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Speciation of fluoride in workroom air during primary production of aluminium

Nils Petter Skaugset,*[ab] Dag G. Ellingsen,[a] Hilde Notø,[a] Lars Jordbekken†[a] and Yngvar Thomassen[ab]

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Exposure to fluorides (F^-) and particulate matter (PM) was assessed by personal sampling with use of Respicon® sampler in Prebake and Søderberg pot rooms in seven aluminium smelters. The inhalable PM mass was dominated by the extra-thoracic aerosol sub-fraction, which contributed with around 70% for both Prebake and Søderberg pot room workers. Quantitative and qualitative differences in exposure were found between pot room workers in smelters using these two technologies. Prebake pot room workers were exposed to 1.4 to 1.7 times higher PM concentrations than Søderberg pot room workers, depending on aerosol sub-fraction. Prebake pot room workers were also exposed to 2.5 to 2.9 higher air concentrations of water-soluble F^- (F_{WS}^-) and 2.8 to 5.3 higher air concentrations of non water-soluble F^- (F_{AS}^-) than Søderberg pot room workers, depending on aerosol sub-fraction. However, exposure to hydrogen fluoride (HF) was 1.3 times higher among Søderberg pot room workers. The relative amount of F_{WS}^-, however, was higher among Søderberg pot room workers, while the relative amount of particulate F^- (sum of F_{WS}^- and F_{AS}^-) was higher among Prebake pot room workers (6.5 *vs.* 3.9%). Exposure to the same PM concentration yielded higher F_{WS}^- and F_{AS}^- air concentrations among Prebake compared to Søderberg pot room workers.

Environmental impact

Workers in the primary aluminium industry are exposed to airborne particulate matter containing inorganic fluorides. The present study gives a comprehensive picture of the air concentrations of particulate matter in the important health related aerosol fractions (inhalable, thoracic and respirable). The particulate matter has been speciated for water-soluble and non water-soluble fluoride present in Prebake and Søderberg pot rooms. The results show that there are differences, both quantitatively and qualitatively between Prebake and Søderberg pot room air contaminants. This study has provided information for improvement of risk characterisation for better worker protection in this industry.

Introduction

About 50 million tons of primary aluminium (Al) metal was produced in 2013.[1] The production is based on the Hall–Héroult electrolytic process where alumina (Al_2O_3) is dissolved in a bath of molten cryolite (Na_3AlF_6) with the addition of aluminium fluoride (AlF_3) and calcium fluoride (CaF_2) in large carbon or graphite coated containers (pots).[2] The anodes are either pre-baked in separate anode plants for use in Prebake pots or formed by continuous feeding of a carbonaceous mixture into the top part of a Søderberg pot. At regular intervals molten Al is siphoned off and transported to the cast house. The Søderberg technology has, however, for several years been globally phased out due to environmental concerns and poorer energy efficiency.[3] About 90% of the global primary Al metal was produced by different modifications of the Prebake-technology in 2010.[1]

Due to the fluorine (F) content of the electrolyte, pot room workers are exposed to a variety of gaseous F^- containing components generated during the electrolytic process, such as hydrogen fluoride (HF), carbon tetrafluoride (CF_4), hexafluoroethane (C_2F_6) and silicon tetrafluoride (SiF_4).[2] Wahnsiedler *et al.*[4] found that direct hydrolysis of HF accounted for about 56% of losses of fluoride (F^-) from the electrolyte (34% from alumina, 19% from air and 3% from the anode), while 41% of the loss was caused by vaporisation of the electrolyte. The main vapour species lost from the electrolyte, $NaAlF_4$, is dissociated into solid particulate $Na_3Al_5F_{14}$ (chiolite) and AlF_3 (aluminium fluoride) on cooling.[2,5]

HF and condensed particulate matter (PM) may be absorbed or adsorbed to alumina, which is used in dry scrubbers for recycling and emission control of F^-.[2] Thus, F^- enriched alumina used in the pots contributes to the work room air contamination. Crushed bath residues may also contribute to

[a]Department of Chemical and Biological Work Environment, National Institute of Occupational Health, P.O.Box 8149 DEP, N-0033 Oslo, Norway. E-mail: nps@stami.no

[b]Department of Environmental Sciences, Norwegian University of Life Sciences, Ås, Norway

† Current address: Bærekraftig arbeidsmiljø WE Sustain AS, Asker, Norway.

the work room air contamination, especially when used to cover the Prebake pot after exchanging anodes.

Work room air concentrations of F^- have been extensively measured in the primary Al producing industry by personal air sampling.[6] Traditionally PM in this industry has been collected by use of the closed-face 37 mm "total dust" aerosol sampler (CFC).[6,7] This sampler, which is still commonly used, has inadequate sampling efficiency for coarse particles; *i.e.* lower sampling efficiency of the extra-thoracic aerosol sub-fraction.[8] The sampling efficiency of the CFC sampler has recently been shown to be similar to a thoracic sampler in Al pot rooms.[9] Although many exposure assessment studies have been performed, little information of F^- concentrations is available in Søderberg and Prebake pot rooms separately. Geometric mean air concentrations of 4.0 and 1.8 mg m^{-3} of PM and 0.7 and 0.3 mg m^{-3} for total F^- (particulate F^- and HF) have, however, been reported for workers in Prebake and Søderberg pot rooms, respectively.[10]

Since both gastrointestinal and pulmonary uptake of F^- contribute to systemic health effects, exposure to bio-accessible amounts of F^- in the different aerosol sub-fractions should be assessed. The gastrointestinal uptake of water-soluble F^- (F_{WS}^-) in humans is almost complete, while pulmonary uptake has been reported to be dependent on solubility and particle size.[11,12] Skeletal fluorosis is a well known occupational disease caused by high uptake of F^-, but is currently rare among Al pot room workers.[13] Painful musculoskeletal disorders possibly caused by F^- exposure have, however, been more frequently reported.[14,15] Exposure to HF and particulate inorganic F^-, alone or in combination with SO_2 has been suggested as causative for respiratory health effects reported among pot room workers in this industry.[16–19]

The aim of this study was to characterize workers' air contaminant exposure in Prebake and Søderberg pot rooms with respect to the distribution of PM, F^- and the solubility in the health related aerosol sub-fractions as defined by Comité Européen de Normalisation (CEN).[20]

Materials and methods

Air sampling strategy

Between 2003 and 2006, aerosol samples were collected by full shift (mean 381 min) personal sampling among workers at seven primary Al smelters in Norway. The air sampling was carried out at six plants in 2003 and one in 2006. The sampling was repeated at two plants, one in 2004 and one in 2006.

Workers with similar work tasks were recruited within specific pre-selected work categories, all on voluntary basis. The workers were stratified into two groups according to the work location; Prebake pot room (261 subjects) and Søderberg pot room (176 subjects). The remaining 167 subjects did not work only in the Prebake or the Søderberg pot room, and where thus classified as Other. Operators in the Prebake pot room carried out work tasks like anode changing, covering of anodes, anode beam raising and cell operation. Søderberg pot room workers were engaged in stud replacement, gas shirt changing, gas burner cleaning, anode effect management and cell operation. Other workers carried out production work tasks such as tapping, anode cleaning, crucible cleaning and anode handling. The workers carried two or three different samplers, mounted in the breathing zone for full shift air sampling.

Sampling equipment

The Respicon® two stage virtual impactor sampler (Helmut Hund GmbH, Wetzlar, Germany) was selected for simultaneous collection of the respirable, tracheo-bronchial and extra-thoracic aerosol sub-fractions as defined by CEN.[20] The required constant 3.11 L min^{-1} air flow rate was achieved using SKC portable high-flow pumps (Cat. no 224-PCXR8, SKC Ltd, Dorset, UK). The gas filter for collection of HF was mounted in series with an IOM sampler. Due to the high pressure drop of the plastic IOM sampler equipped with 5 μm PVC filter resulting in high air flow drop and the IOMs dustiness problems, the number of useable HF samples were reduced to 1038, further details have been published.[9]

The RespiconTM® spectrometer equipped with Hund DSS 8 datalogger was used for direct reading aerosol measurements and the aerosol concentrations were calibrated afterwards, by measuring the mass of the collected aerosol.[21,22] The computer program Respicon™ Transfer and Dataprocessing Software v. 1.61 was used for the calculations.

Gravimetric measurements

The collected PM was measured by weighing the filters before and after sampling using Sartorius MC 5 and MC 210P balances (Sartorius AG, Göttingen, Germany) in a temperature and humidity controlled room (20 ± 1 °C, 40 ± 2% relative humidity). All weighings were made after conditioning the filters for at least 3 days. The Staticmaster®,^{210}Po α-emitter (NRD LLC, Grand Island, NY, USA) was used to discharge the filters prior to weighing at all weighing occasions. Only the aerosol collected on the filters were included in the gravimetric determinations.

The balances were calibrated before each weighing sequence. Accuracy and precision of the measurements were assessed by weighing certified reference masses, 5.0 μm mixed cellulose ester (CA) and 5.0 μm PVC filters which were all kept in a climate controlled room. The detection limits (DLs) calculated as 3 × standard deviation of all field blanks were 0.09 mg per filter used in the Respicon® (n = 331). Thus, DLs of 0.09 mg for the respirable, 0.13 mg for the thoracic and 0.16 mg for the inhalable Respicon® aerosol sub-fractions were achieved. Further details of the gravimetric procedure have been published.[9]

The collected aerosol mass was calculated according to algorithms in the manual without using the suggested 1.5 correction factor for the extra-thoracic aerosol sub-fraction,[23] but in accordance with later recommendations.[8,24]

Measurements of F^-

Water-soluble F^- was defined as the amount of F^- in the collected aerosol mass that dissolved at room temperature in deionised (DI) water (>18.2 MΩ) within 90 min. For the F^- determinations, both filter and wall deposits were included in the leaching procedure. The amount of F^- in the leachates was determined by ion chromatography (IC) using a Dionex DX-500

Table 1 The geometric mean (GM) particulate concentrations (mg m^{-3}) with 95% confidence interval (95% CI) according to aerosol sub-fraction among Prebake pot room workers, Søderberg pot room workers and Other. Same letter in superscript denotes statistically significant differences; $^{b,c,e-h}p < 0.0001$, $^{d}p = 0.03$

	Inhalable			Thoracic			Respirable		
	N^a	GM	95% CI	N^a	GM	95% CI	N^a	GM	95% CI
All	1244	2.86	2.71–3.03	1246	0.90	0.86–0.95	1247	0.42	0.40–0.44
Prebake	537	$4.01^{b,c}$	3.66–4.40	537	$1.17^{e,f}$	1.08–1.26	538	$0.49^{g,h}$	0.46–0.52
Søderberg	386	$2.38^{b,d}$	2.17–2.62	387	0.72^{e}	0.66–0.78	387	0.36^{g}	0.33–0.39
Other	321	$2.03^{c,d}$	1.86–2.23	322	0.78^{f}	0.71–0.86	322	0.39^{h}	0.36–0.42

[a] Number of samples.

ion chromatograph (Dionex, Sunnyvale, CA, USA). Details have been published.[25] The DLs for F_{WS}^- in the respirable, thoracic and inhalable aerosol sub-fractions were 5.0, 7.1 and 8.7 µg per filter, respectively.

Alkaline-soluble fluoride (F_{AS}^-) was defined as the amount of F^- in the collected aerosol mass that remained after leaching the F_{ws}^- and that dissolved in 5 mL 0.5 M potassium hydroxide (KOH) solution at 75 °C within 90 min. The amount of F_{AS}^- in the leachates was determined by ion chromatography (IC) using the same equipment as for F_{WS}^-. The DLs were 20, 28 and 35 µg per filter for F_{AS}^- in the respirable, thoracic and inhalable aerosol sub-fractions, respectively. The F_{WS}^- and F_{AS}^- content of the aerosol sub-fractions were calculated according to the same algorithms as for the aerosol. Field blank filter samples were used for blank corrections.

Analysis of a typical exposed air filter, after leaching with KOH, showed no signs of fluorine in the undissolved particles, the applied leaching procedure was considered to dissolve airborne particles containing fluorine.[25] The determination of F^- by IC from this type of work room environment has previously been shown to be in good agreement with the use of ion-selective electrode.[26]

Gas filters

Impregnated gas filters (10% (w/v) KOH solution on Millipore AP1002500 support pads) were transferred to 15 mL polypropylene tubes (Art. nr. 62.554.001, Sarstedt, Nümbrecht Germany) and bromide was added as internal standard. The filters were then extracted for 2 hours with 10 mL 0.5% (v/v) dihydrogen dioxide and the amount of F^- was determined using the same procedure as for F_{WS}^- and F_{AS}^-. The DL was between 1.0 and 16 µg per filter of F^-, depending on the prepared gas filter batch used.

Statistics

The statistical distributions of the data were considered to be non-normal when the skewness exceeded 2.0. These data were log-transformed to achieve normalisation. Statistical associations between variables were calculated by least square regression analysis, yielding Pearson's correlation coefficients as the measure of association. Samples below DL (3.3, 5.8 and 22% of total number of filters for mass determination, F_{WS}^- and F_{AS}^-, respectively) were substituted with 1/2DL for calculation of respirable, thoracic and inhalable sub-fractions. The time-resolved concentrations from the RespiconTM® were used for

Table 2 The geometric mean (GM) concentrations and 95% confidence (95% CI) interval of F^- (µg m^{-3}) according to aerosol sub-fraction among Prebake pot room workers, Søderberg pot room workers and Other. Same letter in superscript denotes statistically significant differences at $p < 0.0001$

	Inhalable			Thoracic			Respirable		
	N^a	GM	95% CI	N^a	GM	95% CI	N^a	GM	95% CI
F_{WS}^-									
All	1242	147	139–156	1244	72	68–76	1244	38	36–40
Prebake	536	$237^{b,c}$	220–254	537	$114^{e,f}$	106–122	537	$55^{h,i}$	51–58
Søderberg	385	$84^{b,d}$	76–92	385	$39^{e,g}$	35–43	385	$22^{h,j}$	20–25
Other	321	$132^{c,d}$	120–145	322	$70^{f,g}$	63–76	322	$38^{i,j}$	35–41
F_{AS}^-									
All	1237	226	208–245	1241	73	68–78	1242	31	29–33
Prebake	537	$524^{k,l}$	461–595	537	$143^{n,o}$	128–160	538	$51^{q,r}$	47–56
Søderberg	381	$98^{k,m}$	89–108	383	$36^{n,p}$	33–39	383	$18^{q,s}$	16–19
Other	319	$148^{l,m}$	130–169	321	$56^{o,p}$	49–63	321	$25^{r,s}$	23–29

[a] Number of samples.

Table 3 The geometric mean (GM) air concentrations and 95% confidence interval (95% CI) of HF ($\mu g\ m^{-3}$). Same letter in superscript denotes significant differences between the respective groups; $^{b}p < 0.01$, $^{c,d}p < 0.0001$

	N^a	GM	95% CI
All	1038	67	63–72
Prebake	459	$74^{b,c}$	68–81
Søderberg	299	$93^{b,d}$	82–105
Other	280	$41^{c,d}$	36–46

[a] Number of samples.

calculation of cumulative daily exposure related to time, in accordance with a previously described method.[27]

For comparisons of the individual sample pair ratios, analysis of variance (ANOVA) was used. The IBM SPSS Statistics for Windows, Version 21.0 (IBM Corp., Armonk, NY, USA) was used for the statistical calculations. The level of statistical significance was set to 0.05 (two-tailed).

Results

The mean PM concentrations were around 1.4 to 1.7 times higher among Prebake than among Søderberg pot room workers or the group other in all aerosol sub-fractions (Table 1). The measured concentrations of F_{WS}^- and F_{AS}^- were statistically significantly higher among Prebake than among Søderberg pot room workers (Table 2). In contrast, the air concentrations of HF were significantly higher among Søderberg than among the Prebake pot room workers (GM 93 $\mu g\ m^{-3}$ *vs.* 74 $\mu g\ m^{-3}$; $p = 0.003$) (Table 3).

The percentage PM concentration in the thoracic aerosol sub-fraction related to the inhalable sub-fraction was similar among Prebake and Søderberg pot room workers, whereas the percentage was significantly higher among Søderberg (17.6%, CI: 16.5–18.8) than Prebake pot room workers (14.8%, CI: 14.0–15.7) for the respirable sub-fraction (Fig. 1). However there may be an overlap for single observations. Also the relative amount of F_{WS}^- was higher in the respirable sub-fraction among Søderberg (30.0%, CI: 28.5–31.5) compared to Prebake pot room workers (25.6%, CI: 24.6–26.7), whereas for the thoracic sub-fraction the percentages were similar (48.7%, CI: 47.3–50.1 *vs.* 49.6%, CI: 48.6–50.6). The relative amount of F_{AS}^- was lower in the respirable and the thoracic sub-fractions among Prebake than among Søderberg pot room workers (13.5 and 31.1% *vs.* 21.9 and 40.7%). Due to this difference for F_{AS}^-, similar results were observed for the concentrations of particulate F^- (F_{WS+AS}^-). The content of F_{WS+AS}^- in weight percentage of PM concentrations in the different aerosol sub-fractions was higher among Prebake than Søderberg pot room workers (Fig. 2).

The content of F_{WS}^- in weight percentage of F_{WS+AS}^- decreased by increasing particle size of the PM, most obviously for Prebake pot room workers (Table 4). Fig. 3A shows that the percentage F_{WS}^- related to F_{WS+AS}^- in the extra-thoracic sub-fraction is low at high extra-thoracic PM concentrations among the Prebake pot room workers. No obvious association was found for Søderberg pot room workers (Fig. 3B).

Highly statistically significant correlations between PM air concentrations and corresponding air concentrations of F_{WS}^- and F_{AS}^- in all respective sub-fractions were found (Pearson's r between 0.67 and 0.93; $p < 0.001$). Prebake pot room workers experienced higher air concentrations of F_{WS}^- than Søderberg pot room workers in the inhalable aerosol sub-fractions when exposed to the same inhalable PM air concentrations, also observed for the respirable and thoracic sub-fractions (not shown). Prebake pot room workers are also exposed to substantially higher F_{AS}^- air concentrations than Søderberg pot room workers when exposed to the same inhalable PM air concentrations (Fig. 4). This was also observed for respirable and thoracic sub-fractions (not shown).

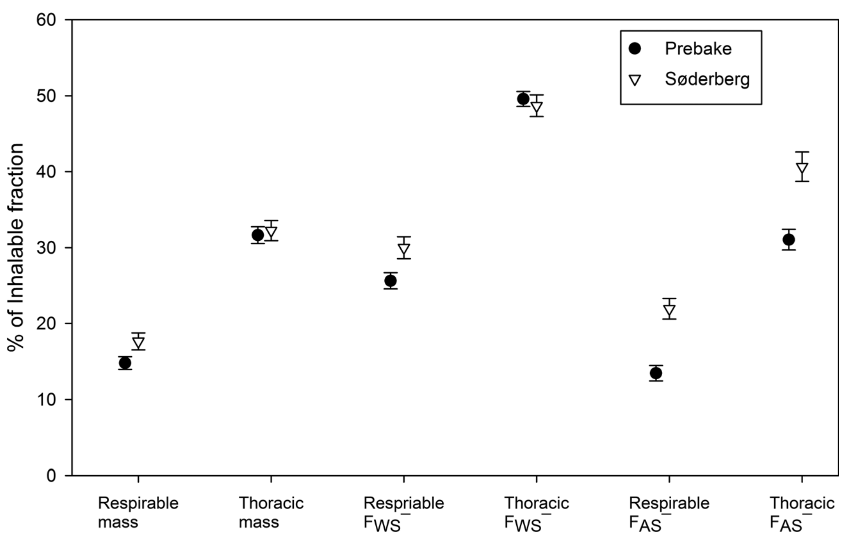

Fig. 1 The arithmetic mean (AM) and confidence interval (95% CI) concentrations of PM, F_{WS}^- and F_{AS}^- in corresponding inhalable aerosol sub-fraction, expressed as percentage.

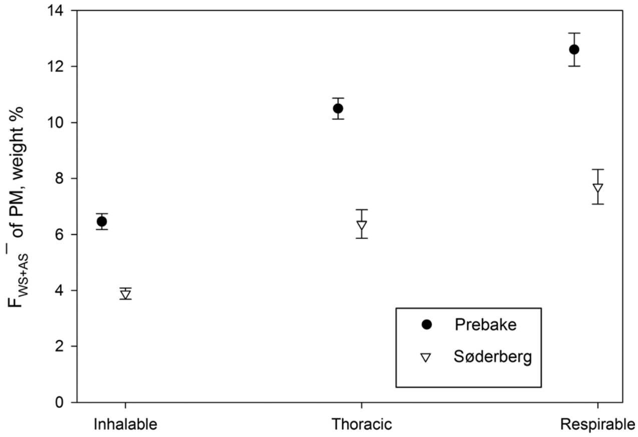

Fig. 2 The arithmetic mean (AM) and confidence interval (95% CI) as weight percentage F_{WS+AS}^- of particulate matter (PM) in corresponding aerosol sub-fractions.

Søderberg pot room workers are exposed to substantially higher air concentration of F_{WS}^- than Prebake pot room workers at the same F_{AS}^- air concentration (Søderberg: $\log(F_{WS}^-) = 0.17 + 0.88 \times \log(F_{AS}^-)$, $r = 0.86$ and Prebake: $\log(F_{WS}^-) = 0.96 + 0.52 \times \log(F_{AS}^-)$, $r = 0.93$). This was also observed for respirable and thoracic sub-fractions.

Data obtained by the Respicon TM® was used for the calculation of the cumulative daily PM exposure. The relative time to reach 50% and 90% of the daily PM exposure, independent of aerosol sub-fraction, was similar among Søderberg ($n = 22$) and Prebake ($n = 19$) pot room workers.

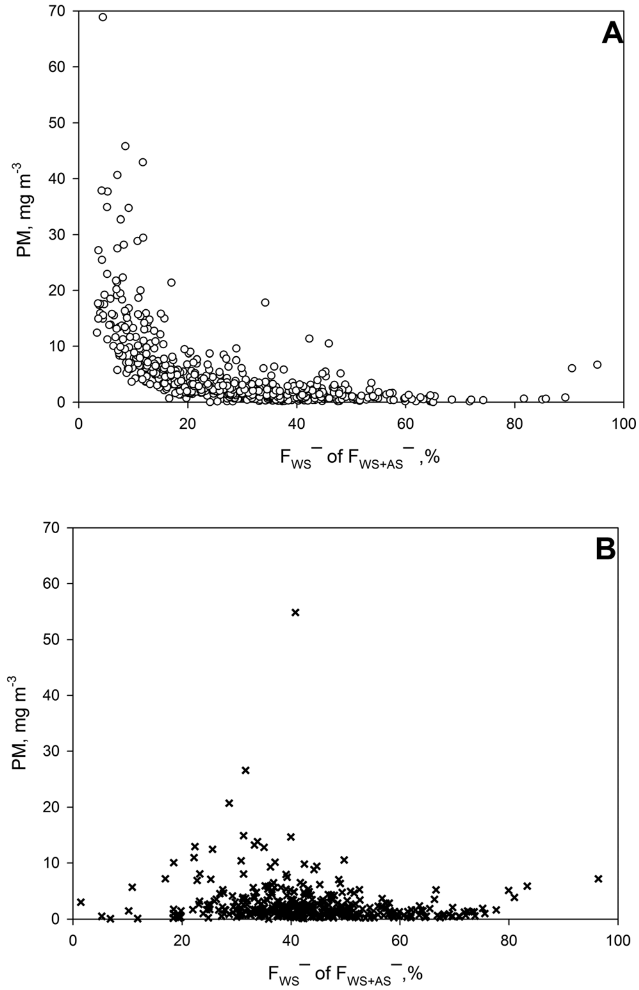

Fig. 3 The weight percentage F_{WS}^- of F_{WS+AS}^- related to the particulate matter (PM) in the extra-thoracic sub-fraction for Prebake (A) and Søderberg (B).

Discussion

This study shows that the highest PM and F^- concentrations in the workroom air are extra-thoracic and higher among Prebake than among Søderberg pot room workers. In contrast, the air concentration of HF was higher among Søderberg pot room workers. There are qualitative differences in the aerosol F^- composition in the two types of pot rooms. The associations between the work room concentrations of F_{WS}^- and F_{AS}^- showed that Søderberg pot room workers were higher exposed to F_{WS}^- than the Prebake pot room workers at the same air concentrations of F_{AS}^-.

Table 4 Arithmetic mean (AM) and 95% confidence interval (95% CI) as percentage F_{WS}^- of F_{WS+AS}^-, according to the defined health related aerosol sub-fractions. Same letter in superscript denotes significant differences between the respective groups; $^b p < 0.001$, $^c p < 0.0001$, $^d p < 0.01$, $^{e-i} p < 0.0001$

	Respirable		Tracheo-bronchial		Extra-thoracic	
	AM	95% CI	AM	95% CI	AM	95% CI
Prebake ($N^a = 532$)	$51^{b,c}$	50–53	$41^{e,f}$	39–42	$28^{h,i}$	27–30
Søderberg ($N^a = 380$)	$55^{b,d}$	54–57	$47^{e,g}$	45–49	43^{h}	42–45
Other ($N^a = 312$)	$59^{c,d}$	57– 61	$52^{f,g}$	50–54	42^{i}	41–44

^{a} Number of samples.

Previous studies have used air samplers not designed to collect health related aerosol sub-fractions. The CFC sampler, which is still commonly used in the Al primary producing industry, has in one large comparison study from the Al producing industry found to have a comparable sampling efficiency as thoracic aerosol sub-fraction of the Respicon® sampler.[9] Earlier studies have reported air concentrations of HF, F^- and "total" F^- during primary production of Al, but mostly not for Prebake and Søderberg pot workers separately. Thus, few data are available for comparison with the present results. Assuming that the particle size distribution has not changed during recent years, the mean thoracic aerosol mass concentration of 0.72 mg m^{-3} measured in this study among Søderberg pot room workers is somewhat lower than previously reported mean concentrations between 0.88 and 5.0 mg m^{-3}.[28,29] The mean thoracic aerosol mass concentration of 1.17 mg m^{-3} among the Prebake pot room workers is in the lower end of the range of previously reported values between 0.47 and 15.7 mg m^{-3}.[7,29,30] The mean air HF concentration of

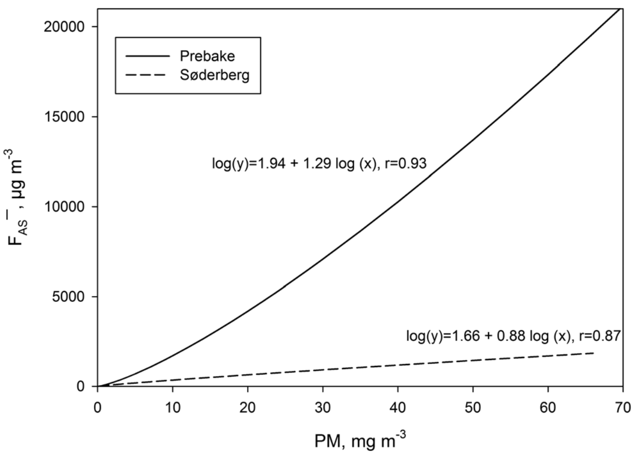

Fig. 4 Associations between inhalable particulate matter (PM) concentrations and F_{AS}^- for Prebake and Søderberg pot room workers.

74 µg m^{-3} among Prebake pot room workers is considerably lower than previously reported concentrations between 0.74 and 0.93 mg m^{-3}.[7,30]

Fluoride containing emissions from the Al reduction process consist primarily of HF and particulate F^-.[2] The electrolyte consists of a molten bath of synthetic cryolite (Na_3AlF_6) with additives. Whereas the mineral cryolite is slightly soluble in water and soluble in alkaline solutions, synthetic cryolite is considered insoluble in water.[31,32] The solubility of the additives AlF_3 and CaF_2 in water is considered negligible.[31] A characterization of individual aerosol particles collected from the workroom air of Al smelter pot rooms reported that the particles with aerodynamic diameter between 0.18 and 10 µm contained a heterogeneous mixture of several phases, foremost aluminium oxide and cryolite.[33]

Previous studies have shown the presence of ultrafine particles in both Søderberg and Prebake pot rooms, and suggested that such particles to a high degree are formed by condensation of vaporized fluorides under supersaturation conditions.[5,25,34] This study shows that the relative amount of F_{WS}^- is dependent on particle size and that the solubility decreases with increasing particle size.

In the Hall–Héroult process there is two basic anode design; the prebaked anodes and the continuously self-baking Søderberg anode. In both technologies the raw material, bath temperature (about 960 °C), potential (4.0–4.5 V) and bath composition are basically the same.[2,35] The main difference being the anode design (Prebake or Søderberg) and the current used (40–600 kA).[2,3]

Most of the emitted F^- containing particles and HF are captured by the hooding system of the Prebake pots, and fed into dry scrubbers. The dry scrubbers remove HF by chemisorption on alumina and entrap F^- condensates; *e.g.* vaporous $NaAlF_4$ and other impurities evolved from the cells.[2,3] This secondary alumina is reused and fed to the pots, thereby reducing the overall F^- consumption.[2] Hence, the use of secondary alumina is likely to contribute to higher F_{WS}^- concentrations in the workroom air. The introduction of dry scrubbers has been associated with higher PM exposure among pot room workers.[28] Fluorides may also evolve from warm electrolyte residue and spent anodes (butts). Butts covered with hot solid electrolyte (crust) are often placed in the Prebake pot room to cool to room temperature, allowing F^- to vaporize and to react with air humidity to form HF.[36] This procedure does not occur in Søderberg pot rooms, since the Søderberg anode is continuously baked. Normal Prebake pot operations require removing of the covers for anode exchange, and covering of new anodes with crushed bath residue mixed with secondary alumina. This Prebake specific work task may explain the higher exposure to F_{AS}^- among Prebake pot room workers, since the crushed bath residue containing cryolite is more soluble in alkaline solutions.[37] The handling of pot covers has been identified as a work operation causing short-term exposure episodes with high PM concentrations.[36]

Fumes are feed through a gas burner before the scrubbers in Søderberg cells. However, some newer versions of Søderberg pots have been equipped with hooded ventilation for the anode. On Søderberg pots, gas skirts are fitted to incinerate hydrocarbons as a part of the ventilation system. Together with an intact crust, this is important for leading the emissions from the warm cells to the dry scrubbers and away from the worker's breathing zone. The crust is regularly punctured to add alumina (point feeding), for siphoning off molten Al and for removal of soot. Larger parts of crust are removed for gas skirt changing. During these operations no extra cell ventilation is added, and a large proportion of the emissions from the cells are released in to the pot room. The Søderberg pot room workers are therefore exposed more directly to the emissions from the cells than the Prebake pot room workers. Because the airborne particles evolving from the hot open cell consists of more F_{WS}^-, this may explain that Søderberg pot room workers are exposed to relatively more F_{WS}^- than Prebake pot room workers. Air concentrations of HF and PM have been shown to be high during gas skirt changing.[36] Covering of bath occurs more irregular and is mainly performed by reusing removed crust (*e.g.* solid bath residue) with added alumina (either secondary or primary) in Søderberg pot rooms. The same aerosol mass concentration yield higher F_{WS}^- and F_{AS}^- among workers in Prebake pot rooms than in Søderberg pot rooms, and the difference is more evident for F_{AS}^-.

This study shows that the percentage F_{WS}^- of the F_{WS+AS}^- is low when the PM in the extra-thoracic aerosol sub-fraction is high, for Prebake pot room workers. Hence, in the extra-thoracic sub-fraction a high percentage of F^- is alkaline soluble at high PM concentrations. This is in agreement with high PM concentrations reported during covering of anodes with alumina and crushed bath residuals.[36] No association between percentage F_{WS}^- of the F_{WS+AS}^- and PM was found for Søderberg pot room workers.

An anode effect (AE) is caused by low alumina concentrations in the electrolyte. This causes a very high cell voltage by formation of an electrically insulating layer of gas underneath the anodes. AE occurs more frequent in Søderberg than in Prebake cells, and may contribute to the relatively higher exposure to F_{WS}^- found among Søderberg pot room workers, since terminating these AE often require manual work on open cells.[2] Other F containing components are also formed during AE events, like the greenhouse gases CF_4 and C_2F_6.[3]

Similar pattern of time-resolved PM exposure among Søderberg and Prebake pot room workers was found, indicating that they are exposed to short-term episodes with high air PM concentrations (not shown). The relative time to reach 90% of the daily total PM exposure is decreasing with increasing aerosol size fraction, which is compatible with shorter settling time for coarse particles.

In this study differences in exposure between workers in Prebake and Søderberg pot rooms are shown. The differences are both quantitative and qualitative, with Prebake pot room workers experiencing higher air concentrations of both PM and F^-. The Søderberg pot room workers experienced higher HF concentrations and are exposed to relatively more $F_{WS}{}^-$ than Prebake pot room workers. Since a high percentage of the exposures to PM are associated with relatively short periods of the work time, is it important to identify these short term episodes in order to reduce the workers' overall exposure.

Conclusions

The PM size distributions of the personal exposure were relatively similar between Prebake and Søderberg technology, although the concentrations were higher in Prebake. The percentage of F^- was higher among Prebake than Søderberg pot room workers.

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