

## TRACE ELEMENT CONCENTRATION IN PARTICULATES FROM POT EXHAUST AND DEPOSITIONS IN FUME TREATMENT FACILITIES

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### Abstract

In dry cleaning of pot exhaust, expensive fluorides are captured and returned to production. At the same time impurities are accumulated in the finer fractions of the secondary alumina fed to the cells. While in secondary alumina the impurity content increased in the finer fractions, raw gas revealed a significant increase in impurities for particles with  $D_i > 1 \mu m$ . Fume particles were sampled using a cyclone with varying cut-sizes and analyzed with help of HD ICP-MS. A statistical approach is used to identify correlations between element concentrations and particle diameters. Maximum impurity concentrations were recorded for fume fractions with particle size  $D_i > 10 \mu m$ . It is expected that an economically feasible way of removing coarse particles from pot exhaust will lead to improved metal quality and increased current efficiency while keeping fluoride losses at a minimum.

### Introduction

Development toward higher cell amperage involves increased resistive heating. To counter the effect of excessive resistive heating, current density and inter-polar distance have to be reduced. However, these measures are restricted to a certain minimum due to cell geometry, short circuiting and extensive back reactions between aluminum and carbon dioxide. The economics of the electrolysis cell can be improved if some of the thermal energy can be recovered. Recent research and development on heat recovery from aluminum electrolysis cells indicate that there will be a shift in the heat profile in modern electrolysis cells, mainly with respect to design of the cells superstructure and exhaust gas system, to break way for heat recovery from pot exhaust [1, 2, 3]. High gas temperatures are necessary to operate compact heat exchangers with sufficient thermal efficiency. However, more emitted cell heat will result in higher pot-room

and off-gas temperatures, with considerable impact on emissions [4, 5]. It is commonly accepted that the quantity of gaseous and particulates emitted is strongly influenced by bath chemistry and operational temperature, which again are dependent on raw material quality, cell design and process techniques [6, 7].

Mapping of impurity distribution in pot exhausts is of interest to develop efficient methods for removal of undesired elements in order to improve metal quality and operate fluoride recycling systems with minimum fluoride losses in a cost-effective manner by reducing deposition (scaling) and corrosion.

While in secondary alumina (fluoride enriched smelter grade alumina) the content of impurity elements increased with decreasing particle size (screen sizes 125, 90, 63, 45, 32  $\mu m$ , and tray) [8], the opposite trend could be observed in raw gas ultra-fines from aluminum electrolysis cells.

Concentrations of the elements Ni, Fe, P, V, Ti, Co, Cu, Zn, and Ga (here called "Impurity Group 1") increase significantly with particle diameters larger than  $D_i > 1 \mu m$ , while the elements S and K accumulated predominantly in sub-micron particles as previously reported [9] (Figure 1(b) and 1(c)). Sub-micron particles consist mainly of quenched bath fumes typical for cryolite-based melts with considerable amounts of  $NaAlF_4$ , S and K.

Varying morphology and high contaminant levels with strong correlation between trace elements, which are found in raw materials, indicated that the coarse particle fraction in the pot exhaust ( $D_i > 1.22 \mu m$ ) is a mixture of dust from alumina, cover-material, splashed bath and other entrained particles such as soot and residuals from anode combustion.

Since it was found that concentrations of Group 1 elements increase significantly with particle diameter in the ultra-fine fraction, the question is if the observed trends also are valid for the raw-gas fraction with  $D_i > 10 \mu m$ . The present work aims at determining amount and composition of particulate

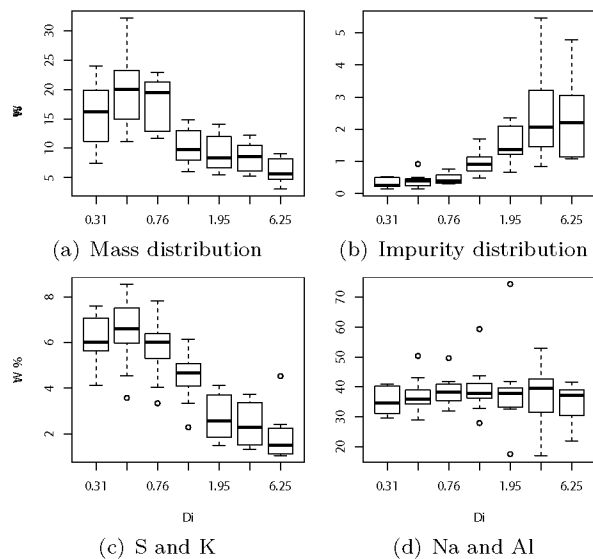


Figure 1: Concentration of Group 1 elements - Total Ultra-Fine content ( $D_i < 10\mu m$ ) approx.  $280\text{-}340\text{ mg}/Nm^3$ .

emissions from industrial electrolysis cells as a basis for evaluation, prediction and extrapolation of consequences for modern gas treatment facilities in primary aluminum industry. The measurement campaigns goals were a) to find indicators bordering the size range which contains the peak concentrations of impurity elements in fumes from aluminum electrolysis b) to gain a better understanding of the formation mechanisms of scale found in fume treatment facilities.

## Experimental

In an attempt to gain information about the impurity distribution in particles with aerodynamic diameters larger than  $10\ \mu m$ , pot exhaust was split into different particle fractions with help of a cyclone and compared to cascade impactor samples and residual fume particles captured on filters. Well mixed fumes from pot-room sections consisting of cell groups with up to 114 aluminum electrolysis cells were sampled upstream to dry-scrubbing facilities. The sampling system TPS4, supplied by Environnement S.A., was used for sampling with different flow rates thereby varying the cyclone's cut-size. Different Split ratios between raw gas coarse and fines fractions were obtained by variation of the sample flow rate (0.5, 0.7, 1.0, and  $1.5\ m^3/min$ ) to alter the cut-size of the cyclone while maintaining isokinetic sampling. The ex-

perimental setup is presented in Figure 2. The coarse particle fraction was separated from the sample flow with help of a standard EPA-cyclone [10] for removal of particles larger than  $10\ \mu m$ . The remaining fume particles passing through the cyclone were captured on filter type Pall Emfab TX40HI20-WW 47 mm (Aerosol retention: 99.9 %). Position 2a marks the location of filter to determine total dust concentration.

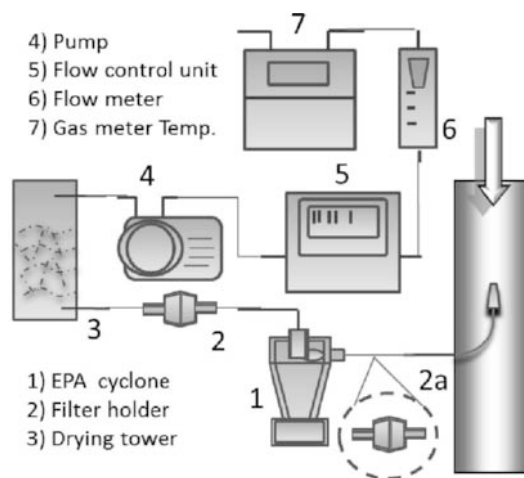


Figure 2: Experimental setup - TPS4 sampling system for isokinetic sampling of pot fumes.

Two measurement campaigns were conducted in May and June 2012. Overall 14 runs over 3 days with sampling duration of 30 to 45 minutes per run for filter measurements while a cyclone sample consists of the particles collected during three filter measurements to accumulate sufficient large amounts of coarse particles for analysis.

The collected fractions were weighed on a Mettler Toledo XP6U Ultra micro-balance and dissolved in solutions containing 65 %  $HNO_3$  and 40 %  $HF$  in a Ultraclave. The acid solutions were diluted to a final volume of 32 ml to 72 ml for element analysis in HR-ICPMS.

## Results and Discussion

### Pot Fume Fractions

An overview of determined dust-loads in the isokinetically sampled fractions is given in Table I.

The total dust concentration measured at the chosen sampling location (Filter position 2a in Figure 2 was  $400\text{ mg}/Nm^3$  ( $\pm 7\%$ )). Typical dust loads for aluminium smelters are  $380\text{ - }500\text{ mg}/Nm^3$  [3, 11].

Table I: Mass Fractions - Particle concentrations

Flow rate	Filter # Cyclon	Conc. [mg/Nm <sup>3</sup> ]	Rel. Stdev
1.5 m <sup>3</sup> /h	Filter 25	282.6	
1.0 m <sup>3</sup> /h	Avg Filter 26-28 Cyclone dust Total	275.9 153.4 429.0	3 %
0.7 m <sup>3</sup> /h	Avg Filter 22-24 Cyclone dust Total	272.3 96.6 368.5	6 %
0.5 m <sup>3</sup> /h	Avg Filter 29-31 Cyclone dust Total	301.1 85.1 386.6	4 %
ELPI setup	Avg Filter 32+33 Cyclone dust Total	346.1 58.5 404.7	31 %
	Avg on Filter	298.9	11 %
	Avg in Cyclone	98.4	41 %
	Total dust	397.2	7 %

Dust deposited in the ca. 90 cm tube connecting the sampling nozzle to the cyclone could not be measured with the chosen experimental setup, due to surrounding air flushing the potential tube-depositions back into the duct, as soon it was disconnected from the filter/cyclone for sample removal. Thus, the total particle concentration is expected to be somewhat higher than reported here due to losses in the sampling nozzle not accounted for. Fume particles passing through the cyclone were captured on a filter. These fines, referred to as filter fines, accumulated to 346.1 mg/m<sup>3</sup> ± 31 % at flow rates of 0.42 m<sup>3</sup>/h, representing the fraction smaller than the cyclone cut-size of approximately 11 μm.

The determined split-ratios and corresponding cyclone cut-sizes are listed in Table II.

Table II: Split ratio determined with TPS4

Flow rate [m <sup>3</sup> /h]	0.42	0.5	0.7	1.0
Cut-size [μm]	11.16	9.86	7.77	6.04
Rel. Mass on Filter	0.86	0.78	0.74	0.64
Rel. Mass in Cyclone	0.14	0.22	0.26	0.36

Figure 3 summarizes the determined contaminant levels over cyclone cut-size measured in coarse and corresponding filter fraction. Increasing the flow rate from 0.42 to 0.5 m<sup>3</sup>/h decreases cut-Size D<sub>50</sub> from 11.16 to 9.86 μm, resulting in a purification of the fine fraction. Simultaneously, the impurity concentration in the coarse fraction is also slightly reduced. The chemical analysis revealed that significantly higher amounts of Group 1 impurity elements are in the coarse particles (Cyclone fraction) with approximately two times the contaminant level concentrated in the coarse fraction compared to the corresponding filter fines.

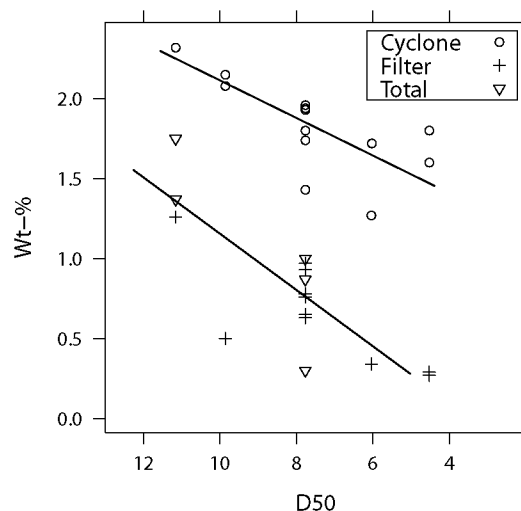


Figure 3: Impurity concentration changes in filter and cyclone samples with varying cut-size.

Further reduction of cyclone cut-size reduces the contaminant level in both fines and coarse fraction. The cut-size reduction from 11.16 to 6.04 μm resulted in change of the mass-ratio of coarse to fine fraction from 1:6 to 1:2, showing that significantly larger amounts of fumes are collected in the cyclone with increasing flow rates. The filter samples get “cleaner” the smaller the cut-off diameter of the cyclone is chosen. However, the purification of the fines with decreasing cut-size seems to level out to approximately 0.3 wt-% at a flow rate of 1.5 m<sup>3</sup>/h.

Although variation in recorded concentrations during repeated measurements can be significant (compare Figure 3 cut-size 7.77 μm), a general trend was observed: Purification of filter fines while simultaneously reducing impurity levels in the coarse cyclone fraction, as cut-size is reduced.

The reduction of impurity concentrations with the reduction of cyclone cut-size in both cyclone and fine fraction follows two steps: Firstly, separation of particle with high impurity levels in the cyclone, before secondly, larger amounts of fume-fines consisting of less contaminated condensates are separated and accumulate in the cyclone fraction when the cut-size is further reduced (compare Figure 4(a) and 4(b)).

Reducing cyclone cut-off will accumulate larger amounts of purer condensates in the cyclone fraction. Even the separation of particles with D<sub>i</sub> = 6.25 μm, which contain the maximum level of impurities of total 2.4 wt-% recorded during impactor measurements (but small fraction weight), does not increase the impurity level in cyclone fraction. This

leads to the assumption that maximum impurity concentration with respect to Group 1 elements (apart from S and K) is located in particles with aerodynamic diameters larger than  $D_i > 10 \mu\text{m}$ .

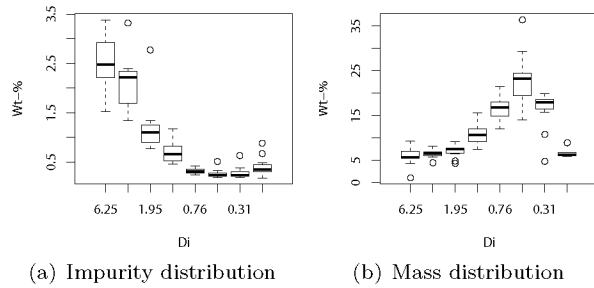


Figure 4: Ultra fines: Distribution Group 1 impurities and mass for particles with  $D_i < 10 \mu\text{m}$ .

### Depositions

Dando and Lindsay [12] report that depositions found in fume treatment plants or secondary alumina handling systems for prebake technology, often referred to as hard gray scale, consist of more than 90 % aluminum, sodium and fluoride. It is stated that the scale is presumably formed of alumina and bath fines together with minor contributions from absorbed fluoride and bath fumes. The authors report that the composition of particulate solids collected at the inlet to an injector scrubber shows a similar chemical composition as the scale, despite the higher degree of crystallinity and higher carbon and sulfur content in the inlet solids. The latter observation is in accordance with the concentrations measured in the work presented here.

Figures 5 and 6 show correlations and concentrations of elements abundant in gray scale as well as in the filter and cyclone fraction of pot exhaust. The graphs are developed using software for statistical computing called “R” [13]. A visual impression of the distribution of measured concentrations of the most abundant element is given in the principal diagonal of the scatter-plot.

Concentrations of Group 1 elements found in the largest particle size fractions of the pot exhaust as well as in the scale sample are significantly higher than reported in specifications for the raw materials (alumina and anodes). The scale sample reveals a similar chemical composition comparable to trace element composition recorded in coarse fume particles captured in the cyclone (Figure 5).

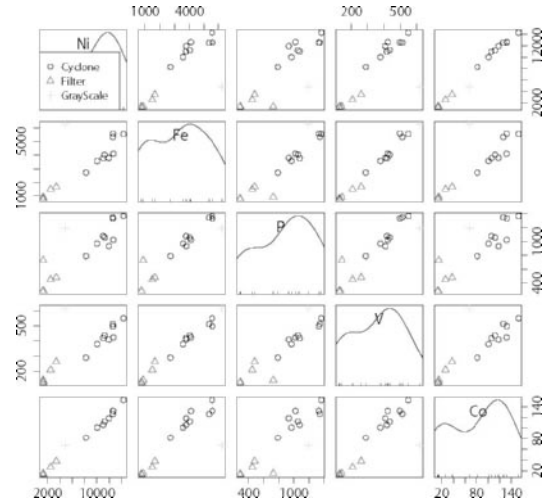


Figure 5: Comparing coarse fume fractions captured in cyclone to fine fume particles and a Gray-scale sample. Concentrations in [ppm]. Trace elements concentrate in the coarse cyclone fraction of the pot fumes.

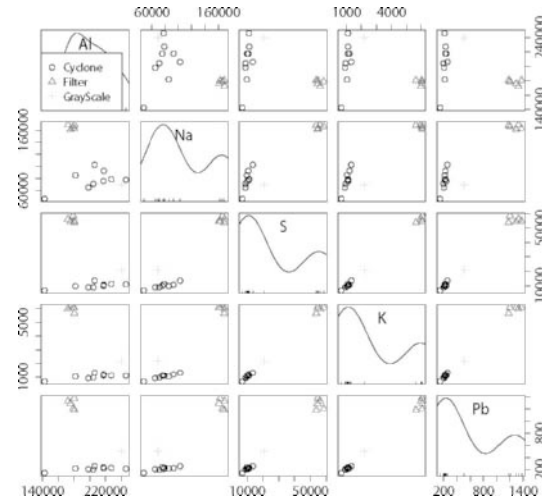


Figure 6: Significant amounts of S, K, and Pb concentrate in the filter fines. Concentrations in [ppm].

While most of the impurity elements concentrate with increasing particle size, lead, sulfur and potassium exhibited an opposite trend (Figure 6). Slightly increased contents of K, S and Pb are recorded in the scale sample assumed to be a contribution of fume fines that diffused into the coarser fraction during deposition.

In Table III the most abundant elements in the scale sample are compared to the fine particle fractions of reacted smelter grade alumina (RSGA) as

well as to the coarse and fine fractions of raw gas particles. The trace element concentration of 1.4 wt-% in the scale is considerably larger (for some elements even orders of magnitude larger) than the 0.45 wt-% measured in ultra-fines of reacted alumina. Considerably higher amounts of S, K and Pb are found in the scale and raw gas filter fractions (Table IV). It becomes obvious that even reacted alumina ultra-fines that have already been in contact with pot fumes do not contain as large amounts of trace elements as measured in the scale.

Table III: Trace elements in pot-fumes, scale sample and ultra fines of reacted smelter grade alumina.

Element [ppm]	Cyclone 0.42 m <sup>3</sup> /h	Filter	Gray scale	RSGA < 10 μm	RSGA < 20 μm
Ni	14283	9574	4815	3615	1341
Fe	5559	1407	6262	388	92
P	1366	740	1190	137	50
V	549	359	620	132	51
Cu	860	178	38	65	26
Ti	131	75	131	56	33
Co	152	84	67	36	13
Ga	193	124	493	36	19
Zn	42	17	21	32	10
[Wt - %]	2.3 %	1.3 %	1.4 %	0.4 %	0.2 %
Ca	9565	1561	1056	684	138
Si	142	512	870	1366	231

Table IV: Concentration of elements abundant in ultra-fines.

Element [ppm]	Cyclone 0.42 m <sup>3</sup> /h	Filter	Gray scale	RSGA < 10 μm	RSGA < 20 μm
S	13555	30324	20752	3969	2314
K	1321	3081	2187	378	143
Pb	255	678	502	77	27
[Wt - %]	1.5 %	3.4 %	2.3 %	0.4 %	0.2 %

If assuming that the major part of the scale is built up from alumina, the concentration of trace elements in the gray scale should be comparably low. If fresh alumina or even reacted alumina (that has already been in contact with the fume) was an essential part of the deposition, then it should have lower concentration of Group 1 elements. However, this is not the case. The trace element analysis shows that the scale sample consist of considerable amounts of coarse particulates originating from pot exhaust.

### Summary and Concluding Remarks

Trace elements, such as Ni, Fe, P, Cr, P, V, Ga, and Ti, originating from entrained particles as soot and residuals from anode combustion and alumina reduction, accumulate in pot fume particle fractions with  $D_i > 1 \mu\text{m}$ . Splitting the fumes in coarse and fine

fractions with help of the cyclone leads to a significant concentration of trace elements in the coarse fraction.

Recorded concentrations in the scale sample as well as coarse particles of raw gas fumes are considerably higher than concentrations reported in specifications for smelter grade alumina or anode materials, even an order of magnitude higher than impurity concentrations measured in reacted alumina ultra-fines with  $D_i < 10 \mu\text{m}$ .

The scale material is chemically similar to the coarse fume particles as captured in the cyclone. A strong correlation between concentration levels in scale sample and the coarse fume particles led to the assumption that the fume from pot exhausts is the main component in depositions found in the scale sample.

Without any doubt the injection of alumina plays an important role in the formation process of scaling layers, since excessive scale formation takes place in the area where alumina is reacted with fumes or reacted alumina is transported. However, smelter grade alumina cannot be considered an essential part of the scale based on trace element analysis presented here. But, it is assumed that the alumina's surface water can be the essential contribution to scale formation. Considerable amounts of loosely bound surface water can evaporate in contact with the warm pot exhaust. Moisture can condensate at designated areas in the fume treatment facilities with large pressure and/or temperature gradients, and react with scale forming elements and compounds in the fumes.

Soluble glass forming elements in the raw gas such as Na, K, Si and loosely bound surface water of the alumina are assumed to be key ingredients for the formation of an amorphous binder matrix as scale forming elements settle and moisture condensates at designated areas in the fume treatment facilities. Potassium sodium sulfur compounds and the role of sulfur in combination with relatively large amounts of trace elements as Ni has to be addressed in further work.

Impurity concentrations of 2.4 wt-% trace elements are recorded in cyclone fractions sampled at the lowest flow rate of 0.4 m<sup>3</sup>/h, corresponding to a cyclone cut-size of 11 μm.

Reduction of cyclone cut-size reduced impurity level in the ultra-fines, and simultaneously diluted contaminant level in the coarse fraction, presumably due to entrainment of cleaner ultra-fine fume-particles into the coarse fraction. These observations support the assumption that the major part of the impurities (except S and K) are in the fractions with

aerodynamic diameters larger than 11  $\mu\text{m}$ .

With 5.5 wt-% a considerable amount of S accumulates in the submicron particle fractions of the fumes, compared to a sulfur content of approximately 1 wt-% in the coarse particle fraction with  $D_i > 10 \mu\text{m}$ .

K as well as Pb accumulate in the sub-micron particles of the fumes to approximately 0.6 and 0.1 wt-% respectively.

More than 25 % of the trace elements (Group 1) can be removed from the pot exhaust by removing approximately 14 wt-% of the total fume particles with  $D_i > 10 \mu\text{m}$  from the raw gas from aluminum electrolysis cells with help of standard cyclones.

It is expected that finding an economically feasible way of removing coarse particles from pot exhaust will increase current efficiency when considerable amounts of P, V and Ti are removed from the secondary alumina.

Since a variety of valuable trace elements are concentrated in the coarse raw gas fractions removal, refining and extraction might become cost efficient when taking into consideration that operation of more efficient heat exchangers becomes feasible with purified raw gas.

It is speculated that removing the coarse fraction from the pot fumes will improve metal quality and current efficiency as well as reduce the scaling potential of raw-gas alumina mixtures, thus, help operating fluoride recycling systems with minimum fluoride losses to the environment in a cost-effective manner. Still, the recycling of valuable fluoride from separated coarse fractions as well as the role of sulfur in the ultra-fines has to be addressed in further work.

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