

## 4. Fluorspar

The mineral fluorspar consists of 51.1% calcium and 48.9% fluorine in its pure form (CaF<sub>2</sub>). In this case, it is colorless and transparent but different colors can be induced by impurities in the crystal structure. Most fluorspar is extracted either in pure veins or in association with lead, silver, or zinc ores. Commercial fluorspar is graded according to its quality and its specification into acid-grade, metallurgical grade and ceramic grade.<sup>1</sup> The largest current producer of fluorspar is China, followed by Mexico.

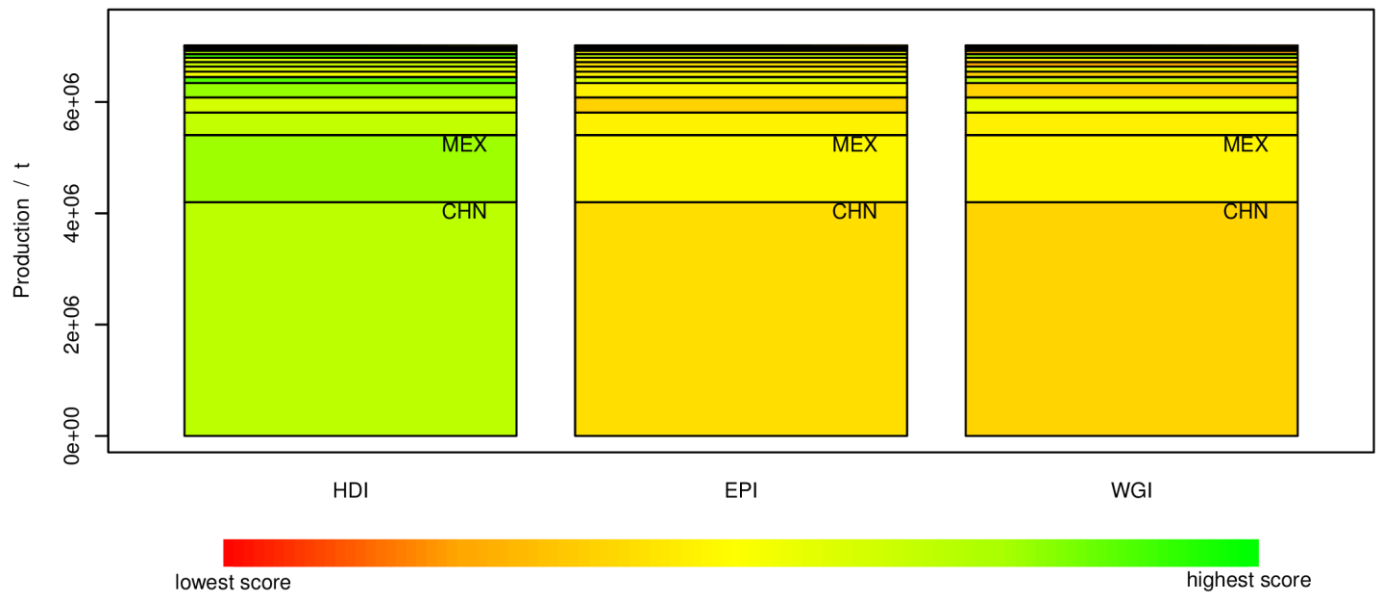


Figure 1: Distribution of fluorspar production<sup>2</sup> and corresponding scores of the producing countries in the Human Development Index (HDI)<sup>3</sup>, Environmental Performance Index (EPI)<sup>4</sup> and World Governance Indicators (WGI)<sup>5</sup>. Both the EPI and WGI are used to assess supply risks with the EU methodology for determining critical raw materials<sup>6</sup>. CHN = China; MEX = Mexico.

After dropping to a price of 0.101 US\$/kg in 2006, the average price of metallurgical grade fluorspar rose to approximately 0.11 US\$/kg\* in 2009. It is estimated that the price fell back to an amount of 0.101 US\$/kg in 2010.<sup>7</sup> The price of acid grade fluorspar is approximately double that value.

\* Price: c.i.f. U.S. port

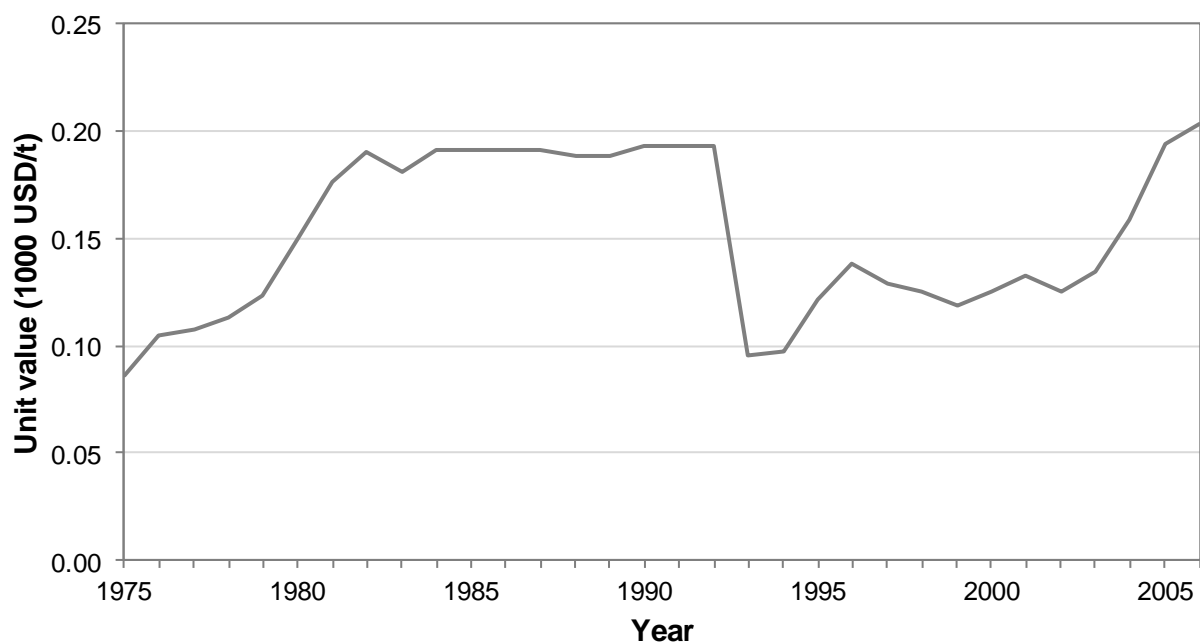


Figure 2: Fluorspar price development during 1975 – 2006. The unit value is defined as the value of 1 t of fluorspar apparent consumption (estimated) <sup>8</sup>.

## Uses and Substitutability

### Hydrofluoric acid

Fluorspar is widely used in the manufacturing of hydrofluoric acid or HF (52% of its end use) which serves as feedstock for many different chemical processes. Hydrofluoric acid from fluorite (acid grade) is used in the synthesis of fluorocarbons (CFCs, HCFCs, HFCs) or fluorine-bearing chemicals such as pharmaceuticals, agrochemicals, non-stick coatings as well as in uranium processing. Another application of hydrofluoric acid is as a catalyst for the petroleum industry.<sup>9</sup> Fluorosilicic acid from the production of phosphoric acid from apatite and fluorapatite has the potential to serve as a substitute for fluorspar as a source of fluorine in HF production.<sup>10</sup> Other possible substitutes are sodium fluoride, and sodium fluorosilicate.<sup>1</sup> Nevertheless, these substitutes are just principle alternatives, since none of them are put into practice yet.

### Steel

The steel sector consumes about 25% of total fluorspar. Metallurgical grade fluorspar is added as flux in the manufacture of steel in open hearth oxygen and electric arc furnaces. Fluorspar lowers the melting point and reduces slag viscosity. It can be substituted with aluminium smelting dross<sup>11</sup>, borax, calcium chloride, iron oxides, manganese ore, silica sand and titanium oxide<sup>10</sup>

### Aluminium

With a market share of 18%, the aluminum sector is the third largest consumer of fluorspar. The reason for this is that aluminum cannot be produced by an aqueous electrolytic process because hydrogen is electrochemically much nobler than aluminum. Thus, liquid aluminum is produced by the electrolytic

reduction of alumina ( $\text{Al}_2\text{O}_3$ ) dissolved in an electrolyte (bath) containing approximately 65% cryolite ( $\text{NaF}_3 \cdot 3\text{NaF}$ ; about 2 kg of cryolite are necessary to produce 1 ton of aluminum). Synthetic cryolite is made from fluorspar ( $\text{CaF}_2$ ) by treating it with sulfuric acid to produce hydrofluoric acid which is then reacted with sodium oxide ( $\text{Na}_2\text{O}$ ) and alumina to produce cryolite. Besides serving as a solvent, cryolite lowers the melting point of the aluminium electrolysis bath to below  $1000^\circ\text{C}$ <sup>1,9</sup>. In addition, aluminium fluoride ( $\text{AlF}_3$ ), also produced using HF, is used in the production of aluminium. In principle, fluorosilic acid, obtained from phosphate rock, can be used to produce HF (and thus synthetic cryolite and  $\text{AlF}_3$ ), but this process has not been implemented on a large scale yet<sup>9</sup>. Therefore, fluorspar cannot be substituted in electrolysis-based aluminium production. A corbothermic reduction process, which does not require fluorspar, is currently being developed by Alcoa (pilot stage).<sup>†</sup>

### Others

In the residual market share (5%) ceramic grade fluorspar is used in milky or coloured glass or glass fibers, which may contain 10 – 20% fluorite. Further applications are enamels for metallic or ceramic substrates containing between 3 – 10% fluorite. Regarding these applications fluorspar is inserted as opacifier. Finally, the addition of ceramic grade fluorspar to raw materials for cement enhances the clinkering temperature to 50 – 150 °C.<sup>9</sup>

### Summary

Fluorspar is used as the main source of fluorine. As such, either the fluorine may be substitutable in a process (e.g. in the steel industry) or alternative sources of fluorine may be used (such as fluorosilicic acid). It is unclear at this time to what extent (by-product) fluorosilicic acid may supplant fluorspar as the principle source of fluorine. In any case, this process would be a slow one.

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<sup>†</sup> SINTEF

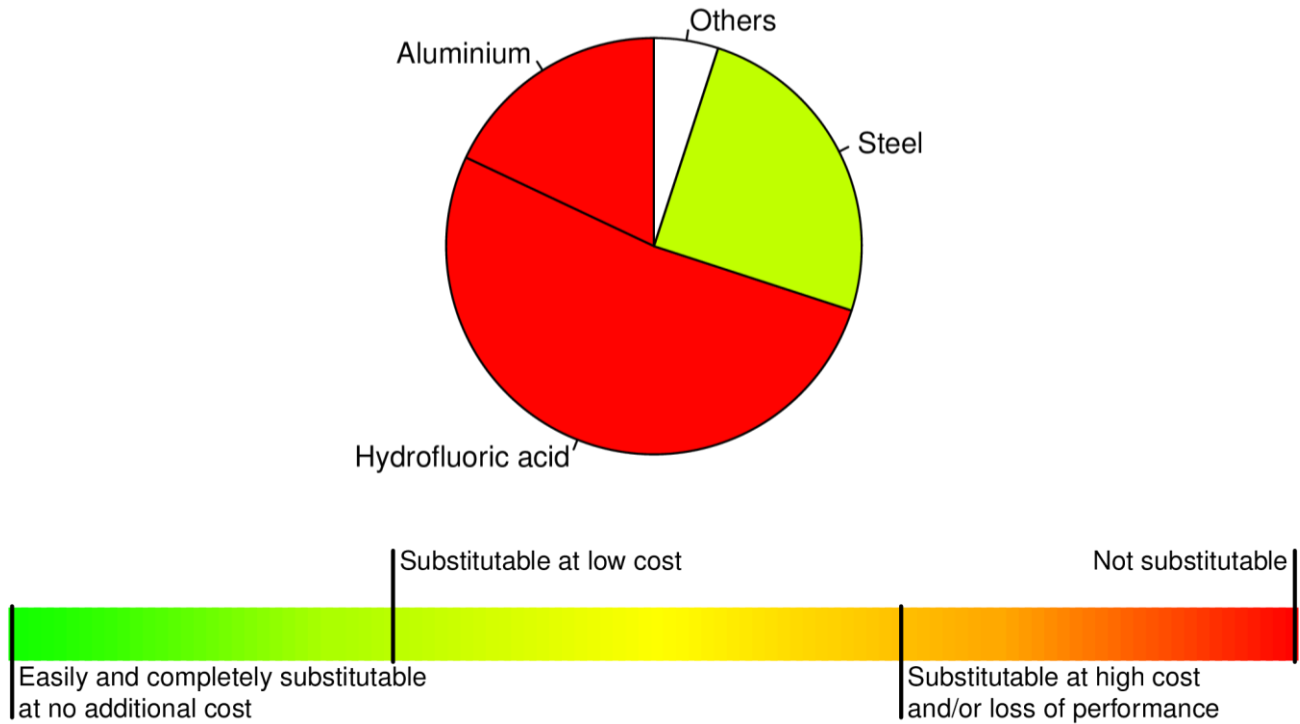


Figure 3: Distribution of end-uses and corresponding substitutability assessment for fluorspar. The manner and scaling of the assessment is compatible with the work of the Ad-hoc Working Group on Defining Critical Raw Materials (2010).

## References

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