

FLUORIDE EMISSIONS FROM FURNACES AND RELEVANCE OF SLAG FLUORIDE CAPACITY

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Introduction

Fluorine emissions, as hydrogen fluoride and particulate fluorides, are a concern in industry due to their impact on health and the environment. Coal-fired power plants are the largest source of anthropogenic HF emissions¹. Also in metallurgy, fluorine is a concern, and special attention is given to impact on workers' health. Typical release limits are concentrations in the order of mg/Nm³, some examples are given in Table 1.

Table 1: Examples of emission limits on HF

	Type of limit	Limit value	Reference
Foundry legislation, France	Concentration	5 mg/Nm ³	2
Foundry legislation, France	Flux	0.5 kg/h	2
Glass/frit manufacture, Ireland	Concentration	5 mg/Nm ³	3
Power plant, USA	Specific	0.18-1.8 g/MWh	4

Legal and recommended exposure limits are even lower, leading to the need for a strict workplace hygiene. As an example from the US,⁵ the OSHA legal airborne permissible exposure limit (PEL) is 3 ppm (2.5 mg/Nm³) averaged over an 8-hour work shift. NIOSH additionally recommends a limit (REL) of 6 ppm for any 15-minute work period. The ACGIH threshold limit values (TLV) are 0.5 ppm averaged over an 8-hour shift and 2 ppm at any time. The odour threshold, for comparison, is as low as 0.04 ppm.

In industries where fluorine containing fluxes (*e.g.* NaF, Na₂SiF₆, KAlF₄, NaAlF₄) are commonly used, HF generation is substantial. Examples of relevant processes are the Hall-Heroult-process for aluminium production, frit production, and brazing. Fluorine containing frit, as a basis for enamels, can pop up in recycling processes and release HF again (*e.g.* 0.9 mg/Nm³ from rotary iron foundry furnace¹). Also the use of coal can contribute significantly (*e.g.* 9-13 mg/Nm³ from cupola furnaces¹). Recycling flue dust may increase the concentration of fluorine in metallurgical flowsheets as well. CaF₂ is a common flux in steelmaking, but less volatile.

HF can effectively be absorbed by targeted or generic off-gas systems. Best available technologies are absorption by a wet gas scrubber or alkaline scrubber.⁶ Although relatively large areas are needed, a removal efficiency of 95%, with resulting HF level of < 1 mg/Nm³ can be achieved with lime, and > 90-95% efficiency can be achieved with sodium bicarbonate as a reagent.

Thermodynamic calculations

Using a thermodynamic viewpoint, a number of aspects of fluoride volatilisation can be clarified. Calculations are performed with FactSage version 7.2. The equilibrium between a certain mineral or slag and a small amount of a gas phase is calculated, and the total release of F to the gas is retrieved.

A first calculation concerns the vapour pressure of F-containing molecules in contact with CaF₂, which is one of the most common and stable fluorides. As can be seen from Figure 1, volatilisation heavily depends on temperature and presence of water vapour. Indeed, apart from simple volatilisation as CaF₂, pyrohydrolysis has a major influence on the F release:



As a result, even the average moisture level in Belgium (8 g/kg) leads to a considerable increase in volatilisation compared to dry air. Presence of steam due to charging of wet material, or from combustion gases, may be an important factor in the decomposition of even the stable CaF₂.

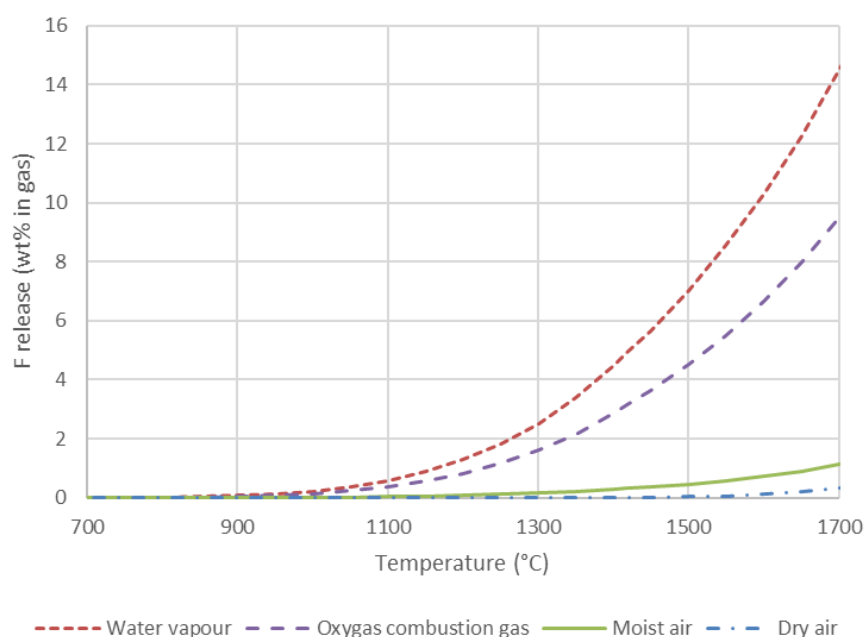


Figure 1: Release of fluorine from CaF₂ in contact with various gases

The behaviour of different fluorides, for which some examples are shown in Figure 2, depends on their thermodynamic stability as well as their vapour pressure. Some fluorides, such as NaF, volatilise easily as a compound. Others, such as ZnF_2 , are more prone to oxidation, and therefore to reaction with water to form HF and their corresponding oxide. Reaction in the furnace to more stable fluorides by e.g. contact with lime may prevent this.

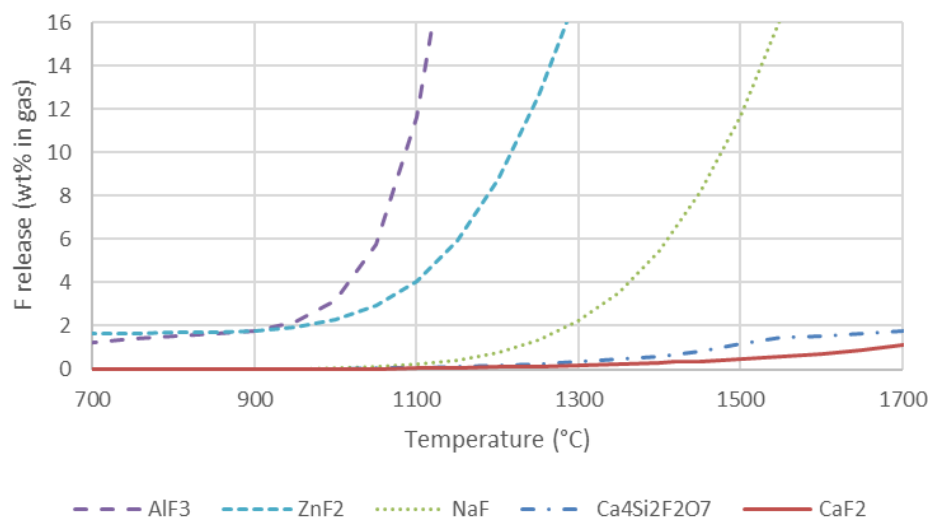


Figure 2: Release of fluorine from different fluoride minerals in contact with moist air

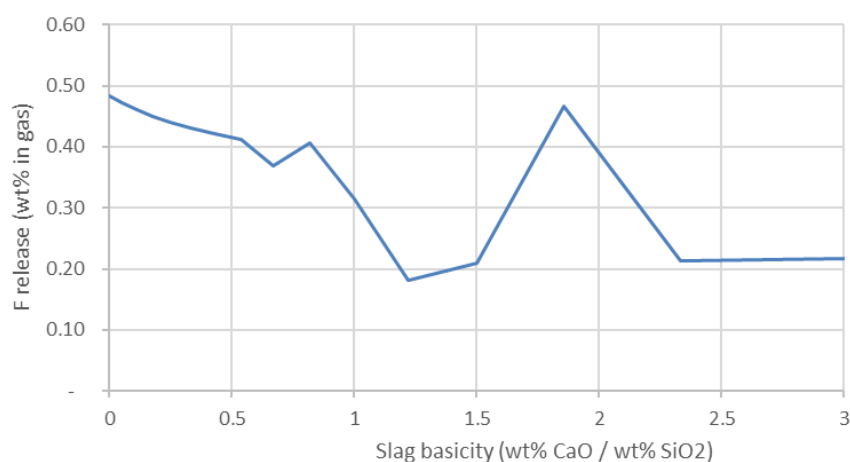


Figure 3: Fluorine content in moist air in contact with CaO-SiO₂ slag, as function of basicity

At high temperatures, fluorides dissolve in the slag. As lime is present in many slag systems, fluorine can typically be assumed to be present as CaF_2 . The activity of CaF_2 and CaO depends on the composition of the slag, and this influences the fluorine release, as shown in Figure 3. However, moisture and fluorine mineralogy during heat-up have a much larger influence and may need attention before optimising the slag composition. Figure 4 shows how the vapour pressure of CaF_2 depends on the composition in a ternary system. In general, a liquid slag with a high lime activity is beneficial for lowering F volatilisation.

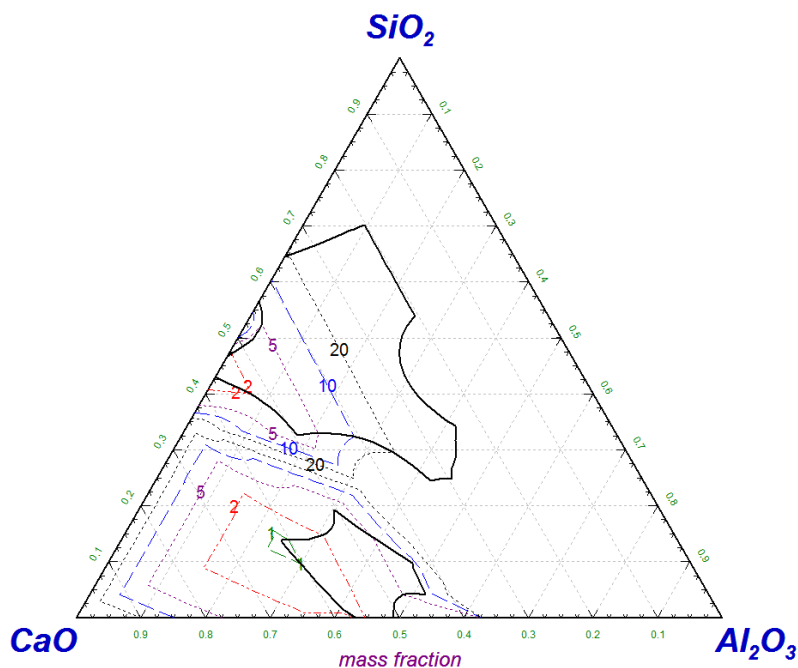


Figure 4: CaF_2 vapour pressure map (ppm) content of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ slag

Conclusions

In this work, the release of HF from metallurgical processes and slags is investigated from a thermodynamic viewpoint. Calculations show that contact with moisture is of the utmost importance, as well as the phase in which F is present. Slag composition is of relevance, mainly due to the ability to capture fluorine in stable fluorides.

References

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