

CALCIUM FLUORIDE

CAS No: 7789-75-5

EINECS No: 232-188-7

SUMMARY RISK ASSESSMENT REPORT (ENVIRONMENT)

Final report, 2008

The Netherlands

FINAL APPROVED VERSION

Rapporteur for the risk assessment of Calciumfluoride 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 Calcium 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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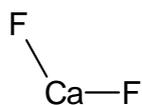
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1 GENERAL SUBSTANCE INFORMATION

1.1 IDENTIFICATION OF THE SUBSTANCE

CAS Number: 7789-75-5
EINECS Number: 232-188-7
IUPAC Name: Calcium fluoride
Synonyms: This dossier is also related to calcium fluoride ore (synonyms: fluorspar or fluorit (CAS: 14542-23-5/ EINECS: 238-575-7)).
Molecular weight: 78.1
Molecular formula: CaF_2
Structural formula:



1.2 PURITY/IMPURITIES, ADDITIVES

Purity: >97%
Impurity: $\leq 1\%$ silicon dioxide
 $\leq 1\%$ calcium carbonate
 $\leq 0.6\%$ diiron trioxide
 $\leq 0.3\%$ barium sulphate
Additives: none

1.3 PHYSICO-CHEMICAL PROPERTIES

Table 1.1 Summary of physico-chemical properties

Property	Value
Physical state	solid
Melting point	1423°C
Boiling point	2786°C
Relative density	3.18 kg/dm ³ at 20°C
Vapour pressure	10.13 hPa at 2100°C
Water solubility	15 mg/l at 18°C
Partition coefficient n-octanol/water (log value)	Not applicable
Granulometry	Variable
Conversion factors	Not applicable
Flash point	Not applicable
Autoflammability	Not applicable
Flammability	Non flammable
Explosive properties	Not explosive
Oxidising properties	No oxidising properties
Viscosity	Not applicable
Henry's constant	1.04E-04
Surface tension	Not applicable

1.4 CLASSIFICATION

Classification and Labelling: no classification

In the RAR on HF (2001) several acute aquatic toxicity studies are reported without specification of the water hardness. Nevertheless, in view of the limited water solubility of CaF₂ (15 mg/l; maximum concentration of F⁻: 7.3 mg/l), none of the EC50 values for fluoride reported will be reached. Therefore, CaF₂ is not classified for the environment.

2

GENERAL INFORMATION ON EXPOSURE

Production

The total amount produced in 2000 in Europe is 335,546 tonnes. The reported total amount imported in 2000 is 519,636 tonnes. The producers reported an exported quantity of 16,700 tonnes. The export may be higher, as the export data from the producers was not complete. In committant, the total amount of CaF₂ used in the year 2000 may be overestimated, but maximally amounts to 838,482 (335,546 + 519,636 – 16,700) tonnes.

Uses

All kinds of applications have been reported for CaF₂, which have been summarised in terms of industrial and use categories in **Table 2.1**.

Table 2.1 Reported industrial and use categories of CaF₂

Industry category	IC no.	Use category	UC no.
Chemical industry: Basic chemicals	2	Other (production of HF)	55
Chemical industry: Chemicals used in synthesis	3	Other (fluorescent powder)	55
Metal Industry	8	Flux agents (for casting)	24
Metal Industry	8	Welding and soldering agents	54
Metal Industry	8	Others (leaching agent) ⁽¹⁾	55
Other (glass and enamel industry)	15	Colouring agents ⁽¹⁾	10
Other (glass and enamel industry)	15	Others (flux agent)	55
Other (cement industry)	15	Process regulators	43

⁽¹⁾ No information is given on the absolute quantities involved with this specific use.

Most of CaF₂ in the EU (91.9%) is used for the production of HF and CaSO₄ by the conversion of dried acid spar with concentrated sulphuric acid at elevated temperatures. Other minor uses are 6.0% as a flux agent (for casting) to reduce melting point and viscosity of slag (UC no. 24), 1.2% for welding, 0.4% in both glass as cement industry and as a colour agent for glasswork (UC no.10). A minor fraction is used for the production of fluorescent powder (0.02%).

Trends

The production and import data for the period 2000 - 2003 show a decreased trend in production and an increased trend in import in the EU. It should be noted that the import data given by CEFIC are much lower than the data provided by the questionnaires (375 versus 519 ktonnes). These differences can probably be explained by the fact that not all importers are members of CEFIC.

Legislative controls

Concerning the production of CaF₂ only dust emissions are expected. In the questionnaires provided by the producers maximum general dust emission limit values in the range of 5 to 10 mg/m³ per 8 hours are reported. For F⁻ maximum values of 2 and 2.5 mg/m³ are reported. If these values are converted to values for CaF₂, also a limit value of approximately 5 mg/m³ dust is obtained. One producer reported also a limit value for aquatic emission of <10 mg F/l.

Since for the downstream use application in the steel industry (flux agent) risks at a local scale considering HF emissions can not be excluded, it should be checked if legislative controls are in place to control these risks and if so, if the risks are controlled sufficiently.

3 ENVIRONMENT

3.1 ENVIRONMENTAL EXPOSURE

Environmental releases

Two producers provided information on the fluoride emission to water (as total particles in suspension or unspecified). The calculated emission factors are 28.9 and 233 g/t. Based on a total production in the EU of 335,546 tonnes, the resulting emission of fluoride from CaF_2 -production to the aquatic environment will range from 9.7 to 78t.

Emissions of HF could not be established with the emission data provided and are taken forward from the RAR on HF (2001) applying an extrapolation factor of 1.9, resulting in a total (continental) atmospheric emission for both production as downstream use for the year 2000 of 18 tonnes HF. Applying the 10% rule a total regional emission of 1.8 tonnes HF can be assumed. Assuming 365 production days, the total daily regional emission amounts to 4.9 kg/d, which can be considered negligible compared to a release of 675 kg/d (2,463 tonnes / $365 * 10\%$) resulting from aluminium production.

Environmental fate

Fluorides are emitted to the atmosphere as gaseous compounds (75%) or as solids in the form of aerosols (25%). Gaseous fluorides in the atmosphere are predominantly HF (and SiF_4). HF is removed relatively rapidly from the atmosphere by both dry and wet deposition with a half-life of ca. 14 hours and ca. 12 hours for dry and wet deposition, respectively. Fluoride aerosol is eliminated slowly predominantly (65%) by wet deposition with a half-life of 50 hours. For dry deposition of fluoride aerosol a half-life of 12 days is reported. Fluorides in air are deposited in the general vicinity of an emission source. When HF (F) is released in fresh water at pH above 5, the free ion is the main fluoride species when calcium concentrations are low. At lower pH, the proportion of fluoride ion decreases, while HF_2^- and non-dissociated HF increase. In the presence of phosphate insoluble fluorapatite is formed, a large part of which is transferred to the bottom sediments.

CaF_2 is released during production and industrial use to waste water, where it is expected to precipitate, especially when the $\text{pH} > 4.5$. Even when fluoride is emitted as free ions to waste water, this emission is not expected to result in considerable atmospheric HF emission, as only a fraction of fluoride occurs as HF, especially when the pH is above 5. Therefore it can be concluded that the release of HF from water to the atmosphere can be considered negligible. In addition, CaF_2 is also released as dust during the production and downstream use, which is expected to deposit in the vicinity of the production and downstream user sites to both, surface water as soil. In soil CaF_2 tends to accumulate within the surface layer, but maybe displaced throughout the root zone, even in calcareous soils. In soils with $\text{pH} < 6$ fluoride is considered to be immobile as it predominantly occurs in the form of fluoride containing minerals. At a pH above 6, the fluoride ion is the dominant species.

Fluoride accumulates, food-dependently in skeletal tissues of both aquatic and terrestrial vertebrates and invertebrates. Bioaccumulation occurs in marine organisms and, to a lesser extent, 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:

- The F-emissions to water from the CaF₂ industry are in general low; additionally due to its low solubility, CaF₂ dissociation in water is minimal.
- F-emissions to water from the CaF₂ production (i.e. mining companies) may result in levels that exceed the current Predicted No Effect Concentration (PNEC) water for fluoride (one case actually reported). The number of those mining companies, however, is known to be limited and furthermore it is assumed that the emissions from the mining activities are known to (and regulated by) local authorities. It should be borne in mind that high fluoride water levels in mine areas may also be related to high natural background levels in those regions;
- F-emissions to water for the HF production, being the most important use source of CaF₂, were already addressed in the HF report;
- 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;

In the RAR on HF (2001), the Predicted Environmental Concentrations (PEC) values for the terrestrial compartment (calculated from the deposition of HF) were found to be negligible compared to background concentrations. The same conclusion can be drawn based on the HF production figures for the year 2000, although the HF emission is twice as high. The same conclusion can be drawn when the emission of CaF₂ is taken into account, as the emission is comparable to the emission of HF, for which already a high deposition rate was used.

The emission information derived calculated levels of HF nearby industrial sources range from 0.013 to 3.05 µg/m³ (section 3.1.5.1.2). It can be concluded that these levels do correspond with the measured data (0.03 to 4.6 µg/m³). The total emission within the EU for 2001 of 11,945 tonnes results in a PEC_{regional} of 0.20 µg/m³ for the atmosphere derived with EUSES 2.0.3 (2005). The calculated PEC_{regional} is in the same order of magnitude as the mean measured concentration for the Netherlands of 0.07 µg/m³. As the calculated PEC_{regional} is comparable to the mean measured concentration in the Netherlands, it was decided to use this value (0.20 µg/m³) to derive the PEC_{local} for the steel production sites, the production site for welding consumables, the AlF₃ production plants and 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 toxicity tests are available for algae, Daphnia and fish. However, the reliability of the most available data is very poor as it involves not standardised toxicity studies, in addition few is reported about the test conditions. 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 EC₅₀-value of 43 mg F/l for freshwater algae have been taken into consideration for the derivation of PNEC for the aquatic environment.

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 CaF₂, 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 TRA for CaF₂, 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 using an extrapolation factor.

Non compartment specific effects relevant to the food chain

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. As explained in the RAR on AlF₃, the air concentration causing a risk for the terrestrial compartment atmosphere is much higher than the one that will cause a risk for the atmosphere. 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, with respect to the use of CaF_2 by the steel industry as flux agent. Therefore, for the downstream use flux agent on a local scale conclusion (ii) is drawn. For all other minor uses (0.8% of the total EU volume) no conclusion is drawn with respect to HF emissions, since they are considered to be of minor importance.

Atmosphere

The regional PEC derived with EUSES 2.0.3, combining the fluoride emissions from both intentional and unintentional sources was found to be $0.2 \mu\text{g}/\text{m}^3$, which equals the established $\text{PNEC}_{\text{plant-air}} = 0.2 \mu\text{g}/\text{m}^3$. As the Dutch mean 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. Based on realistic worst-case emission factors provided by the industry, the use of CaF_2 in the metal industry as a flux agent leads to local air concentrations ranging from 0.032 to $3.05 \mu\text{g}/\text{m}^3$. For the class of five steel production sites which use up to 500 tons of CaF_2 a (maximum) C_{local} of $0.095 \mu\text{g}/\text{m}^3$ is derived. Adding this maximum local concentration up with the $\text{PEC}_{\text{regional}}$ (resulting in a $\text{PEC}_{\text{local}}$ of $0.30 \mu\text{g}/\text{m}^3$) leads to a maximum RCR of 1.5. Since the $\text{PEC}_{\text{regional}}$ equals the PNEC, each local atmospheric emission of HF leads to exceeding of the PNEC. However, in view of the limited contribution of the local air concentrations to the exceeding of the PNEC, conclusion (ii) is drawn for these five sites. The use of CaF_2 by the metal industry with respect to welding can be split up in the use for the production of welding consumables and the use as a flux agent for welding. From the latter emissions are considered to be small on a local scale, due to wide distribution of this application across the EU. In addition, at the production of welding consumables no HF is emitted. Therefore, conclusion (ii) is drawn at the local scale for both scenarios.

Conclusion (iii) is drawn for the following downstream uses of CaF_2 :

The local environmental risk characterisation of the downstream use of CaF_2 (HF production) is described in the RAR on HF (2001). The calculated PEC in atmosphere exceeds the PNEC (conclusion iii).

For the eight steel production sites which use above 500 tons of CaF_2 as a flux agent (classes with upper thresholds ranging from 1,000 to 16,000 tonnes) conclusion iii is drawn. The upper threshold of the class 500 to 1,000 tonnes of CaF_2 results in a C_{local} of $0.19 \mu\text{g}/\text{m}^3$, a $\text{PEC}_{\text{local}}$ of $0.39 \mu\text{g}/\text{m}^3$ and an RCR of 2.0. Since this local air concentration is considered to be equal to the PNEC conclusion (iii) is drawn.

For all other minor uses (0.8% of the total EU volume) no conclusion is drawn with respect to HF emissions, since they are considered to be of minor importance.

Non compartment specific effects relevant to the food chain

No emissions of HF are expected during the production of CaF_2 . Therefore, no specific effect relevant to the food chain are expected (conclusion ii). Based on realistic worst-case emission factors provided by the industry, the use of CaF_2 in the metal industry as a flux agent leads to local air concentrations ranging from 0.032 to $3.05 \mu\text{g}/\text{m}^3$. For the five steel production sites which use up to 1,000 tons of CaF_2 a (maximum) C_{local} of $0.19 \mu\text{g}/\text{m}^3$ is derived. Adding this maximum local concentration up to the $\text{PEC}_{\text{regional}}$ (resulting in a (maximum) $\text{PEC}_{\text{local}}$ of $0.39 \mu\text{g}/\text{m}^3$) the atmospheric NOEC for livestock of $0.3 \mu\text{g}/\text{m}^3$ for the winter season is exceeded by

a factor 1.3. In view of the limited contribution of the local air concentrations to the exceeding of the NOEC, conclusion (ii) is drawn for these sites. For the ten steel production sites which use up to 3,500 tons of CaF_2 as a flux agent a (maximum) $\text{PEC}_{\text{local}}$ of $0.87 \mu\text{g}/\text{m}^3$ (C_{local} : $0.67 \mu\text{g}/\text{m}^3 + \text{PEC}_{\text{regional}}$: $0.2 \mu\text{g}/\text{m}^3$) is derived. The NOEC for livestock for the grazing season of $0.8 \mu\text{g}/\text{m}^3$ is exceeded by a factor 1.08. In view of the marginal exceeding of the NOEC, conclusion (ii) is drawn for these sites. The use of CaF_2 by the metal industry with respect to welding can be split up in the use for the production of welding consumables and the use as a flux agent for welding. From the latter emissions are considered to be small on a local scale, due to wide distribution of this application across the EU. In addition, at the production of welding consumables no HF is emitted. Therefore, conclusion (ii) is drawn at the local scale for both scenarios.

Conclusion (iii) is drawn for the following downstream uses of CaF_2 :

The local environmental risk characterisation with respect to non compartment specific effects relevant to the food chain of the main downstream use of CaF_2 (HF production) is described in the RAR on HF. The calculated PEC in atmosphere exceeds the atmospheric NOECs for livestock of $0.8 \mu\text{g}/\text{m}^3$ and $0.3 \mu\text{g}/\text{m}^3$ for the grazing season and winter season, respectively (conclusion iii). It was emphasized that wildlife is probably more susceptible to fluorides than livestock.

For the eight steel production sites which use above 1,000 tons of CaF_2 as a flux agent (classes with upper thresholds ranging from 1,500 to 16,000 tonnes) conclusion iii is drawn for the winter season. The upper threshold of the class 1,000 to 1,500 tonnes of CaF_2 results in a C_{local} of $0.29 \mu\text{g}/\text{m}^3$, a $\text{PEC}_{\text{local}}$ of $0.49 \mu\text{g}/\text{m}^3$ and an RCR of 1.6. Since this local air concentration is considered to be equal the atmospheric NOEC for livestock of $0.3 \mu\text{g}/\text{m}^3$ for the winter season conclusion (iii) is drawn.

For the three steel production sites which use more than 6,500 tons of CaF_2 as a flux agent (up to 16,000 tonnes) conclusion (iii) is drawn for the summer season on a local scale, in view of the calculated $\text{PEC}_{\text{local}}$ of $1.44 \mu\text{g}/\text{m}^3$ (up to $3.25 \mu\text{g}/\text{m}^3$).

For all other minor uses (0.8% of the total EU volume) no conclusion is drawn, since they are considered to be of minor importance.

4

HUMAN HEALTH

4.1

HUMAN HEALTH (TOXICITY)

Exposure assessment

(Hydrogen) fluoride emissions are resulting from CaF_2 use. The flux agent scenario shows the highest realistic local HF concentration derived from CaF_2 use. The H atom hardly has any influence on the HF concentration, therefore the concentration of HF and F^- are considered equivalent. For man exposed indirectly, the yearly average concentration is taken, including the regional exposure. This concentration would lead to an intake of $3.25 \mu\text{g F}^-/\text{m}^3 \times 20 \text{ m}^3/\text{day} / 70 \text{ kg bw} = 1 \mu\text{g F}^-/\text{kg bw}/\text{day}$.

Risk characterisation

The background intake via food and drinking water of the fluoride-ion is circa $85 \mu\text{g}/\text{kg bw}$ day. In analogy with F^- intake via air for HF, the F^- intake via air for CaF_2 use is put in the context of the daily F^- intake. The intake of F^- of $1 \mu\text{g}/\text{kg bw}/\text{day}$ for the flux agent scenario is negligible 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 an 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 HF on a local scale and the down stream use of CaF_2 by the steel industry as flux agent with respect to HF emissions on a local scale.

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 HF on a local scale, the class of five steel production sites which use up to 500 tons of CaF_2 and the use of CaF_2 by the metal industry with respect to welding.

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 the eight steel production sites which use above 500 tons of CaF_2 as a flux agent and the local environmental risk characterisation of the downstream use of CaF_2 (HF production) is described in the RAR on HF.

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 the use of CaF_2 in the metal industry as a flux agent, the ten steel production sites which use up to 3,000 tons of CaF_2 as a flux agent and the use of CaF_2 by the metal industry with respect to welding.

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 local environmental risk characterisation with respect to non compartment specific effects relevant to the food chain of the main downstream use of CaF_2 (HF production) is described in the RAR on HF, the eight steel production sites which use above 1,000 tons of CaF_2 as a flux agent and the three steel production sites which use more than 6,500 tons of CaF_2 as a flux agent.

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.

