# Fluorochemicals from Fluorspar via a Mechanochemical Process Bypassing HF

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## **1.** Fluorochemical Industry

Fluorochemicals are important molecules used in our everyday lives. For centuries, the first step in accessing all fluorochemicals has been the energy intensive conversion of fluorspar (CaF<sub>2</sub>) to highly toxic and corrosive hydrogen fluoride (HF) gas. A paradigm shift would be to access essential fluorochemicals directly from fluorspar by passing HF, in a way that is cheaper, safer and greener. Our aim was to find a solution to this long-standing challenge.



**2.** Method: Mechanochemical Activation of CaF<sub>2</sub>

1 CaF<sub>2</sub> is insoluble in water and all organic solvents. **Mechanochemistry** (e.g. ball milling) can be used to harness reactivity of insoluble salts.

Inspired by **biomineralization** (e.g. bone formation), where **Ca<sup>2+</sup>** ions form strong bonds with phosphate ions  $(PO_4^{3-})$ , we sought to replace fluoride (F-) ions in CaF<sub>2</sub> for **PO<sub>4</sub><sup>3-</sup>** to release fluoride.

> $CaF_2 + K_2HPO_4$ ball milling

biomineral in teeth & bones  $CaHPO_4$  - calcium hydrogen phosphate

 $Ca_5(PO_4)_3OH$  - apatite

highly stable salt

Griding acidspar (>97%  $CaF_2$ ) with 3 dipotassium phosphate (K<sub>2</sub>HPO<sub>4</sub>) salt in a ball mill enables **F<sup>-</sup> release** from CaF<sub>2</sub>, **increasing its solubility**.

**F**<sup>-</sup> **release** + Ca<sup>2+</sup> **phosphate** by-product (e.g. CaHPO<sub>4</sub>)

The resultant powder is a **new**, **easy to handle** used to make fluorochemicals in a manner that **Fluoromix**<sup>™</sup>

#### 3. New Fluorinating Species

**Powder X-ray diffraction** was used to elucidate the composition of **Fluoromix**<sup>TM</sup>, which contains CaF, and 2 new crystalline salts **X** and Y.



**X** is  $K_3(HPO_4)F$ , independently prepared by ball milling  $KF + K_2HPO_4$ . Y is  $K_{2-x}Ca_{v}(PO_{3}F)_{a}(PO_{4})_{b}$  prepared by ball milling X + CaHPO<sub>4</sub>. Both X and Y possess fluorinating ability and are in Fluoromix<sup>TM</sup>.

## **4.** Fluorochemicals from **Fluoromix**<sup>™</sup>

Fluoromix<sup>™</sup> successfully installs F atoms into

fluorinating reagent (**Fluoromix**<sup>™</sup>) that can be

completely **bypasses HF production**.



(Hetero)fluoroarenes

organic molecules by halogen exchange. It was used to synthesize a variety of fluorochemicals with **S-F and C-F bonds** including:

- Widely used **fluorinating reagents** •
- Fluorochemicals used to make **drugs and** agrochemicals
- Industrially relevant **chemical building blocks** ullet

# **Conclusions & Outlook**

Mechanochemical activation of acidspar (>97% CaF<sub>2</sub>) with  $K_2HPO_4$  affords a fluorinating reagent (Fluoromix<sup>™</sup>) for the construction of S-F and C-F bonds without the requirement of HF. Complementary approaches to accessing fluorine content from waste fluorochemicals will form the focus of future work towards developing **circular solutions** to fluorine chemistry with **global challenges in mind**.



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