

ALUMINIUM FLUORIDE

CAS No: 7784-18-1

EINECS No: 232-051-1

SUMMARY RISK ASSESSMENT REPORT (ENVIRONMENT)

Final report, 2008

The Netherlands

FINAL APPROVED VERSION

Rapporteur for the risk assessment of Aluminiumfluoride is the Ministry of Housing, Spatial Planning and the Environment (VROM) in consultation with the Ministry of Social Affairs and Employment (SZW) and the Ministry of Public Health, Welfare and Sport (VWS). Responsible for the risk evaluation and subsequently for the contents of this report is the rapporteur.

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PREFACE

This report provides a summary, with conclusions, of the risk assessment report of the substance Aluminium fluoride that has been prepared by the Netherlands in the context of Council Regulation (EEC) No. 793/93 on the evaluation and control of existing substances.

For detailed information on the risk assessment principles and procedures followed, the underlying data and the literature references the reader is referred to the comprehensive Final Risk Assessment Report (Final RAR) that can be obtained from the European Chemicals Bureau¹. The Final RAR should be used for citation purposes rather than this present Summary Report.

¹ European Chemicals Bureau – Existing Chemicals – <http://ecb.jrc.it>

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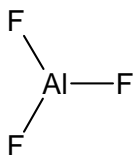
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GENERAL SUBSTANCE INFORMATION

1.1

IDENTIFICATION OF THE SUBSTANCE

CAS Number: 7784-18-1
EINECS Number: 232-051-1
IUPAC Name: Aluminium fluoride
Synonyms: aluminum fluoride, aluminium trifluoride, aluminum trifluoride
Molecular weight: 83.98
Molecular formula: AlF_3
Structural formula:



1.2

PURITY/IMPURITIES, ADDITIVES

Purity: >97% (wet production process)
>90% (dry production process)
Impurities: For both qualities the balance is aluminium oxide or aluminium hydroxide depending on the production process used.
Additives: none

1.3 PHYSICO-CHEMICAL PROPERTIES

Table 1.1 Summary of physico-chemical properties

Property	Value	Remarks
Physical state	solid	
Melting point	1257° C	Melting point is not relevant because of sublimation. No decomposition below 600°C.
Boiling point	1537° C	
Relative density	850 or 1,500 kg/m ³ at 20° C ⁽¹⁾	
Vapour pressure	1.3 hPa at 1238° C	
Water solubility	5.3 – 9.4 mg/l at 25° C	pH = 5.9 for saturated solution
Partition coefficient n-octanol/water (log value)	Not applicable	
Granulometry	>0.090 mm 74% >0.063 mm 18% >0.045 mm 4% <0.045 mm 4%	
Conversion factors	Not applicable	
Flash point	Not applicable	
Autoflammability	Not applicable	
Flammability	Non flammable	
Explosive properties	Not explosive	
Oxidizing properties	No oxidising properties	
Viscosity	Not applicable	
Henry's constant	7.03E-06	
Surface tension	Not applicable	
Additional remark	Not combustible/ does not support combustion	

⁽¹⁾ depending on the filling process if shaking is applied or not

1.4 CLASSIFICATION

Classification and Labelling: no classification

Aluminium chloride, several aluminium alkyls and HF are already listed on Annex I with no classification and labelling for the environment. The aluminium substances were not classified because aluminium precipitates at an environmental pH range. Toxicity is only observed at a low pH. Therefore, no classification for the environment is concluded for AlF₃.

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GENERAL INFORMATION ON EXPOSURE

Production

The total EU production of all AlF_3 is 106,677 tonnes. The total quantity imported amounts to 14,244 tonnes. A total quantity of 57,095 tonnes is exported. The total amount of AlF_3 within the EU for the year 2000 is $(106,677 + 14,244 - 57,095 =) 63,826$ tonnes.

Uses

The industrial and use categories of AlF_3 are IC8, UC40 and UC43. The main use of AlF_3 is as a temperature-regulating agent, a pH-regulator and as a solubility enhancer of aluminium oxide in the electrolyte solution in the production process of aluminium. The use of AlF_3 as such results in a lowering of the energy consumption in the aluminium pot. The raw material (aluminium oxide) is melted and split in aluminium and oxygen. The minor downstream uses of AlF_3 are for metal treatment and for optical coating as an essential component of anti-reflective coatings and in semiconductors. A total of 52 tonnes of AlF_3 was sold to traders, for which it is also assumed that it is used for other purposes than aluminium production. As no other significant uses were reported, neither by producers nor by downstream users, it is assumed that the main application is for production of aluminium, which is in general agreement with the information provided by the producers (> 99.6% used for aluminium production). As a consequence the risk assessment will focus on this particular use.

Trends

Very limited data was submitted on trends and expected production volumes and fluoride emissions in the future. It is assumed that the total EU production of AlF_3 will be more or less the same in the next five years (2006 – 2010). In addition, no further reduction in fluoride emissions is expected based on this information.

Legislative controls

All primary aluminium production plants are according to the European Integrated Pollution Prevention and Control (IPPC) Bureau Directive 96/61/EC. The reference document prescribes different emission limit values for primary aluminium electrolysis ($<0.2 \text{ mg HF/Nm}^3$)¹ and primary aluminium smelters ($<1 \text{ mg total fluoride/Nm}^3$) under application of Best Available Techniques (BAT). However, these standards cannot be related to the emission data in this RAR. The on-site monitoring programs are not evaluated within the scope of this RAR. In addition, OSPAR prescribes an emission limit value for the primary aluminium industry of 0.4 kg HF per ton produced aluminium. It should be noted that the current maximum emission under BAT prescribed by OSPAR does not warrant environmental concentrations below the PNEC of $0.2 \text{ }\mu\text{g/m}^3$. In the WHO Air Quality Guideline for Europe it is concluded that the available information does not permit the derivation of an air quality guideline value for fluoride(s). In addition, it is recognised that fluoride levels in ambient air should be less than $1 \text{ }\mu\text{g/m}^3$ to prevent effects on livestock and plants and that these concentrations will also sufficiently protect human health.

3

ENVIRONMENT

3.1

ENVIRONMENTAL EXPOSURE

Environmental releases

Over 99.6% of all AlF_3 is used by the aluminium industry. For 28 out of 32 sites the fraction present in the gaseous HF form is specified. The ratios between total F and HF range from 10.9 to 88.4% (see Table 3.1.1). The average fluoride emission of a primary aluminium smelter within the EU consists for 53% of HF and 47% of particulate fluoride. In cases where the HF emission is not specified, the maximum proportion of HF is taken as a worst-case estimate for the HF emission. The summation of the fluoride emissions results in a total of 4,929 tonnes for the year 2002. Assuming that all of the AlF_3 within the EU (63,826t) is used by the primary aluminium industry this results in a total emission of 2,463 ton HF per year. As the reported emissions can not directly be related to production levels (only the production capacity is given) in Table 3.1.1, the total HF emission reported for 2002 is considered to be representative for the year 2000. The total amount of HF released to the atmospheric compartment in the EU during production (1.2 t/y) and industrial use (2,463 t/y) of AlF_3 amounts to 2,464 tonnes HF for the year 2000. It can be concluded that a negligible fraction of HF is released to the atmosphere during the production of AlF_3 (1.2 t/y) compared to the total annual emission of HF of 11,945 t/y within the EU.

Environmental fate

AlF_3 is not photodegradable, but abiotic hydrolysis of AlF_3 does occur. Many complexes can be formed and occur in water such as $\text{Al}(\text{OH})_3$, $\text{AlF}_3(\text{OH})^-$, $\text{Al}(\text{OH})_4^-$, AlOH^{2+} , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})\text{F}^+$, AlF_2^+ , AlF^{2+} and AlF_4^- . The forming of complexes is dependent on several factors such as pH, water hardness and temperature. In hard water (>50 mg CaCO_3/l), fluoride precipitates with Ca as CaF_2 (especially when $\text{pH}>4.5$). In water AlF_3 complexes are generally the most dominant inorganic aluminium species. Free aluminium and aluminium hydroxide complexes are present in relatively smaller amounts. In the low pH range formation of AlF_3 complexes will dominate, whereas hydrolytic species will predominate at higher pH levels. Fluoride ions, being similar in size to hydroxyl ions, will readily substitute in these complexes, although the complexes formed with OH^- are much stronger than with F^- ions.

Fluoride accumulates, food-dependently in skeletal tissues of both aquatic and terrestrial vertebrates and invertebrates. Bioaccumulation occurs in marine organisms and, to a lesser extend, fresh water organisms. Reported BCF-values for marine organisms range up to approximately 150 and 60 for fish and crustacea, respectively. The most important exposure route for plants is uptake from the atmosphere. Concentrations in plants in the vicinity of a HF production plant range up to approximately 200 mg/kg, with mean levels between 20 and 50 mg/kg dry weight. Generally, lowest fluoride levels are found in herbivores and (somewhat) higher levels in predators.

Environmental concentrations

No risk assessment for the water compartment (including sediment and wastewater treatment systems) was performed based on several reasons:

- F-emissions to water from the AlF_3 industry are in general lower than the air emissions;
- no information was received that fluorides constitute a water problem at a regional scale in the EU;
- fluoride emissions from unintentional sources, in particular those from the fertiliser industry (phosphate ore), by far exceed the emissions from the intentional emissions of fluoride to water at a regional scale. The contribution of unintentional sources is also expected to be high for the atmospheric F emissions, but to a relatively lower extent as for water;
- The toxicity of AlF_3 complexes is primarily related to the aluminium (free F has a much lower aquatic toxicity than Al ions). It thus seems more obvious to assess these risks in a possible future RA of aluminium and aluminium compounds.

Based on a regional air concentration of $0.20 \mu\text{g HF/m}^3$ and the higher deposition velocity a regional soil concentration is calculated of 0.04 mg F/kg . The data provided by the downstream users can not be used for deriving a C_{local} as no information was given on the exact position where these measurements were performed (i.e. distance to the emission source). When the measured data are compared with the calculated data, they seem to differ considerably, at first sight. The range of the calculated data from 0.65 to $27 \mu\text{g/m}^3$ is approximately 3 to 6 times higher as the range of measured data from 0.2 to $4.55 \mu\text{g/m}^3$. As it is most of the times not clear at what distance from the emission source these concentrations in air have been measured, it seems plausible that this difference can be explained by distance to the emission source. The predicted HF levels are calculated for a distance of 100 metres from the emission source with OPS-Pro 4.1. For some of the monitoring data for fluoride the distance to the aluminium production plants is known. The Norwegian reported fluoride concentrations in the range 0.5 to $3.3 \mu\text{g/m}^3$ at approximately 700 metres from the emission source. In 1987 and 1988 at 1.65 km from an aluminium plant in the USA the mean concentration of fluoride was 0.79 and $0.85 \mu\text{g/m}^3$, respectively. These measurements seem to confirm the assumption that the differences can at least partially be explained by the greater distance. According to the Norsk Elektro Optikk the typical concentration levels in dry scrubber outlets of aluminium plants is in the range of 0.1 to 10 mg HF/m^3 . Comparable emissions ($2\text{-}4 \text{ mg/m}^3$), also measured in a chimney, from a HF plant result in mean measured atmospheric fluoride concentrations of $0.3\text{-}0.4 \mu\text{g/m}^3$ at a distance of 500 metres from this site. Taking these data into account, it can be concluded that the calculated atmospheric concentrations of HF at a distance of 100 metres from the emission source are in general agreement with monitoring data of aluminium smelters.

The total emission within the EU for 2001 of 11,945 tonnes results in a $\text{PEC}_{\text{regional}}$ of $0.20 \mu\text{g/m}^3$ for the atmosphere derived with EUSES 2.0.3 (2005). The calculated $\text{PEC}_{\text{regional}}$ is in the same order of magnitude as the mean measured concentration for the Netherlands of $0.07 \mu\text{g/m}^3$. As the calculated $\text{PEC}_{\text{regional}}$ is comparable to the mean measured concentration in the Netherlands, it was decided to use this value ($0.20 \mu\text{g/m}^3$) to derive the $\text{PEC}_{\text{local}}$ for the aluminium production plants.

3.2 EFFECTS ASSESSMENT

Aquatic compartment (incl. sediment)

As no risk assessment for the aquatic environment (both freshwater and marine) is performed, no PNECs will be derived for the aquatic compartment. Various results of GLP and non-GLP toxicity tests are available for algae, Daphnia and fish. All reported tests are performed with AlF_3 . Toxicity can be expected from free Al and F ions, but also from aluminium fluoride-complexes, which will also occur in view of the water solubility (5.3 – 9.4 mg/l). There are several factors, which influence the toxicity to a large extent, such as pH, water hardness and temperature. Reference is made to the RAR on HF, which presents toxicity data for the F ion and EHC 194, which presents toxicity data on the Al^{3+} ion. In the RA on HF long-term NOEC-values of 4 and 8.9 mg F/l for fish and Daphnia, respectively, and the lowest EC_{50} -value of 43 mg F/l for freshwater algae have been taken into consideration for the derivation of PNEC for the aquatic environment. In WHO document 194 the lowest reported toxicity values or effect concentration for Al are 96-h LC_{50} of 0.095, 0.48 and EC_{50} of 5 mg Al/l for the American flagfish, the polychaete *Ctenodrilus serratu*, and the alga *Chlorella pyrenoidosa*, respectively.

Terrestrial compartment

The PNEC for the terrestrial compartment derived in a RAR for HF, will be taken forward without revision in the risk assessment for AlF_3 , since no additional data are available. The PNEC for HF of 11 mg/kg was based on the lowest available NOEC, i.e. 106 mg/kg for nitrification divided by an assessment factor of 10. The background F concentrations in the above-mentioned test systems were very low. So theoretically, the PNEC of 11 mg/kg is a concentration that must be added to the neutral background concentration in soil.

Atmosphere

The PNEC derived for plants and atmosphere derived in a RAR for HF, will be taken forward without revision in the risk assessment for AlF_3 , since no additional data are available: $\text{PNEC}_{\text{plant-air}} = 0.2 \mu\text{g}/\text{m}^3$. The PNEC has been derived from the lowest NOEC for highly sensitive plant species, without making use of an extrapolation factor.

Non compartment specific effects relevant to the food chain

The fluoride NOECs, as derived earlier in the HF RAR for both plants (air) and livestock/wildlife (food-air), will be taken forward without revision in the TRA for AlF_3 . The atmospheric NOECs for livestock (and plants) are 0.8 μg and 0.3 $\mu\text{g}/\text{m}^3$ (daily averages) for the grazing season and winter season, respectively, based on a maximum acceptable F level in feed of 55 mg/kg dry weight. It was concluded that wild herbivores are or may be more susceptible to fluoride toxicity than domestic live stock, on a dietary F content basis. This greater susceptibility is probably due to larger variation in F intake by wild animals, in conjunction with the influence of other stress-inducing factors in the environment. Thus atmospheric NOECs derived for livestock may provide an insufficient guarantee for the protection of wild fauna.

3.3 RISK CHARACTERISATION

Terrestrial compartment

The potential risk for the terrestrial compartment is caused by the atmospheric deposition of fluoride, which is directly related to the air concentration. The air concentration causing a risk for the terrestrial compartment via atmospheric deposition is much higher than the one that will cause a risk for the atmospheric compartment. Consequently, the risk for the terrestrial compartment will be subordinated to the risks assessed for plants for atmospheric HF and in concomitant all emission reduction measures necessary to reduce the risk for plants, will automatically reduce the risk for the terrestrial compartment as well. For this reason it is considered redundant to perform a detailed risk assessment for the terrestrial compartment. As an indication all sites with a PEC in the atmosphere higher than $63 \mu\text{g}/\text{m}^3$ result in a soil concentration higher than the PNEC of $11 \text{ mg}/\text{kg}$ (estimated with EUSES 2.0.3). Since the highest calculated local concentration is $27 \mu\text{g}/\text{m}^3$, no PEC/PNEC ratios above 1 are expected. The levels for the AlF_3 producers were found to be negligible compared to background concentrations (conclusion ii). It should be noted that the PNEC used for the terrestrial compartment is based on toxicity data for HF and does not take into account the possible toxicity of aluminium. The risks from aluminium ions for the terrestrial compartment should be considered in a possible future risk assessment for aluminium compounds.

Atmosphere

The PNEC for plant-air is $0.2 \mu\text{g}/\text{m}^3$ (RAR HF). For the risk characterisation the ambient background F concentration in air ($\text{PEC}_{\text{regional}}$) has been added to the PEC-values. A $\text{PEC}_{\text{regional}}$ $0.20 \mu\text{g}/\text{m}^3$ has been calculated with EUSES 2.0.3. For AlF_3 production site 4 and the formulation site 5 conclusion (ii) is applicable, as there is minimal and no emission to air, respectively. For AlF_3 production sites 1, 2 and 3 the PEC local exceeds the PNEC due to the contribution of the regional background concentration. However, in view of the limited contribution of the local air concentration to the exceeding of the PNEC, conclusion (ii) is drawn for these sites. The regional PEC based on both intentional and unintentional sources is $0.20 \mu\text{g}/\text{m}^3$, which equals the established $\text{PNEC}_{\text{plant-air}} = 0.2 \mu\text{g}/\text{m}^3$. As the Dutch mean measured concentration of $0.07 \mu\text{g}/\text{m}^3$ confirms that the PNEC is not exceeded conclusion (ii) is drawn for the regional scale.

Conclusion (iii) applies to all primary aluminium production sites (downstream use of AlF_3) at the local scale. At almost all primary aluminium production sites fluoride monitoring programs are in place. The monitoring programs are not evaluated within the scope of this RAR. It can be concluded that by adaptation of the OPS model with more realistic conditions for the primary aluminium smelters (i.e. multiple source emission and higher emission height), the HF air concentrations in the surrounding of all EU primary aluminium smelters still exceed the PNEC. It is assumed that further refinement of the model calculations based on additional site-specific information (e.g. specific plant configurations and meteorological information) will not lower the $\text{PEC}_{\text{local}}$ sufficiently to affect the conclusion (iii) in the risk characterisation. Local risk reduction measures should be tailor made, taking into account additional site-specific information (e.g. the specific plant configurations and relevant meteorological information).

Non compartment specific effects relevant to the food chain

For AlF_3 production sites no risk is indicated for the winter season and the grazing season (conclusion ii) for the non compartment specific effects relevant to the food chain.

Local air concentrations around the primary aluminium production sites exceed the atmospheric NOECs for livestock of $0.8 \mu\text{g}$ and $0.3 \mu\text{g}/\text{m}^3$ for the grazing season and winter season, respectively (conclusion iii). It is emphasized that wildlife is probably more susceptible to fluorides than livestock. Since the risk for non compartment specific effects relevant to the food chain is determined by the deposition via the atmosphere any reduction measures needed to reduce the risk for the atmosphere will also reduce the risk for these specific effects.

4

HUMAN HEALTH

4.1

HUMAN HEALTH (TOXICITY)

Exposure assessment

(Hydrogen) fluoride emissions are resulting from AlF_3 use. Pragmatically, the concentration of HF and F^- are considered equivalent. For man exposed indirectly, the yearly average concentration is taken, including regional exposure. This concentration would lead to an intake of $27.2 \mu\text{g F}^-/\text{m}^3 \times 20 \text{ m}^3/\text{day}/70 \text{ kg bw} = 7.7 \mu\text{g F}^-/\text{kg bw}/\text{day}$.

Risk characterisation

The background intake via food and drinking water of the fluoride-ion is circa $85 \mu\text{g F}^-/\text{kg bw}$ day. In analogy with F^- intake via air for HF, the F^- intake via air from AlF_3 use is put into the context of the overall F^- intake. The intake of F^- of $7.7 \mu\text{g}/\text{kg bw}/\text{day}$ is marginal compared to the total daily fluoride intake (conclusion ii). The regional air concentration of F^- is $0.2 \mu\text{g F}^-/\text{m}^3$. This concentration would lead to an intake of $6 \times 10^{-2} \mu\text{g F}^-/\text{kg bw}/\text{day}$ which is negligible compared to overall intake of fluoride via food and drinking water of $85 \mu\text{g F}^-/\text{kg bw}/\text{day}$ (conclusion ii).

5 RESULTS

5.1 ENVIRONMENT

Terrestrial compartment

Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.

Conclusion (ii) for the terrestrial compartment applies to all EU primary aluminium production sites at a local scale. Also for the AlF_3 producers conclusion (ii) is drawn at a local scale. At the regional scale the PEC derived with EUSES taking into account a higher deposition velocity did not exceed the PNEC (conclusion ii).

Atmosphere

Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.

This conclusion applies to AlF_3 production sites 1 to 5 and the regional scale.

Conclusion (iii) There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

Conclusion (iii) applies to all primary aluminium production sites (downstream use of AlF_3) at the local scale.

Non compartment specific effects relevant to the food chain

Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.

This conclusion applies to AlF_3 production sites for the winter season and the grazing season.

Conclusion (iii) There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

This conclusion applies to the primary aluminium production sites for the grazing season and winter season at local scale.

5.2 HUMAN HEALTH

Humans exposed via the environment

Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.

This conclusion applies to both local and regional scales.

