn and emission of pot fume, and is also a regulator of top cell heat transfer [2]. Furthermore, the role of dust sources from within the pot compared to those external to the pot (e.g. re-circulating settled dust, raw material spillages, emissions from spent anodes or bath cavity cleanings) are also not well understood.

In 2004, a 'Scoping Study on Potroom Dust' [8] surveyed a wide range of reported mechanisms of dust generation. Three common factors behind dust generation were extracted: (i) the properties of material sources of dust in the process (including aeratability and fines content); (ii) the smelting technology used (including materials transport and pot gas extraction systems); and (iii) the work practices applied within the potroom. These elements have formed the framework behind the current research on potroom dust.

Research Background, Objective & Scope

With the completion of the scoping study [8], the Light Metals Research Centre was commissioned by AMIRA International to conduct a full plant-based study on potroom dust, entitled '*P791a*: *Potroom Dust, Character & Causes*'. The study aimed to provide a deeper understanding of the mechanisms behind potroom dust generation and focused on several key questions:

- What are the composition and material sources of dust?
- What are the key mechanisms that generate potroom dust (with respect to raw materials properties, smelter technologies and work practices used)?
- Do the same mechanisms of dust generation apply to any general smelter or are they site-specific?
- Can strategies be developed to better manage these mechanisms of dust generation?

The potroom dust study consisted of six sampling campaigns at four different pre-bake, point-fed smelters, in collaboration with three industry partners. Each smelter had varying sets of raw materials properties, technologies and work practices, allowing the study to make broad conclusions across a range of smelting technologies and scenarios. To provide a greater, 'big-picture' understanding of potroom dust generation, the study focused on all air-suspended particulates in the potroom, ranging from 0.1 to 100 μ m in particle size. This differed from the fluoride-specific focus of many environmental studies. Similarly, it differed in approach to occupational hygiene studies which target only fine, respirable particles. The presence of non-process related dust (rust, marine aerosols) was also of interest, but understanding the mechanisms behind such compounds was considered outside the scope of the study. Older Söderberg technology smelters were also excluded from the scope of the study.

The first challenges were to develop a sampling methodology that allowed collection of representative samples of dust, and to develop an analysis methodology that allowed fingerprinting of the sources of dust even when those sources had overlapping components (e.g. bath components in both cover material and pot fume). This paper presents a sound methodology to capture and measure the composition of potroom dust, and presents useful visualisation tools that allow us to understand variation in dust composition: firstly, across different locations or elevations in a potroom and secondly, as a function of the material sources of dust across different smelters.

Sampling & Analysis Methodology

In order to build a representative picture of the dust compositions in a potroom, sampling activities incorporated not only *airborne dust* in a potroom (air-suspended particulate) but also *settled dust* (accumulated material on surfaces that can potentially be reaerated or re-circulated). To examine the spatial variation in dust composition across any potroom, samples were taken across a range of potroom locations and elevations (as shown in Figure 1A). *Material sources* of dust were also taken for compositional 'fingerprinting' and comparison against collected dust.

Sampling of Airborne Dust, Settled Dust & Dust Sources

For compositional analyses, airborne dust was collected using *Tisch TE-2000P* high volume samplers as shown in Figure 1B. High sampling flowrates (up to 350 L/min) and large filter areas

(110mm Whatman GF/C) enabled collection of large samples of dust for compositional analyses. Spatial variations in airborne dust across a potroom were examined using two sets of samplers operating simultaneously (refer to Figure 1A). Dust as a function of *elevation* was examined by sampling at the operating potroom floor (between two-pots) and the potroom roof level. Airborne dust generation was also examined as a function of *proximity to sources of dust* (raw material fill stations, potroom doorways, the tap-end of pots, etc). To capture the average composition of airborne dust over time, sampling durations were also designed to match the typical cycle of potroom operations, which varied from 24 to 48 hours across the four smelters.



Figure 1: Photos showing: [A] dust sampling locations in a typical potroom for airborne (x) and settled dust (•); [B] Tisch TE-2000P high volume sampler used to collect airborne dust.

In contrast, settled dust on surfaces was collected through both: (i) manual sweepings using a brush and pan and (ii) 'passive' collections of dust over 2-3 weeks using low-form aluminium trays. Samples were taken across a wide range of potroom surfaces (as illustrated in Figure 1A), spanning from the basement, to the potroom floor and up to roof/rafters level.

The likely material sources of dust (feed alumina, anode cover material, crushed bath) were collected either at the pot or from material conveyors or silos. Pot fume samples were also collected, as represented by condensed fume (condensed material from internal pot-superstructure surfaces) and particulate drawn from inlet ducts of GTCs (gas treatment centres) or dry scrubbers.

Analyses of Dust Compositions

X-Ray Diffraction (XRD) was the primary analysis method for determining the composition of dust. Settled dust and dust sources (generally loose particulates) were powdered, doped with a 10% wt silicon internal standard and scanned using a *Rigaku MiniFlex II* diffractometer (Cu-K α radiation, 2 θ range 10-70°C, step size 1°/min). Levels of major component phases in settled dust and dust sources were then estimated using an '*Internal Standard Method*' as described by Brandt and Kinneging [13]. For airborne dust however, XRD scans were carried out directly on dust adhering to filter surfaces. Levels of major dust phases were then semi-quantitatively estimated using *Bruker EVA S-Q* software. For all samples, the major component phases analysed were:

- Bath-related compounds: cryolite (Na₃AlF₆), chiolite (Na₅Al₃F₁₄) and calcium chiolite (Na₂Ca₃Al₂F₁₄),
- Transitional aluminas $(\gamma, \gamma' \text{ and } \theta Al_2O_3)$,
- Corundum (a-Al₂O₃) and graphitic carbon (C).

Minor component phases in each sample were qualitatively estimated by comparing diffracted peak heights for each phase against major diffraction peaks. Minor phases analysed were: bath fume or atmolite (NaAlF₄), uncalcined alumina or gibbsite (Al(OH)₃) and aluminium hydroxyfluorides – tracer phases for fluorinated alumina aged over time in a humid environment (Al₂(OH)₃F₃ and AlF_{1.65}(OH)_{1.35}.xH₂O) [14].

Challenges in Characterising Dust Compositions

While the above methods allowed characterisation of the component phases in each sample of dust, piecing this information together to identify the dominant material source(s) was a further challenge. This was made difficult by the high level of overlap between the components of each material source. Transitional aluminas, for example, are found in both feed alumina and cover material. To overcome this challenge, the study developed two methods to visualise the composition of dust. The first method relied on the presence of 'tag' components to give an initial indication of the predominant source of a dust sample, i.e.:

- Feed alumina = transitional aluminas (low levels of corundum, often contains gibbsite);
- Cover material = mixtures of bath phases, corundum and transitional aluminas;
- Crushed bath = high levels of bath phases (low levels of corundum);
- Pot fume = also high levels of bath phases, but distinct from crushed bath as it contains carbon and NaAlF₄;
- Hydroxyfluoride signals = indicate the presence of aged dust (i.e. with a long residence time in the potroom) that contains fluorinated alumina.

Composition was then plotted against location to visualise how the possible sources varied as a function of position in the smelter. In the second method, composition of the dust samples was plotted on a 'ternary diagram' to more clearly identify the primary sources. Together, these provided a clear understanding of (i) how dust varied as a function of location in a potroom and (ii) the overall contribution of each material source to dust in any smelter.

Results & Discussion

The two visualisation methods for understanding the composition of potroom dust are presented as follows. For the purposes of comparison, the four case study smelters have been designated Case Study A, B, C and D.

Visualising Dust Compositions Spatially across a Potroom

For each smelter, dust compositions (for both airborne and settled dust) across a number of potroom cross-sections were presented using a combination of bar-charts and tables – an example is shown in Figure 2. For each dust sample, levels of major phases (% wt) were plotted on a horizontal bar chart, whereas minor phases were shown in a table (showing qualitative dot-levels ranging from: not present, trace levels, substantial levels, to significant levels). For simplicity, all bath-related compounds were grouped under 'transition aluminas'.

These charts provided snapshot profiles of how the composition of airborne and settled dust varied as a function of potroom location or elevation, e.g. from the basement, to the operating floor and up to the roof level (for more detailed treatment, refer to



Figure 2: A snapshot profile of *airborne dust, settled dust* and *sources of dust* in a potroom, across a range of elevations. Note that: (i) settled dust includes both dust sweepings and dust collected passively on trays; (ii) normalised compositions (% wt) of major phases are shown in the centred bar chart, whereas (iii) qualitative levels of minor phases are indicated by dots (•) in the table on the right.

a recent publication [15]). More importantly, these charts provided comparisons of how individual dust samples related to the material sources of dust. One might observe that at this smelter, airborne dust resembles mixtures of crushed bath (match in terms of high levels of bath and lower levels of corundum) and pot fume (also contain carbon and NaAlF₄). In contrast, settled dust appears closer to a mixture of cover material and feed alumina, with varying contributions from each at different potroom locations. While this bar-chart and table visualisation is very useful in studying the spatial variation of individual dust compositions for larger data sets (>70 samples were obtained from at least two case study smelters).

Visualising the Overall Contribution of Dust Sources

To better visualise large sets of dust compositions in relation to their material sources, ternary or three-phase diagrams were used. This involved normalising levels (% wt) of bath phases, corundum and transitional aluminas in each sample to 100% and plotting them on triangular axes. The three phases were selected on the basis of their prevalence and distinctiveness as components of dust. Example ternary diagrams are shown in Figure 3 and Figure 4, for Case Study Smelters A and D, respectively. It should be noted that while the ternary diagram provides a clear representation of bath and alumina-based components, the analysis does exclude carbon and any other minor components in dust. To interpret these ternary diagrams:

- Each symbol on the diagram represents the composition of one dust or material source sample – larger symbols represent material sources, whereas smaller symbols represent airborne and settled dust.
- A 'mixing line' drawn between the compositions of feed alumina and crushed bath is used to represent mixtures of these two material sources.
- A shaded, triangular region denotes where dust is a mixture of cover material and partially hydrolysed bath fume or vapour (NaAlF₄). Complete hydrolysis of bath fume, as given by equation 1 below, forms a solid-phase mixture of 33% wt alumina and 67% wt cryolite [16].

 $3NaAlF_{4}(g) + 3H_{2}O(g) = Na_{3}AlF_{6}(s) + Al_{2}O_{3}(s) + 6HF(g)$ (1)

The ternary diagrams provided an ability to capture and convey a 'big-picture' view of dust compositions for any smelter.

Similarities in the Composition of Dust Sources

With the use of ternary diagrams (Figure 3 and Figure 4), it is clear that the material sources of dust were very similar in composition from one smelter to another. At all four smelters:

- Feed alumina was predominantly transitional aluminas (>90% wt) with very low levels of corundum.
- Crushed bath was high in bath (70% wt), lower in corundum (>20% wt).
- Cover material, being a mixture of feed alumina and crushed bath, was located on the alumina-crushed bath 'mixing line'. However it varies in composition as a function of bath-to-alumina blend ratio.
- Condensed pot fume under pot superstructures was predominantly bath-rich. In contrast, particulate drawn from GTC inlet ducts (also representing pot fume) resembled cover or mixtures of cover and feed alumina.

General Composition of Settled Dust

Overall, settled dust was found to be either predominantly cover material or a mixture of cover + feed alumina (refer to Figure 3 and Figure 4). The exact role of feed alumina and cover material in settled dust appeared to be highly dependent on two smelting technology factors, namely: the method of alumina delivery to the pot and the granulometry of cover material used in the potroom.

In Case Study A where alumina was *conveyed* to the pot and cover material was particularly '*fine*' in particle size, settled dust was predominantly cover material. This is shown in Figure 3, where the majority of settled dust compositions fall in the vicinity of cover material. In contrast, in Case Study D where alumina was loaded to the pot *by crane* and cover material was particularly '*coarse*', settled dust was roughly a 50/50 mixture of cover material and feed alumina. This is shown in Figure 4 where the bulk of settled dust compositions fall half-way between these two material sources. Average compositions of settled dust across the four smelters are summarised in Table I.

This finding demonstrates the influence of smelting technology in the generation of settled dust. In smelters where feed alumina was loaded by crane (as opposed to being conveyed), alumina was a greater contributor to settled dust. This is consistent with observed spillages of alumina on various potroom surfaces in these smelters. In contrast, at smelters where anode cover was particularly 'fine', cover material played a more dominant role in settled dust than alumina. This is consistent with expectation that fine cover is more easily aerated and therefore more likely to generate dust [2].

General Composition of Airborne Dust

The ternary diagrams have also provided a very clear distinction between airborne and settled dust. Overall, airborne dust consisted of much higher levels of bath (ranging 50-80% wt) and lower levels of total alumina. The majority of airborne dust compositions was also located in the shaded triangular regions in each diagram, denoting mixtures of cover and bath fume (refer to Figure 3 and Figure 4). These observations linked fine crushed bath particles (from anode cover) and bath fume as the two dominant sources of airborne dust. The significant level of particulate fluorides reported in potroom dust correlates well with this [1, 2, 6]. Table I gives a summary of compositions.

Interestingly, airborne dust compositions did not vary significantly from one smelter to another. However, there were slight influences towards higher bath content in airborne dust where cover material was '*fine*' (as opposed to 'coarse') and slight influences towards less bath content where alumina was loaded by overhead crane (as opposed to being conveyed). These trends were similar to those found in settled dust, but on a smaller scale.

Minor Compounds in Potroom Dust

The presence of minor compounds in airborne and settled dust (as shown in the bar-chart and table visualisations in Figure 2) can provide further understanding of how dust is generated. Firstly, the presence and activity of *alumina fines* in potroom dust cannot be discounted – this is shown by minor levels of uncalcined alumina or gibbsite (generally concentrated in the finer fractions of alumina supplied to smelters [9]) in potroom dust. Secondly,



Figure 3: Ternary Diagram for Case Study Smelter A, showing the composition of airborne dust (\$\2014) and settled dust (\$\xi\$) in a potroom compared to its material sources (n = 79 samples in total).



Figure 4: Ternary Diagram for Case Study Smelter D, showing the composition of airborne dust (\diamond) and settled dust ($\dot{\alpha}$) in a potroom compared to its material sources (n = 49 samples in total).

Table I: Composition of settled and airborne dust across four case study smelters categorised in terms of the delivery method for Feed Alumina and the Granulometry of Anode Cover Material.

Case Study	Delivery Mechanism for Feed Alumina to Pot	Granulometry of Cover Material	Composition of Settled Dust	Composition of Airborne Dust
Α	Conveyed to Pot	'Fine'	Predominantly Cover Material	Mostly Bath Fines + Fume
B	Conveyed to Pot	'Fine'	Predominantly Cover Material	Mostly Bath Fines + Fume
C	Loaded by Crane to Pot	'Coarse'	Mostly Cover + some Feed Alumina	Mostly Bath Fines + Fume
D	Loaded by Crane to Pot	'Coarse'	50% Cover + 50% Feed Alumina	Mostly Bath Fines + Fume

aeration or *re-circulation of aged, settled dust* from potroom surfaces (as opposed to 'newly generated dust') is an active mechanism of dust generation; this is indicated by the presence of aluminium hydroxy-fluorides (tracer phases for aged, fluorinated alumina [14]) in both settled and airborne dust. Finally, minor levels of bath fume/atmolite and carbon soot provide further evidence that *pot fume* is a contributor to potroom dust generation.

Conclusions

New characterisation and visualisation techniques (bar-charts and ternary diagrams) have provided a means to understand the composition of dust as a function of its material sources. They have also provided understanding in how dust compositions vary spatially as a function of location in a potroom. These techniques have uncovered a remarkable level of similarity in the composition of dust across four smelter case studies. In general, dust settled on potroom surfaces was composed of mixtures of cover material and feed alumina; however, the contribution of each was dependent on the granulometry of cover and the method of alumina delivery used in each potroom. In contrast, airborne dust in the potroom was dominated by high levels of bath (in the form of crushed bath fines and hydrolysed bath fume), with only minor levels of alumina. The current study on potroom dust has therefore provided a greater understanding of the composition (and therefore the material sources) of dust in a general pre-bake, point-fed smelter.

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References

- Less, L.N. and J. Waddington, "The Characterisation of Aluminium Reduction Cell Fume", *TMS Light Metals*, ed. T.G. Edgeworth, New York, 1971, 499-508.
- Hyland, M.M. and M.P. Taylor, "Origins and Effects of Potroom Dust", *TMS Light Metals*, ed. H. Kvande, San Francisco, CA, 2005, 141-145.
- 3. Heinrich, U., W. Koch, and W. Dunkhorst, "Characterization of the Exposure to Ultrafine Particles at

Workplaces of a Primary Aluminium Smelter" (Final Report, Fraunhofer ITEM Project No: 112 062: Hannover, 2004).

- Hoflich, B.L.W., et al., "Characterization of Individual Aerosol Particles in Workroom Air of Aluminium Smelter Potrooms", Journal of Environmental Monitoring, 2005, 7(5), 419-424.
- 5. OSPAR Convention, OSPAR Recommendation 98/2 on Emission and Discharge Limit Values for Existing Aluminium Electrolysis Plants, 1998.
- Dernedde, E., "Estimation of Fluoride Emissions to the Atmosphere", TMS Light Metals, ed. B. Welch, San Antonio, TX, 1998, 317-322.
- Hyland, M., "Tracking Sources of Airborne Dust including Nanoparticles: A Case Study from the Aluminium Industry", Australian Institute of Occupational Hygienists (AIOH), 24th Annual Conference, Gold Coast, 2006.
- Light Metals Research Centre, "Project P791: Potroom Dust Scoping Study" (Final Report, prepared for AMIRA International Ltd, 2004).
- 9. Perander, L.M., et al., "The Nature and Impacts of Fines in Smelter-Grade Alumina", JOM, 2009, 61(11), 33-39.
- Kjar, A.R., "Matching Alumina Properties with Reduction Requirements," JOM, 1994, 46(8), 24-26.
- Chambers, A.J., O.J. Scott, and M. Ooms, "Measurement of Dustiness and Flowability of Alumina", *Alumina Technology Workshop*, University of New South Wales, 1985, 271-296.
- Gaertner, H., A.P. Ratvik, and T.A. Aarhaug, "Particulate Emissions from Electrolysis Cells", *TMS Light Metals*, ed. S.J. Lindsay, San Diego, CA, 2011, 345-350.
- 13. Brandt, C.G. and A.J. Kinneging, X-Ray Powder Diffraction: A Practical Guide to Quantitative Phase Analysis, 2nd ed (Netherlands: PANalytical B.V, 2007).
- Gillespie, A.R., M.M. Hyland, and J.B. Metson, "The Surface Chemistry of Secondary Alumina from the Dry Scrubbing Process", *TMS Light Metals*, ed. R.D. Peterson, 2000, 345-350.
- 15. Wong, D.S., N.I. Tjahyono, and M.M. Hyland, "Methodologies for Fingerprinting Sources of Dust in Aluminium Smelters", *Conference of Metallurgists*, Montreal, 2011.
- Haupin, W. and H. Kvande, "Mathematical Model of Fluoride Evolution from Hall-Heroult Cells", *TMS Light Metals*, ed. S.K. Das, Denver, CO, 1993: 257-263.