

Occurrence of fibrous sodium aluminumtetrafluoride particles in potrooms of the primary aluminum industry

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GYLSETH B, BJØRSETH O, DUGSTAD Ø, GJØNNES J. Occurrence of fibrous sodium aluminumtetrafluoride particles in potrooms of the primary aluminum industry. *Scand J Work Environ Health* 10 (1984) 189—195. Inorganic fibrous particles have been found in the work environment of the primary aluminum industry. Based on scanning electron microscopic analysis, the concentrations ranged from 9 to 720 fibers/cc. The fibers were generally thinner than 0.1 μm in diameter and shorter than 5 μm . By electron microscopy, energy dispersive X-ray microanalysis, and selected area electron diffraction the fibers were identified as sodium aluminumtetrafluoride.

Key terms: electron microscopy, fiber concentrations, sodium aluminumtetrafluoride fibers.

As a result of research conducted by Stanton and co-workers (14) other mineral fibers than asbestos have also been focused on from an occupational health point of view. Stanton et al demonstrated that both synthetic and natural mineral fibers may possess a carcinogenic potential when implanted in the pleural cavity of animals. Though their route of administration was unphysiological and cannot be directly compared to inhalation, the results have gained great importance with respect to further research and the occupational and medical evaluation of workplaces where such fibers occur. The endemic occurrence of malignant pleural mesotheliomas in some small villages in Turkey (2), where fibrous zeolites (erionite) are found in the rocks, has given further strength to the hypothesis that other minerals than asbestos may also be carcinogenic.

The Norwegian aluminum industry has, for a long period, been the subject of great interest due to an anticipated increased risk of fluorosis due to fluoride exposure, allergic alveolitis caused probably by a mixed dust and gas exposure, and cancer due to exposure to polycyclic aromatic hydrocarbons. During a routine industrial hygiene survey in one plant, fibrous particles were observed in the airborne dust in the potrooms.

In this study we report on the identification and quantification of such inorganic fibers in the work atmosphere of the primary aluminum industry.

Materials and methods

Samples from the work environment

Short-term samples from the work environment were taken by both personal and stationary sampling. For the personal samples air was filtered through Nuclepore membranes (diameter 37 mm, pore size 0.2 μm) at a flow rate of 1.8 l/min for 1—9 min. These specimens were used for the quantitative analysis of airborne fiber concentrations. For the stationary samples Nuclepore membranes (diameter 47 mm, pore size 0.2 μm) were used with a flow rate of 15 l/min during sampling periods of 10—30 s. These samples were used for the qualitative analysis.

Bulk samples

From one of the plants samples of reacted alumina and cryolite from a pot with prebaked anodes were obtained. A sample of chiolite ($\text{Na}_5\text{Al}_3\text{F}_{14}$) was obtained from the Norwegian Institute of Technology.

Analytical methods

Phase contrast microscopy at $40 \times$ objective (magnification of $500 \times$) is recommended as the standard method for the analysis of fibers in the work environment. The fibers we were looking at were mostly far below the limit of the visibility of our phase contrast microscope (fibers 0.25 μm in diameter), and therefore only electron microscopic techniques were used. Pieces of the Nuclepore membranes (air samples and filtered bulk samples) were coated with a thin film of gold or carbon to make the specimens conductive. The carbon-coated specimens were attached to 200-mesh electron microscopy grids and placed on a polyurethane sponge soaked in chloroform. After

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one night the Nuclepore membrane was dissolved, and the particles were left embedded in an electron transparent carbon film. These samples were first analyzed in a Jeol 100 CX transmission electron microscope (TEM) fitted to a Link 860 X-ray microanalyzer [used for energy dispersive X-ray microanalysis (EDS)] for the determination of chemical composition. Fiber dimensions were measured from micrographs taken at different magnifications. The same samples were also subject to selected area electron diffraction (SAED) analysis in a Jeol 200 CX TEM. The gold-coated samples were analyzed for fiber density in a Jeol JSM-35 scanning electron microscope (SEM) equipped with a Princeton gamma tech 1000 X-ray microanalyzer. The fibers were counted directly from the screen in the slow scanning mode at a magnification of $4,500\times$. One hundred fibers or 100 fields, whichever was obtained first, were counted. The chemistry and morphology of the bulk samples were also analyzed by SEM.

The solubility of the fibers was investigated by the resuspension of some of the membranes in distilled water or 1 M hydrochloric acid, respectively, and then treated for 5 min in an ultrasonic bath. The suspension was then refiltered on Nuclepore membranes 25 mm in diameter and $0.2\text{ }\mu\text{m}$ in pore size and analyzed in the SEM.

Results

Electron microscopy

The fibers were found in high concentrations during the crust-breaking operation. The results are given in table 1. Figure 1 shows characteristic fibers as seen in the SEM, whereas figures 2 and 3 show the same type of fibers photographed in the TEM.

Forty-three fibers were measured from different micrographs, and the geometric mean for diameter and length was calculated. The mean diameter was 0.053 (range $0.027\text{--}0.114$) μm and the mean length was 0.87 (range $0.23\text{--}9.71$) μm .

Energy dispersive X-ray microanalysis

General EDS revealed sodium and aluminum as the only elements present. Fluorine was probably another element present; however, it was not detected by this method.

The relation between the peak heights for sodium (Na) and aluminum (Al) will be less than the corresponding molar concentrations due to instrumental factors. Peak heights were measured from the spectra shown in figure 4, and the data are presented in table 2. The Na:Al peak height ratio of two fiber samples was found to be 0.20 and 0.21, neither of which corresponds to cryolite or chiolite, with ratios of 0.80 and 0.40, respectively. Based on the cryolite standard, every Na atom corresponds to a peak height of 14 mm and every Al atom to a peak height of 54 mm,

ie, Na:Al = 0.26. If chiolite is used as a standard, the corresponding Na:Al ratio is 0.24. These results indicate that the fibers consist of equal amounts of Na and Al as in sodium aluminumtetrafluoride (NaAlF_4).

Selected area electron diffraction

Diffraction patterns from individual fibers consisted of spotty rings and arcs, as well as diffraction spots. The fibers hence are not single crystals. Dark field pictures taken with diffraction spots also indicated the fibers to be composed of many small single crystals, probably of the same type as seen in figure 3. Most of the diffraction features are weak and difficult to measure with great accuracy. Four distinct reflections gave the d values 6.24, 3.70, 2.87, and $2.41\text{ }\text{\AA}$. The latter three could be attributed to several or all the possible crystal modifications cryolite, chiolite and NaAlF_4 . The first and strongest, at $6.24\text{ }\text{\AA}$ (001), only corresponds to NaAlF_4 (15). The diffraction patterns were thus taken as a strong indication of the presence of this compound.

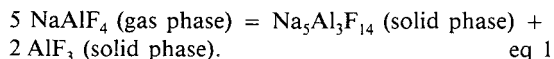
Solubility

Fibers without apparent signs of chemical attack were detected after 5 min of sonication in both distilled water and 1 M hydrochloric acid. This finding suggests that the fibers are resistant to these liquids.

Discussion

It is evident that short thin fibers are produced during primary aluminum production. The crystals are probably produced during the recrystallization of fumes from the electrolyte. These particles will, to some extent, follow the pot gases and are collected in the dry-filtration process and thus recycled to the pots along with the reacted alumina. (Fibers were detected in the sample of reacted alumina.)

Howard (5) first demonstrated the existence of NaAlF_4 in the gas phase in rapidly cooled vapors with the use of X-ray powder diffractometry. He claimed that the compound was unstable over 470°C and that the dissociation occurred according to the following equation:



Ginsberg & Resch (4) studied rapidly cooled vapors over melted NaF/AlF_3 between temperatures ranging from $800\text{--}1,200^\circ\text{C}$ by X-ray diffractometry. They only observed diffraction lines from NaAlF_4 in the NaAlF_4 melt composition, while both NaAlF_4 and $\text{Na}_5\text{Al}_3\text{F}_{14}$ were observed over melted cryolite. On the basis of this information, they assumed that the dissociation according to the aforementioned equation was not probable and suggested that it was

NaAlF₄ (gas phase) and NaF (gas phase) that formed chiolite during the condensation phase.

Rolin & Houriez (9) suggested on the other hand that NaAlF₄ (gas phase) dissociates according to equation 1 at temperatures below 920°C, while the

predominant reaction at temperatures above 920°C is:

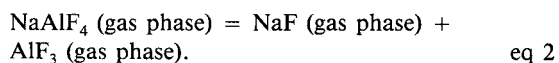
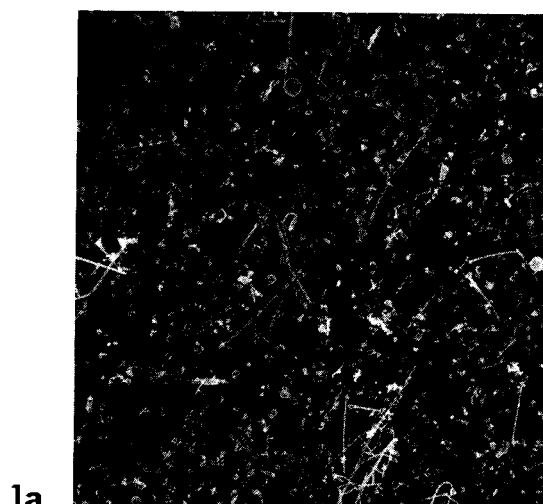


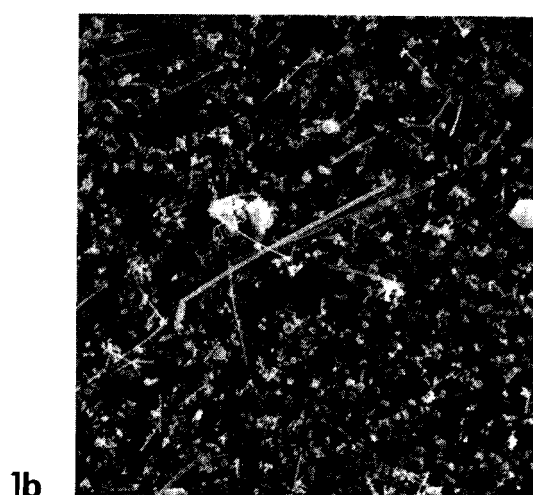
Table 1. Air samples analyzed by scanning electron microscopy at a magnification of 4,500 ×.

Location	Air volume (l)	Fiber concentration (fibers/cc)
Just behind the crust breaker	1.5	640
Two pots behind crust breaker (prebaked)	16.2	190
Four pots behind crust breaker (prebaked)	14.4	390
Filling of secondary aluminum	8.6	9
Two pots behind crust breaker (Søderberg)	7.5	720



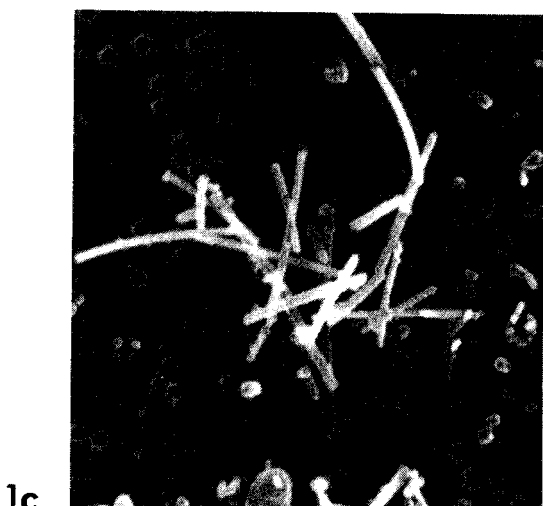
1a

5 μm



1b

5 μm

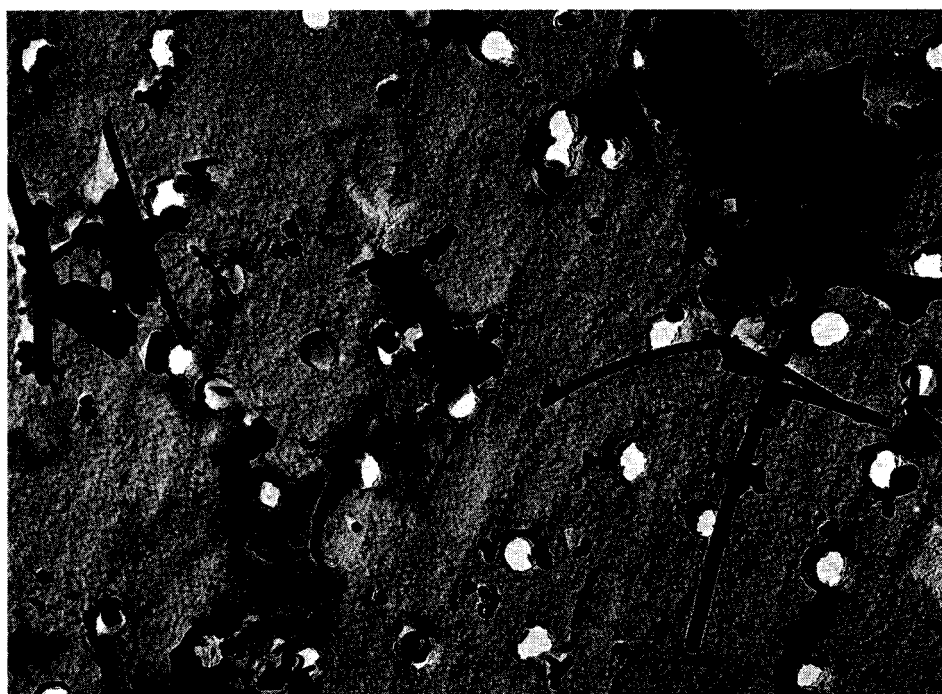


1c

1 μm

Figure 1a—c. Typical sodium aluminumtetrafluoride fibers as seen in the scanning electron microscope at different magnifications.

2a



1 μm

2b



1 μm

Figure 2a—b. Typical sodium aluminotetrafluoride fibers as seen in the transmission electron microscope at different magnifications.



Figure 3. High magnification transmission electronmicrograph of one big fiber and several single crystal microfibers.

Table 2. Peak heights measured from energy dispersive X-ray spectra both from fibers and from standards of chiolite and cryolite.

Particle	Method	Sodium (mm)	Aluminum (mm)	Sodium: aluminum
Cryolite (Na_3AlF_6)	Scanning electron microscopy — energy dispersive X-ray microanalysis	43	53	0.80
Fiber (?)	Scanning electron microscopy — energy dispersive X-ray microanalysis	10	49	0.20
Fiber (?)	Transmission electron microscopy — energy dispersive X-ray microanalysis	15	70	0.21
Chiolite ($\text{Na}_5\text{Al}_3\text{F}_{14}$)	Scanning electron microscopy — energy dispersive X-ray microanalysis	45	113	0.40

The formation and stability of NaAlF_4 have been further investigated and discussed in several other reports (3, 4, 6, 7, 10, 11, 12, 13).

An increased lung cancer risk (observed:expected = 1.6) has been reported in the Norwegian aluminum industry (including the plant where we measured the fibers) by Andersen et al (1). This increased cancer risk could, according to them, be attributed to several factors, among which are exposure to polycyclic aromatic hydrocarbons, a higher proportion of smokers among employees than the referents, and intercounty cancer variations in the reference population. It was emphasized that the cancer incidence of

a reference population is a critical methodological problem. The observed:expected ratio of 1.6 found by Andersen et al was based on the reference incidence rates observed in the counties where the plants are located. If, however, the estimation were based on national rates, the corresponding ratio would be 1.07. More recently Rockette & Arena (8) did not find any increased lung cancer risk in their study of aluminum reduction plant workers.

We have reported high concentrations of fibrous particles in the work environment of the primary aluminum industry; such high concentrations have previously not been described. These fibers showed re-

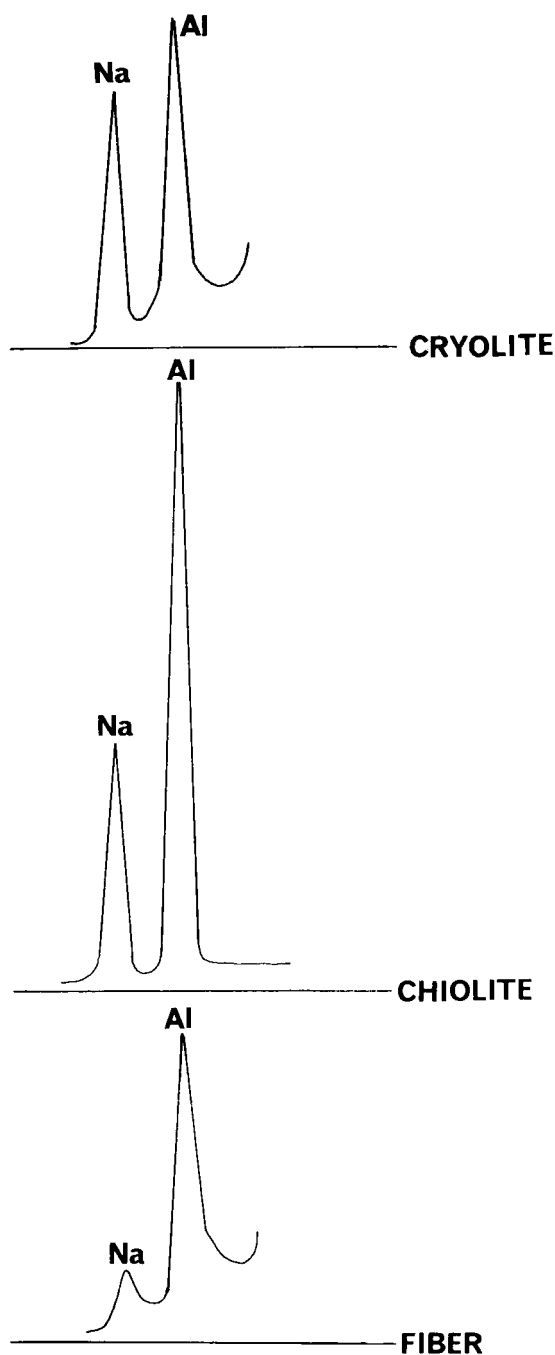


Figure 4. Energy dispersive X-ray spectra of standard cryolite and chlorite and one of the fibers.

sistance against dilute hydrochloric acid; however the solubility of such fibers in physiological model solutions or lung fluids has not been established. The dimensions of the fibers were rather small, and, if the dimensions are considered the most important factor from a toxicologic point of view, such fibers should not represent any carcinogenic risk. However, little is known about the health effects of short and thin

durable inorganic fibers, and whether or not such fibers do represent a contribution to a health risk can so far only be a matter of speculation. In order to promote prevention, further research should be initiated, including toxicologic tests and, from an epidemiologic point of view, recordings of the concentration of these fibers at work sites in the primary aluminum industry.

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