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(54) Title: PREPARATION OF FLUOROCHEMICALS

(57) Abstract: Processes for the preparation of fluorochemicals are described, in which a fluoride source is pulverised together with an activator and optionally a sequestrant. Fluorochemicals resulting from the processes are also described.

PREPARATION OF FLUOROCHEMICALS

INTRODUCTION

[0001] The present invention relates to processes for preparing fluorochemicals, as well as to the fluorochemicals resulting therefrom. The processes of the invention can avoid the need to use hydrofluoric acid as an intermediate for fluorochemical production.

BACKGROUND OF THE INVENTION

[0002] Fluorochemicals are present in our daily life with applications in the metallurgical industry, Li-ion batteries, electrical appliances, luminescent nanoparticles and electronics, fluoropolymers (PTFE known as Teflon or ETFE), refrigerants (HFOs), air conditioning, as well as agrochemicals, anesthetics, and pharmaceuticals. Often, fluorine atoms incorporated in organic fluorochemicals are derived from the naturally occurring mineral fluorspar (calcium fluoride, CaF_2) by applying a workflow commencing with its conversion into highly toxic hydrogen fluoride (HF). Specifically, metallurgical grade fluorspar (Metspar, 60-96% CaF_2, ~ 40% of total fluorspar production) can be employed as a flux in steelmaking, while acid grade fluorspar (Acidspar, ≥97% CaF_2, ~ 60% of total fluorspar production), can be used in the manufacture of hydrofluoric acid (HF) and/or aluminium trifluoride (AlF_3).

[0003] Industrial practice for the manufacture of organic fluorochemicals can rely upon energy-intensive treatment of acid grade calcium fluoride (Acidspar) with sulfuric acid at elevated temperatures to generate hydrogen fluoride gas which can either be stored for use as liquified gas, or diluted in water for use as an aqueous solution. Safety of HF-based processes can be a concern of both producers and users, for example, due to HF being a highly dangerous and corrosive acid which requires extreme caution for safe handling.

[0004] Developing alternative routes for accessing value-added fluorochemicals can be extremely challenging, e.g., due to the high lattice energy of CaF_2 (~2640 $kJ \cdot mol^{-1}$, or ~1320 $kJ \cdot mol^{-1}$ for each mole of fluoride generated).

[0005] The present invention was devised with the foregoing in mind.

SUMMARY OF THE INVENTION

[0006] According to a first aspect of the present invention there is provided a process for the preparation of a fluorochemical, the process comprising the step of:

pulverising together a fluoride source, an activator and a sequestrant,
wherein the fluoride source is at least one selected from CaF_2, SrF_2 and BaF_2, the activator is at least one selected from NaOH, Na_2O, Na_2O_2 and NaO_2, and the sequestrant is at least one selected from TiO_2, MoO_3, WO_3, Pb_3O_4 and PbO_2.

[0007] According to a second aspect of the present invention there is provided a pulverised mixture obtained, directly obtained or obtainable by the process of the first aspect of the invention.

[0008] According to a third aspect of the present invention there is provided a mixture comprising: sodium fluoride or a sodium metallate fluoride, and a mixed metal oxide.

[0009] According to a fourth aspect of the present invention there is provided a process for the preparation of a fluorochemical, the process comprising the step of:
pulverising together a fluoride source and an activator,
wherein the fluoride source is at least one selected from CaF_2, SrF_2, BaF_2 and MgF_2, and the activator is Na_2S.

[0010] According to a fifth aspect of the present invention there is provided a pulverised mixture obtained, directly obtained or obtainable by the process of the fourth aspect of the invention.

[0011] According to a sixth aspect of the present invention there is provided a mixture comprising: sodium fluoride, and a sulphide of Ca, Sr, Ba or Mg.

[0012] According to a seventh aspect of the present invention there is provided a process for the preparation of a fluorochemical, the process comprising the step of:
pulverising together a fluoride source and an activator,
wherein the fluoride source is at least one selected from CaF_2, SrF_2, BaF_2 and MgF_2, and the activator is at least one selected from LiOH, Li_2O, Li_2O_2, LiO_2, NaOH, Na_2O, Na_2O_2, NaO_2, KOH, K_2O_2, KO_2, CsOH (including $CsOH{\cdot}H_2O$), Cs_2O, Cs_2O_2, Cs_2O_3, CsO_2 and CsO_3.

[0013] According to an eighth aspect of the present invention there is provided a pulverised mixture obtained, directly obtained or obtainable by the process of the seventh aspect of the invention.

[0014] According to a ninth aspect of the present invention there is provided a mixture comprising: a metal fluoride, wherein the metal is lithium, sodium, potassium or caesium; and an oxide or hydroxide of Ca, Sr, Ba or Mg.

[0015] According to a tenth aspect of the present invention there is provided a process for the preparation of a fluorochemical, the process comprising the step of:
pulverising together a fluoride source and an activator,

wherein the fluoride source is MgF_2, and the activator is at least one selected NaOH, Na_2O, Na_2O_2 and NaO_2.

[0016] According to an eleventh aspect of the present invention there is provided a pulverised mixture obtained, directly obtained or obtainable by the process of the tenth aspect of the invention.

[0017] According to a twelfth aspect of the present invention there is provided a mixture comprising: sodium fluoride and at least one of MgO and $Mg(OH)_2$.

[0018] CaF_2 and MgF_2 are particularly suitable fluoride sources. The CaF_2 may be in its naturally occurring form (i.e., fluorspar) or may be a synthetic, industrially produced material having fewer impurities (e.g., acidspar or metspar). Alternatively, the CaF_2 may be present within a waste product (e.g., the CaF_2 may be CaF_2 sludge) or may have been obtained (e.g., purified) from such a waste product. The MgF_2 may be derived from waste fluorochemicals.

DETAILED DESCRIPTION OF THE INVENTION

[0019] Throughout the entirety of the description and claims of this specification, where subject matter is described herein using the term “comprise” (or “comprises” or “comprising”), the same subject matter instead described using the term “consist of” (or “consists of” or “consisting of”) or “consist essentially of” (or “consists essentially of” or “consisting essentially of”) is also contemplated.

[0020] Throughout the description and claims of this specification, the singular encompasses the plural unless the context otherwise requires. In particular, where the indefinite article is used, the specification is to be understood as contemplating plurality as well as singularity, unless the context requires otherwise.

[0021] Features described in conjunction with a particular aspect, embodiment or example of the invention are to be understood to be applicable to any other aspect, embodiment or example described herein unless incompatible therewith. All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive. The invention is not restricted to the details of any of the specific embodiments recited herein. The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

[0022] Unless otherwise specified, where the quantity or concentration of a particular component of a given product is specified as a weight percentage (wt.% or %w/w), said weight percentage refers to the percentage of said component by weight relative to the total weight of the product as a whole. It will be understood by those skilled in the art that the sum of weight percentages of all components of a product will total 100 wt.%. However, where not all components are listed (e.g. where a product is said to "comprise" one or more particular components), the weight percentage balance may optionally be made up to 100 wt.% by unspecified ingredients.

[0023] As described hereinbefore, in a first aspect the present invention provides a process for the preparation of a fluorochemical, the process comprising the step of:
pulverising together a fluoride source, an activator and a sequestrant,
wherein the fluoride source is at least one selected from CaF_2, SrF_2 and BaF_2, the activator is at least one selected from NaOH, Na_2O, Na_2O_2 and NaO_2, and the sequestrant is at least one selected from TiO_2, MoO_3, WO_3, Pb_3O_4 and PbO_2.

[0024] Through rigorous investigations, the inventors have arrived at a solution to the long-standing problem described hereinbefore by devising a process that allows fluoride sources, such as calcium fluoride and others, to be directly converted into fluorochemicals without the need for converting them into HF using sulfuric acid. This is achieved by reacting the fluoride source with an activator and a sequestrant according to the conditions described herein (e.g. ball milling, or other mechanochemical technique). The process of the invention therefore allows for the preparation of value-added fluorochemicals using more environmentally-friendly and sustainable techniques.

[0025] The process of the invention involves reacting the fluoride source with the other recited reactants using a high-energy mixing technique, such as one that is sufficient to mechanically reduce the particle size of (e.g. crush) the reactants and bring them into contact with one another in such a manner that causes a chemical reaction to occur, thereby changing their chemical composition. Pulverising together the reactants achieves this objective. It will, however, be appreciated that synonymous high-energy mixing techniques resulting in a chemical reaction between the reactants and a reduction in their particle size (and/or an increased surface area to volume ratio of the reactants), such as crushing together, grinding together, milling together, mashing together, macerating together and the like, are embraced by the invention. It will be understood that the fluoride source, activator and sequestrant may be pulverised together in any order. For example, all three components may be pulverised together simultaneously. Alternatively, two components (e.g., the fluoride source and the activator) may be pulverised

together, to which is then added the third component (e.g., the sequestrant) with further pulverising.

[0026] The process may be a mechanochemical process and/or the pulverising step may be conducted under mechanochemical conditions. Mechanochemistry is a developing area of chemical synthesis and is widely understood to refer to chemical transformations that are initiated by and/or sustained by the application of a mechanical stress to one or more solid reactants.

[0027] The pulverising step may be conducted in a ball mill, a pestle and mortar or a twin-screw extruder (TSE). Other techniques and apparatuses suitable for carrying out the pulverising step will be familiar to one skilled in the art, e.g., those skilled in the art of mechanochemistry, including an ultrasonic bath, a mechanical press, and/or resonant acoustic mixing (RAM).

[0028] In particular embodiments, the pulverising step is conducted in a ball mill. Exemplary ball mills include a planetary ball mill, a vibratory ball mill, an attritor ball mill or a tumbling ball mill. Most suitably, the ball mill is a vibratory ball mill.

[0029] The person skilled in the art of ball milling will be able to select appropriate conditions, including ball size and weight, and vessel size. For example, a stainless steel vessel and one or more stainless steel balls may be used. Alternatively, a zirconia vessel and one or more zirconia balls may be used. A ball, or balls, (each) weighing 2-20 g (e.g., 3 g, 4 g, 7 g or 16 g) may, for example, be used.

[0030] The pulverising step may be carried out for any suitable period of time. For example, the pulverising step may be carried out for 0.5 – 12 hours.

[0031] In particular embodiments, the pulverising step comprises ball milling the reactants together at a frequency of 0.5 – 80 Hz. More suitably, the pulverising step comprises ball milling the reactants together at a frequency of 5 – 65 Hz. Even more suitably, the pulverising step comprises ball milling the reactants together at a frequency of 15 – 45 Hz. Most suitably, the pulverising step comprises ball milling the reactants together at a frequency of 20 – 40 Hz (e.g., 28 – 38 Hz).

[0032] In its simplest sense, the pulverising step is conducted in the absence (or substantial absence) of any solvent. However, the use of some solvent is known to offer advantages in some solid state (e.g. mechanochemical) reactions. Examples of such techniques include solvent-assisted mechanochemistry (sometimes termed liquid-assisted mechanochemistry, e.g. liquid-assisted grinding). Suitably, the pulverising step is conducted in less than 500 wt% of a solvent relative to the combined mass of the reactants. Thus, if 1 g each of the fluoride source, the activator and the sequestrant are used, the pulverising step may be conducted in less than 15 g of solvent. More suitably, the pulverising step is conducted in less than 200 wt% of a solvent

relative to the combined mass of the reactants. Even more suitably, the pulverising step is conducted in less than 50 wt% of a solvent relative to the combined mass of the reactants. Yet more suitably, the pulverising step is conducted in less than 10 wt% of a solvent relative to the combined mass of the reactants. Most suitably, the pulverising step is conducted in the absence (or substantial absence) of any solvent. The pulverising step may therefore be described as being conducted in the solid state.

[0033] The fluoride source may be at least one selected from the group consisting of CaF_2, SrF_2 and BaF_2. The fluoride source is most suitably CaF_2 (e.g., fluorspar, metspar or acidspar, of which acidspar is typically used).

[0034] The activator is suitably NaOH or Na_2O. Most suitably, the activator is Na_2O.

[0035] Without wishing to be bound by theory, it is believed that the sequestrant promotes the formation of the fluorochemical by sequestering the alkaline earth metal species that is formed when the fluoride source reacts with the activator. Therefore, during the pulverising step, the sequestrant may sequester the alkaline earth metal of the fluoride source. The sequestrant is most suitably TiO_2.

[0036] In particular embodiments, the fluoride source is CaF_2, the activator is NaOH or Na_2O, and the sequestrant is TiO_2.

[0037] The pulverising step results in the formation of at least one fluorochemical. As used herein, the term fluorochemical denotes a fluorine-containing compound that is not the fluoride source. In the context of the first aspect of the invention, the fluorochemical is suitably at least one of sodium fluoride and a sodium metallate fluoride. It will be understood that the precise nature of the fluorochemical will depend on the particular sequestrant(s) used. When TiO_2, Pb_3O_4 or PbO_2 is used as a sequestrant, sodium fluoride is typically formed as a fluorochemical. When MoO_3 or WO_3 is used as a sequestrant, a sodium metallate fluoride (e.g., sodium tungstate fluoride or sodium molybdate fluoride) is typically formed as a fluorochemical. The aforementioned fluorochemicals may have a variety of industrial uses. For example, sodium fluoride can be used as a fluorinating reagent in organic synthesis.

[0038] The pulverising step may result in the formation of a pulverised mixture. The pulverised mixture may comprise the fluorochemical and a mixed metal oxide. The mixed metal oxide is typically insoluble in solvents that dissolve the fluorochemical, thereby allowing the latter to be readily purified, if required, by solvent extraction and/or filtration. The mixed metal oxide typically comprises a first metal, M^1, derived from the fluoride source (i.e., Ca, Sr or Ba) and a second metal, M^2, derived from the sequestrant (i.e., Ti, Mo, W or Pb).

[0039] When TiO_2 is used as a sequestrant, a mixed metal oxide of formula M^1TiO_3 is typically formed. When MoO_3 or WO_3 is used as sequestrant, a mixed metal oxide of formula $M^1M^2O_4$ is typically formed. When PbO_2 or Pb_3O_4 is used as sequestrant, a mixed metal oxide of formula $M^1{}_2PbO_4$ is typically formed.

[0040] The pulverised mixture may further comprise a residual quantity of (unreacted) fluoride source, activator and/or sequestrant.

[0041] In particular embodiments, the fluoride source is CaF_2, the sequestrant is TiO_2, the fluorochemical is sodium fluoride and the mixed metal oxide is $CaTiO_3$.

[0042] In some instances, the pulverising step is conducted in the absence of aluminium oxide. Suitably, the pulverising step is conducted in the absence of any aluminium-containing species.

[0043] The pulverising step (and optionally any other steps forming the process) may be conducted at low temperature, for example at a temperature lower than 300°C, more suitably lower than 250°C, and even more suitably lower than 200°C. In many instances, the pulverising step (and optionally any other steps forming the process) may be conducted at a temperature lower than 100°C.

[0044] The process of the invention allows for the formation of a fluorochemical without the need for strong mineral acids (e.g. HF, HCl and H_2SO_4), which would typically be used to leach fluoride, thereby forming HF. Therefore, in some instances, the pulverising step (and optionally any other steps forming the process) may be conducted in the absence of a mineral acid. In some instances, HF is not formed during the pulverising step (optionally nor is it formed during any other steps forming the process).

[0045] As described hereinbefore, in a second aspect the present invention provides a pulverised mixture obtained, directly obtained or obtainable by the process of the first aspect of the invention.

[0046] As described hereinbefore, in a third aspect the present invention provides a mixture comprising: sodium fluoride or a sodium metallate fluoride, and a mixed metal oxide. It will be appreciated that the sodium metallate fluoride and the mixed metal oxide may have any of those definitions discussed hereinbefore in relation to the first aspect of the invention.

[0047] The mixture may further comprise at least one of a fluoride source and a sequestrant. It will be appreciated that the fluoride source and the sequestrant may have any of those definitions discussed hereinbefore in relation to the first aspect of the invention.

[0048] The mixture is suitably a solid mixture (e.g., comprising particles of the sodium fluoride or sodium metallate fluoride, the mixed metal oxide, and of any fluoride source or sequestrant present).

[0049] In particular embodiments, the mixture comprises sodium fluoride, $CaTiO_3$, and optionally at least one of CaF_2 and TiO_2.

[0050] As described hereinbefore, in a fourth aspect the present invention provides a process for the preparation of a fluorochemical, the process comprising the step of:
pulverising together a fluoride source and an activator,
wherein the fluoride source is at least one selected from CaF_2, SrF_2, BaF_2 and MgF_2, and the activator is Na_2S.

[0051] Through rigorous investigations, the inventors have arrived at a solution to the long-standing problem described hereinbefore by devising a process that allows fluoride sources, such as calcium fluoride and others, to be directly converted into fluorochemicals without the need for converting them into HF using sulfuric acid. This is achieved by reacting the fluoride source with an activator according to the conditions described herein (e.g. ball milling, or other mechanochemical technique). The process of the invention therefore allows for the preparation of value-added fluorochemicals using more environmentally-friendly and sustainable techniques.

[0052] The process of the invention involves reacting the fluoride source with the other recited reactants using a high-energy mixing technique, such as one that is sufficient to mechanically reduce the particle size of (e.g. crush) the reactants and bring them into contact with one another in such a manner that causes a chemical reaction to occur, thereby changing their chemical composition. Pulverising together the reactants achieves this objective. It will, however, be appreciated that synonymous high-energy mixing techniques resulting in a chemical reaction between the reactants and a reduction in their particle size (and/or an increased surface area to volume ratio of the reactants), such as crushing together, grinding together, milling together, mashing together, macerating together and the like, are embraced by the invention.

[0053] The process may be a mechanochemical process and/or the pulverising step may be conducted under mechanochemical conditions. Mechanochemistry is a developing area of chemical synthesis and is widely understood to refer to chemical transformations that are initiated by and/or sustained by the application of a mechanical stress to one or more solid reactants.

[0054] The pulverising step may be conducted in a ball mill, a pestle and mortar or a twin-screw extruder (TSE). Other techniques and apparatuses suitable for carrying out the pulverising step will be familiar to one skilled in the art, e.g. those skilled in the art of mechanochemistry, including an ultrasonic bath, a mechanical press and/or resonant acoustic mixing (RAM).

[0055] In particular embodiments, the pulverising step is conducted in a ball mill. Exemplary ball mills include a planetary ball mill, a vibratory ball mill, an attritor ball mill or a tumbling ball mill. Most suitably, the ball mill is a vibratory ball mill.

[0056] The person skilled in the art of ball milling will be able to select appropriate conditions, including ball size and weight, and vessel size. For example, a stainless steel vessel and one or more stainless steel balls may be used. Alternatively, a zirconia vessel and one or more zirconia balls may be used. A ball, or balls, (each) weighing 2-20 g (e.g., 3 g, 4 g, 7 g or 16 g) may, for example, be used.

[0057] The pulverising step may be carried out for any suitable period of time. For example, the pulverising step may be carried out for 0.5 – 12 hours.

[0058] In particular embodiments, the pulverising step comprises ball milling the reactants together at a frequency of 0.5 – 80 Hz. More suitably, the pulverising step comprises ball milling the reactants together at a frequency of 5 – 65 Hz. Even more suitably, the pulverising step comprises ball milling the reactants together at a frequency of 15 – 45 Hz. Most suitably, the pulverising step comprises ball milling the reactants together at a frequency of 20 – 40 Hz (e.g., 28 – 38 Hz).

[0059] In its simplest sense, the pulverising step is conducted in the absence (or substantial absence) of any solvent. However, the use of some solvent is known to offer advantages in some solid state (e.g. mechanochemical) reactions. Examples of such techniques include solvent-assisted mechanochemistry (sometimes termed liquid-assisted mechanochemistry, e.g. liquid-assisted grinding). Suitably, the pulverising step is conducted in less than 500 wt% of a solvent relative to the combined mass of the reactants. Thus, if 1 g each of the fluoride source and the activator are used, the pulverising step may be conducted in less than 10 g of solvent. More suitably, the pulverising step is conducted in less than 200 wt% of a solvent relative to the combined mass of the reactants. Even more suitably, the pulverising step is conducted in less than 50 wt% of a solvent relative to the combined mass of the reactants. Yet more suitably, the pulverising step is conducted in less than 10 wt% of a solvent relative to the combined mass of the reactants. Most suitably, the pulverising step is conducted in the absence (or substantial absence) of any solvent. The pulverising step may therefore be described as being conducted in the solid state.

[0060] The fluoride source may be at least one selected from the group consisting of CaF_2, SrF_2, BaF_2 and MgF_2. The fluoride source is most suitably CaF_2 (e.g., fluorspar, metspar or acidspar, of which acidspar is typically used).

[0061] A sequestrant may be pulverised together with the fluoride source and the activator, wherein the sequestrant is at least one selected from TiO_2, MoO_3, WO_3, Pb_3O_4 and PbO_2. When

used, the sequestrant is suitably TiO_2. The sequestrant may promote the formation of the fluorochemical by sequestering the alkaline earth metal species that is formed when the fluoride source reacts with the activator. Therefore, during the pulverising step, the sequestrant may sequester the alkaline earth metal of the fluoride source. It will be understood that the fluoride source, activator and sequestrant may be pulverised together in any order. For example, all three components may be pulverised together simultaneously. Alternatively, two components (e.g., the fluoride source and the activator) may be pulverised together, to which is then added the third component (e.g., the sequestrant) with further pulverising.

[0062] The pulverising step results in the formation of at least one fluorochemical. In the context of the fourth aspect of the invention, the fluorochemical is suitably sodium fluoride. Sodium fluoride has a variety of industrial uses. For example, sodium fluoride can be used as a fluorinating reagent in organic synthesis.

[0063] The pulverising step may result in the formation of a pulverised mixture. The pulverised mixture may comprise the fluorochemical and a sulphide of a metal, M^1 derived from the fluoride source (i.e., Ca, Sr, Ba or Mg). The sulphide of metal, M^1 is typically insoluble in solvents that dissolve the fluorochemical, thereby allowing the latter to be readily purified, if required, by solvent extraction and/or filtration.

[0064] The pulverised mixture may further comprise a residual quantity of (unreacted) fluoride source, activator and/or sequestrant.

[0065] In particular embodiments, the fluoride source is CaF_2, the fluorochemical is sodium fluoride and the sulphide of metal, M^1 is CaS.

[0066] In some instances, the pulverising step is conducted in the absence of aluminium oxide. Suitably, the pulverising step is conducted in the absence of any aluminium-containing species.

[0067] The pulverising step (and optionally any other steps forming the process) may be conducted at low temperature, for example at a temperature lower than 300°C, more suitably lower than 250°C, and even more suitably lower than 200°C. In many instances, the pulverising step (and optionally any other steps forming the process) may be conducted at a temperature lower than 100°C.

[0068] The process of the invention allows for the formation of a fluorochemical without the need for strong mineral acids (e.g. HF, HCl and H_2SO_4), which would typically be used to leach fluoride, thereby forming HF. Therefore, in some instances, the pulverising step (and optionally any other steps forming the process) may be conducted in the absence of a mineral acid. In some instances, HF is not formed during the pulverising step (optionally nor is it formed during any other steps forming the process).

[0069] As described hereinbefore, in a fifth aspect the present invention provides a pulverised mixture obtained, directly obtained or obtainable by the process of the fourth aspect of the invention.

[0070] As described hereinbefore, in a sixth aspect the present invention provides a mixture comprising: sodium fluoride and a sulphide of Ca, Sr, Ba or Mg.

[0071] The mixture may further comprise at least one of a fluoride source and an activator. It will be appreciated that the fluoride source and the activator may have any of those definitions discussed hereinbefore in relation to the fourth aspect of the invention.

[0072] The mixture is suitably a solid mixture (e.g., comprising particles of the sodium fluoride, the sulphide of Ca, Sr, Ba or Mg, and of any fluoride source or activator present).

[0073] In particular embodiments, the mixture comprises sodium fluoride, CaS, and optionally at least one of CaF_2 and Na_2S.

[0074] As described hereinbefore, in a seventh aspect the present invention provides a process for the preparation of a fluorochemical, the process comprising the step of:
pulverising together a fluoride source and an activator,
wherein the fluoride source is at least one selected from CaF_2, SrF_2, BaF_2 and MgF_2, and the activator is at least one selected from LiOH, Li_2O, Li_2O_2, LiO_2, NaOH, Na_2O, Na_2O_2, NaO_2, KOH, K_2O_2, KO_2, CsOH (including $CsOH{\cdot}H_2O$), Cs_2O, Cs_2O_2, Cs_2O_3, CsO_2 and CsO_3.

[0075] Through rigorous investigations, the inventors have arrived at a solution to the long-standing problem described hereinbefore by devising a process that allows fluoride sources, such as calcium fluoride and others, to be directly converted into fluorochemicals without the need for converting them into HF using sulfuric acid. This is achieved by reacting the fluoride source with an activator according to the conditions described herein (e.g. ball milling, or other mechanochemical technique). The process of the invention therefore allows for the preparation of value-added fluorochemicals using more environmentally-friendly and sustainable techniques.

[0076] The process of the invention involves reacting the fluoride source with the other recited reactants using a high-energy mixing technique, such as one that is sufficient to mechanically reduce the particle size of (e.g. crush) the reactants and bring them into contact with one another in such a manner that causes a chemical reaction to occur, thereby changing their chemical composition. Pulverising together the reactants achieves this objective. It will, however, be appreciated that synonymous high-energy mixing techniques resulting in a chemical reaction between the reactants and a reduction in their particle size (and/or an increased surface area to

volume ratio of the reactants), such as crushing together, grinding together, milling together, mashing together, macerating together and the like, are embraced by the invention.

[0077] The process may be a mechanochemical process and/or the pulverising step may be conducted under mechanochemical conditions. Mechanochemistry is a developing area of chemical synthesis and is widely understood to refer to chemical transformations that are initiated by and/or sustained by the application of a mechanical stress to one or more solid reactants.

[0078] The pulverising step may be conducted in a ball mill, a pestle and mortar or a twin-screw extruder (TSE). Other techniques and apparatuses suitable for carrying out the pulverising step will be familiar to one skilled in the art, e.g. those skilled in the art of mechanochemistry, including an ultrasonic bath, a mechanical press and/or resonant acoustic mixing (RAM).

[0079] In particular embodiments, the pulverising step is conducted in a ball mill. Exemplary ball mills include a planetary ball mill, a vibratory ball mill, an attritor ball mill or a tumbling ball mill. Most suitably, the ball mill is a vibratory ball mill.

[0080] The person skilled in the art of ball milling will be able to select appropriate conditions, including ball size and weight, and vessel size. For example, a stainless steel vessel and one or more stainless steel balls may be used. Alternatively, a zirconia vessel and one or more zirconia balls may be used. A ball, or balls, (each) weighing 2-20 g (e.g., 3 g, 4 g, 7 g or 16 g) may, for example, be used.

[0081] The pulverising step may be carried out for any suitable period of time. For example, the pulverising step may be carried out for 0.5 – 12 hours.

[0082] In particular embodiments, the pulverising step comprises ball milling the reactants together at a frequency of 0.5 – 80 Hz. More suitably, the pulverising step comprises ball milling the reactants together at a frequency of 5 – 65 Hz. Even more suitably, the pulverising step comprises ball milling the reactants together at a frequency of 15 – 45 Hz. Most suitably, the pulverising step comprises ball milling the reactants together at a frequency of 20 – 40 Hz (e.g., 28 – 38 Hz).

[0083] In its simplest sense, the pulverising step is conducted in the absence (or substantial absence) of any solvent. However, the use of some solvent is known to offer advantages in some solid state (e.g. mechanochemical) reactions. Examples of such techniques include solvent-assisted mechanochemistry (sometimes termed liquid-assisted mechanochemistry, e.g. liquid-assisted grinding). Suitably, the pulverising step is conducted in less than 500 wt% of a solvent relative to the combined mass of the reactants. Thus, if 1 g each of the fluoride source and the activator are used, the pulverising step may be conducted in less than 10 g of solvent. More suitably, the pulverising step is conducted in less than 200 wt% of a solvent relative to the

combined mass of the reactants. Even more suitably, the pulverising step is conducted in less than 50 wt% of a solvent relative to the combined mass of the reactants. Yet more suitably, the pulverising step is conducted in less than 10 wt% of a solvent relative to the combined mass of the reactants. Most suitably, the pulverising step is conducted in the absence (or substantial absence) of any solvent. The pulverising step may therefore be described as being conducted in the solid state.

[0084] The activator may be at least one selected from LiOH, Li_2O, Li_2O_2 and LiO_2. For example, the activator may be LiOH or Li_2O. A sequestrant (e.g. TiO_2) may be used, as described below.

[0085] The activator may be at least one selected from NaOH, Na_2O, Na_2O_2 and NaO_2. For example, the activator may be NaOH or Na_2O. A sequestrant (e.g. TiO_2) may be used, as described below.

[0086] The activator may be at least one selected from KOH, K_2O_2 and KO_2. For example, the activator may be KOH. A sequestrant (e.g. TiO_2) may be used, as described below.

[0087] The activator may be at least one selected from CsOH (including hydrated forms), Cs_2O, Cs_2O_2, Cs_2O_3, CsO_2 and CsO_3. For example, the activator may be $CsOH{\cdot}H_2O$. A sequestrant (e.g. TiO_2) may be used, as described below.

[0088] The activator is suitably NaOH, Na_2O, KOH, CsOH (including $CsOH{\cdot}H_2O$), LiOH or Li_2O. A sequestrant (e.g. TiO_2) may be used, as described below.

[0089] The fluoride source may be at least one selected from the group consisting of CaF_2, SrF_2, BaF_2 and MgF_2. The fluoride source is most suitably CaF_2 (e.g., fluorspar, metspar or acidspar, of which acidspar is typically used).

[0090] In some instances, when the activator is KOH or NaOH, the fluoride source is not CaF_2.

[0091] A sequestrant may be pulverised together with the fluoride source and the activator, wherein the sequestrant is at least one selected from TiO_2, MoO_3, WO_3, Pb_3O_4 and PbO_2. When used, the sequestrant is suitably TiO_2. The sequestrant may promote the formation of the fluorochemical by sequestering the alkaline earth metal species that is formed when the fluoride source reacts with the activator. Therefore, during the pulverising step, the sequestrant may sequester the alkaline earth metal of the fluoride source. It will be understood that the fluoride source, activator and sequestrant may be pulverised together in any order. For example, all three components may be pulverised together simultaneously. Alternatively, two components (e.g., the fluoride source and the activator) may be pulverised together, to which is then added the third component (e.g., the sequestrant) with further pulverising.

[0092] The pulverising step results in the formation of at least one fluorochemical. In the context of the seventh aspect of the invention, and depending on the nature of the activator, the

fluorochemical is suitably lithium fluoride, sodium fluoride, potassium fluoride and/or caesium fluoride. Lithium fluoride, potassium fluoride and caesium fluoride have a variety of industrial uses. For example, lithium fluoride is widely used as a flux in the ceramic and metallurgical fields, and has applications in the battery industry. Sodium fluoride, potassium fluoride and caesium fluoride are highly versatile reagents for organic synthesis. Sodium fluoride is also useful in water fluoridation, as well as an ingredient in toothpaste. When a sequestrant is used, the fluorochemical may be at least one of an alkali metal (i.e., Li, Na, K or Cs) fluoride and an alkali metal (i.e., Li, Na, K or Cs) metallate fluoride. Examples of particular alkali metal metallate fluorides include alkali metal tungstate fluoride (which may be formed when WO_3 is used as sequestrant) or alkali metal molybdate fluoride (which may be formed when MoO_3 is used as sequestrant).

[0093] The pulverising step may result in the formation of a pulverised mixture. The pulverised mixture may comprise the fluorochemical and an oxide or hydroxide of a metal, M^1 derived from the fluoride source (i.e., Ca, Sr, Ba or Mg). The oxide or hydroxide of metal, M^1 typically has a different solubility profile to the fluorochemical, thereby allowing the latter to be readily purified, if required, by solvent extraction and/or filtration.

[0094] The pulverised mixture may further comprise a residual quantity of (unreacted) fluoride source, activator and/or sequestrant.

[0095] In particular embodiments, the fluoride source is CaF_2, the fluorochemical is lithium fluoride and the oxide or hydroxide of metal, M^1 is CaO or $Ca(OH)_2$.

[0096] In particular embodiments, the fluoride source is CaF_2, the fluorochemical is sodium fluoride and the oxide or hydroxide of metal, M^1 is CaO or $Ca(OH)_2$.

[0097] In particular embodiments, the fluoride source is CaF_2, the fluorochemical is potassium fluoride and the oxide or hydroxide of metal, M^1 is CaO or $Ca(OH)_2$.

[0098] In particular embodiments, the fluoride source is CaF_2, the fluorochemical is caesium fluoride and the oxide or hydroxide of metal, M^1 is CaO or $Ca(OH)_2$.

[0099] In some instances, the pulverising step is conducted in the absence of aluminium oxide. Suitably, the pulverising step is conducted in the absence of any aluminium-containing species.

[00100] The pulverising step (and optionally any other steps forming the process) may be conducted at low temperature, for example at a temperature lower than 300°C, more suitably lower than 250°C, and even more suitably lower than 200°C. In many instances, the pulverising step (and optionally any other steps forming the process) may be conducted at a temperature lower than 100°C.

[00101] The process of the invention allows for the formation of a fluorochemical without the need for strong mineral acids (e.g. HF, HCl and H_2SO_4), which would typically be used to leach fluoride, thereby forming HF. Therefore, in some instances, the pulverising step (and optionally any other steps forming the process) may be conducted in the absence of a mineral acid. In some instances, HF is not formed during the pulverising step (optionally nor is it formed during any other steps forming the process).

[00102] As described hereinbefore, in an eighth aspect the present invention provides a pulverised mixture obtained, directly obtained or obtainable by the process of the seventh aspect of the invention.

[00103] As described hereinbefore, in a nineth aspect the present invention provides a mixture comprising: at least one of lithium fluoride, sodium fluoride, potassium fluoride and caesium fluoride; and an oxide or hydroxide of Ca, Sr, Ba or Mg.

[00104] The mixture may further comprise at least one of a fluoride source and an activator. It will be appreciated that the fluoride source and the activator may have any of those definitions discussed hereinbefore in relation to the seventh aspect of the invention.

[00105] The mixture may further comprise an alkali metal (i.e., Li, Na, K or Cs) metallate fluoride, examples of which are discussed hereinbefore.

[00106] The mixture is suitably a solid mixture (e.g., comprising particles of: (i) the lithium fluoride, sodium fluoride, potassium fluoride and/or caesium fluoride; (ii) the oxide or hydroxide of Ca, Sr, Ba or Mg, and (iii) any fluoride source or activator present).

[00107] In particular embodiments, the mixture comprises lithium fluoride, at least one of CaO and $Ca(OH)_2$, and optionally at least one of CaF_2, Li_2O and LiOH. A lithium metallate fluoride may also be present.

[00108] In particular embodiments, the mixture comprises sodium fluoride, at least one of CaO and $Ca(OH)_2$, and optionally at least one of CaF_2, Na_2O and NaOH. A sodium metallate fluoride may also be present.

[00109] In particular embodiments, the mixture comprises potassium fluoride, at least one of CaO and $Ca(OH)_2$, and optionally at least one of CaF_2 and KOH. A potassium metallate fluoride may also be present.

[00110] In particular embodiments, the mixture comprises caesium fluoride, at least one of CaO and $Ca(OH)_2$, and optionally at least one of CaF_2 and CsOH (e.g., $CsOH \cdot H_2O$). A caesium metallate fluoride may also be present.

[00111] As described hereinbefore, in a tenth aspect the present invention provides a process for the preparation of a fluorochemical, the process comprising the step of:
pulverising together a fluoride source and an activator,
wherein the fluoride source is MgF_2, and the activator is at least one selected NaOH, Na_2O, Na_2O_2 and NaO_2.

[00112] Through rigorous investigations, the inventors have arrived at a solution to the long-standing problem described hereinbefore by devising a process that allows fluorochemicals to be produced from the fluoride source, magnesium fluoride without the need for converting the fluoride source into HF using sulfuric acid. This is achieved by reacting the fluoride source with an activator according to the conditions described herein (e.g. ball milling, or other mechanochemical technique). The process of the invention therefore allows for the preparation of value-added fluorochemicals using more environmentally-friendly and sustainable techniques.

[00113] The process of the invention involves reacting the fluoride source with the other recited reactants using a high-energy mixing technique, such as one that is sufficient to mechanically reduce the particle size of (e.g. crush) the reactants and bring them into contact with one another in such a manner that causes a chemical reaction to occur, thereby changing their chemical composition. Pulverising together the reactants achieves this objective. It will, however, be appreciated that synonymous high-energy mixing techniques resulting in a chemical reaction between the reactants and a reduction in their particle size (and/or an increased surface area to volume ratio of the reactants), such as crushing together, grinding together, milling together, mashing together, macerating together and the like, are embraced by the invention.

[00114] The process may be a mechanochemical process and/or the pulverising step may be conducted under mechanochemical conditions. Mechanochemistry is a developing area of chemical synthesis and is widely understood to refer to chemical transformations that are initiated by and/or sustained by the application of a mechanical stress to one or more solid reactants.

[00115] The pulverising step may be conducted in a ball mill, a pestle and mortar or a twin-screw extruder (TSE). Other techniques and apparatuses suitable for carrying out the pulverising step will be familiar to one skilled in the art, e.g. those skilled in the art of mechanochemistry, including an ultrasonic bath, a mechanical press and/or resonant acoustic mixing (RAM).

[00116] In particular embodiments, the pulverising step is conducted in a ball mill. Exemplary ball mills include a planetary ball mill, a vibratory ball mill, an attritor ball mill or a tumbling ball mill. Most suitably, the ball mill is a vibratory ball mill.

[00117] The person skilled in the art of ball milling will be able to select appropriate conditions, including ball size and weight, and vessel size. For example, a stainless steel vessel and one or more stainless steel balls may be used. Alternatively, a zirconia vessel and one or more zirconia

balls may be used. A ball, or balls, (each) weighing 2-20 g (e.g., 3 g, 4 g, 7 g or 16 g) may, for example, be used.

[00118] The pulverising step may be carried out for any suitable period of time. For example, the pulverising step may be carried out for 0.5 – 12 hours.

[00119] In particular embodiments, the pulverising step comprises ball milling the reactants together at a frequency of 0.5 – 80 Hz. More suitably, the pulverising step comprises ball milling the reactants together at a frequency of 5 – 65 Hz. Even more suitably, the pulverising step comprises ball milling the reactants together at a frequency of 15 – 45 Hz. Most suitably, the pulverising step comprises ball milling the reactants together at a frequency of 20 – 40 Hz (e.g., 28 – 38 Hz).

[00120] In its simplest sense, the pulverising step is conducted in the absence (or substantial absence) of any solvent. However, the use of some solvent is known to offer advantages in some solid state (e.g. mechanochemical) reactions. Examples of such techniques include solvent-assisted mechanochemistry (sometimes termed liquid-assisted mechanochemistry, e.g. liquid-assisted grinding). Suitably, the pulverising step is conducted in less than 500 wt% of a solvent relative to the combined mass of the reactants. Thus, if 1 g each of the fluoride source and the activator are used, the pulverising step may be conducted in less than 10 g of solvent. More suitably, the pulverising step is conducted in less than 200 wt% of a solvent relative to the combined mass of the reactants. Even more suitably, the pulverising step is conducted in less than 50 wt% of a solvent relative to the combined mass of the reactants. Yet more suitably, the pulverising step is conducted in less than 10 wt% of a solvent relative to the combined mass of the reactants. Most suitably, the pulverising step is conducted in the absence (or substantial absence) of any solvent. The pulverising step may therefore be described as being conducted in the solid state.

[00121] The activator is suitably NaOH or Na_2O. Most suitably, the activator is Na_2O.

[00122] A sequestrant may be pulverised together with the fluoride source and the activator, wherein the sequestrant is at least one selected from TiO_2, MoO_3, WO_3, Pb_3O_4 and PbO_2. When used, the sequestrant is suitably TiO_2. The sequestrant may promote the formation of the fluorochemical by sequestering the alkaline earth metal species that is formed when the fluoride source reacts with the activator. Therefore, during the pulverising step, the sequestrant may sequester the alkaline earth metal of the fluoride source. It will be understood that the fluoride source, activator and sequestrant may be pulverised together in any order. For example, all three components may be pulverised together simultaneously. Alternatively, two components (e.g., the fluoride source and the activator) may be pulverised together, to which is then added the third component (e.g., the sequestrant) with further pulverising.

[00123] The pulverising step results in the formation of at least one fluorochemical. In the context of the nineth aspect of the invention, the fluorochemical is suitably sodium fluoride. Sodium fluoride has a variety of industrial uses. For example, sodium fluoride can be used as a fluorinating reagent in organic synthesis.

[00124] The pulverising step may result in the formation of a pulverised mixture. The pulverised mixture may comprise the fluorochemical and an oxide or hydroxide of Mg. The oxide or hydroxide or Mg are typically insoluble in solvents that dissolve the fluorochemical, thereby allowing the latter to be readily purified, if required, by solvent extraction and/or filtration.

[00125] The pulverised mixture may further comprise a residual quantity of (unreacted) fluoride source, activator and/or sequestrant.

[00126] In particular embodiments, the activator is Na_2O, the fluorochemical is sodium fluoride and the oxide or hydroxide of Mg is MgO or $Mg(OH)_2$ (e.g., MgO).

[00127] In some instances, the pulverising step is conducted in the absence of aluminium oxide. Suitably, the pulverising step is conducted in the absence of any aluminium-containing species.

[00128] The pulverising step (and optionally any other steps forming the process) may be conducted at low temperature, for example at a temperature lower than 300°C, more suitably lower than 250°C, and even more suitably lower than 200°C. In many instances, the pulverising step (and optionally any other steps forming the process) may be conducted at a temperature lower than 100°C.

[00129] The process of the invention allows for the formation of a fluorochemical without the need for strong mineral acids (e.g. HF, HCl and H_2SO_4), which would typically be used to leach fluoride, thereby forming HF. Therefore, in some instances, the pulverising step (and optionally any other steps forming the process) may be conducted in the absence of a mineral acid. In some instances, HF is not formed during the pulverising step (optionally nor is it formed during any other steps forming the process).

[00130] As described hereinbefore, in an eleventh aspect the present invention provides a pulverised mixture obtained, directly obtained or obtainable by the process of the tenth aspect of the invention.

[00131] As described hereinbefore, in a twelfth aspect the present invention provides a mixture comprising: sodium fluoride and an oxide or hydroxide of Mg.

[00132] The mixture may further comprise at least one of a fluoride source and an activator. It will be appreciated that the fluoride source and the activator may have any of those definitions discussed hereinbefore in relation to the seventh aspect of the invention.

[00133] The mixture is suitably a solid mixture (e.g., comprising particles of the sodium fluoride, the oxide or hydroxide of Mg, and of any fluoride source or activator present).

[00134] In particular embodiments, the mixture comprises sodium fluoride, MgO, and optionally at least one of MgF_2, NaOH and Na_2O.

[00135] The following numbered statements 1 to 89 are not claims, but instead describe particular aspects and embodiments of the invention:

1. A process for the preparation of a fluorochemical, the process comprising the step of: pulverising together a fluoride source, an activator and a sequestrant,
wherein the fluoride source is at least one selected from CaF_2, SrF_2 and BaF_2, the activator is at least one selected from NaOH, Na_2O, Na_2O_2 and NaO_2, and the sequestrant is at least one selected from TiO_2, MoO_3, WO_3, Pb_3O_4 and PbO_2.

2. The process as defined in statement 1, wherein the pulverising step is conducted in the absence of a solvent.

3. The process as defined in statement 1 or 2, wherein the pulverising step is a mechanochemical reaction.

4. The process as defined in statement 1, 2 or 3, wherein the pulverising step is conducted in a ball mill, a pestle and mortar or a twin-screw extruder.

5. The process as defined in any one of the preceding statements, wherein the pulverising step is conducted in a ball mill.

6. The process as defined in any one of the preceding statements, wherein the fluoride source is CaF_2 (e.g., fluorspar).

7. The process as defined in any one of the preceding statements, wherein the activator is NaOH or Na_2O.

8. The process as defined in any one of the preceding statements, wherein the activator is Na_2O.

9. The process as defined in any one of the preceding statements, wherein the sequestrant is TiO_2.

10. The process as defined in any one of the preceding statements, wherein the fluorochemical is sodium fluoride or a sodium metallate fluoride.

11. The process as defined in statement 10, wherein the sodium metallate fluoride is sodium tungstate fluoride or sodium molybdate fluoride.

12. The process as defined in any one of the preceding statements, wherein the pulverising step results in the formation of a pulverised mixture comprising the fluorochemical, a mixed metal oxide and optionally at least one of residual fluoride source and residual sequestrant.

13. The process as defined in statement 12, where the mixed metal oxide comprises a first metal selected from Ca, Sr and Ba, and a second metal selected from Ti, Mo, W and Pb.

14. The process as defined in any one of the preceding statements, wherein the pulverising step is conducted in the absence of aluminium oxide or in the absence of any aluminium-containing species.

15. The process as defined in any one of the preceding statements, wherein the pulverising step (and optionally any other steps forming the process) is conducted at a temperature lower than 300°C.

16. The process as defined in any one of the preceding statements, wherein the pulverising step (and optionally any other steps forming the process) is conducted in the absence of a mineral acid; and/or HF is not formed during the pulverising step (optionally nor is it formed during any other steps forming the process).

17. The process as defined in any one of the preceding statements, further comprising the step of isolating the fluorochemical resulting from the pulverising step by solvent extraction and/or filtration.

18. A pulverised mixture obtained, directly obtained or obtainable by the process as defined in any one of statements 1 to 16.

19. A mixture comprising:

sodium fluoride or a sodium metallate fluoride, and
a mixed metal oxide.

20. The mixture as defined in statement 19, wherein the mixture is a solid mixture.

21. The mixture as defined in statement 19 or 20, wherein the mixed metal oxide comprises a first metal selected from Ca, Sr and Ba, and a second metal selected from Ti, Mo, W and Pb.

22. The mixture as defined in any one of statements 19, 20 or 21, wherein the mixed metal oxide is $CaTiO_3$.

23. The mixture as defined in any one of statements 19 to 22, further comprising at least one of a fluoride source and a sequestrant, wherein the fluoride source is one or more selected from CaF_2, SrF_2 and BaF_2, and the sequestrant is one or more selected from TiO_2, MoO_3, WO_3, Pb_3O_4 and PbO_2.

24. The mixture as defined in statement 23, wherein the fluoride source is CaF_2.

25. The mixture as defined in statement 23 or 24, wherein the sequestrant is TiO_2.

26. A process for the preparation of a fluorochemical, the process comprising the step of:
pulverising together a fluoride source and an activator,
wherein the fluoride source is at least one selected from CaF_2, SrF_2, BaF_2 and MgF_2, and the activator is Na_2S.

27. The process as defined in statement 26, wherein the pulverising step is conducted in the absence of a solvent.

28. The process as defined in statement 26 or 27, wherein the pulverising step is a mechanochemical reaction.

29. The process as defined in statement 26, 27 or 28, wherein the pulverising step is conducted in a ball mill, a pestle and mortar or a twin-screw extruder.

30. The process as defined in any one of statements 26 to 29, wherein the pulverising step is conducted in a ball mill.

31. The process as defined in any one of statements 26 to 30, wherein the fluoride source is CaF_2 (e.g., fluorspar).

32. The process as defined in any one of statement 26 or 31, wherein a sequestrant is pulverised together with the fluoride source and the activator, wherein the sequestrant is at least one selected from TiO_2, MoO_3, WO_3, Pb_3O_4 and PbO_2.

33. The process as defined in statement 32, wherein the sequestrant is TiO_2.

34. The process as defined in any one of statements 26 to 33, wherein the fluorochemical is sodium fluoride.

35. The process as defined in any one of statements 26 to 34, wherein the pulverising step results in the formation of a pulverised mixture comprising the fluorochemical, a sulphide of Ca, Sr, Ba or Mg, and optionally residual fluoride source.

36. The process as defined in any one of statements 26 to 35, wherein the pulverising step is conducted in the absence of aluminium oxide or in the absence of any aluminium-containing species.

37. The process as defined in any one of the statements 26 to 36, wherein the pulverising step (and optionally any other steps forming the process) is conducted at a temperature lower than 300°C.

38. The process as defined in any one of the statements 26 to 37, wherein the pulverising step (and optionally any other steps forming the process) is conducted in the absence of a mineral acid; and/or HF is not formed during the pulverising step (optionally nor is it formed during any other steps forming the process).

39. The process as defined in any one of statements 26 to 38, further comprising the step of isolating the fluorochemical resulting from the pulverising step by solvent extraction and/or filtration.

40. A pulverised mixture obtained, directly obtained or obtainable by the process as defined in any one of statements 26 to 38.

41. A mixture comprising:

sodium fluoride, and
a sulphide of Ca, Sr, Ba or Mg.

42. The mixture as defined in statement 41, wherein the mixture is a solid mixture.

43. The mixture as defined in statement 41 or 42, further comprising a fluoride source, wherein the fluoride source is one or more selected from CaF_2, SrF_2, BaF_2 and MgF_2.

44. The mixture as defined in statement 41, 42 or 43, wherein the fluoride source is CaF_2.

45. A process for the preparation of a fluorochemical, the process comprising the step of: pulverising together a fluoride source and an activator,
wherein the fluoride source is at least one selected from CaF_2, SrF_2, BaF_2 and MgF_2, and the activator is at least one selected from LiOH, Li_2O, Li_2O_2, LiO_2, NaOH, Na_2O, Na_2O_2, NaO_2, KOH, K_2O_2, KO_2, CsOH (including $CsOH{\cdot}H_2O$), Cs_2O, Cs_2O_2, Cs_2O_3, CsO_2 and CsO_3.

46. The process as defined in statement 45, wherein the pulverising step is conducted in the absence of a solvent.

47. The process as defined in statement 45 or 46, wherein the pulverising step is a mechanochemical reaction.

48. The process as defined in statement 45, 46 or 47, wherein the pulverising step is conducted in a ball mill, a pestle and mortar or a twin-screw extruder.

49. The process as defined in any one of statements 45 to 48, wherein the pulverising step is conducted in a ball mill.

50. The process as defined in any one of statements 45 to 49, wherein the activator is at least one selected from LiOH, Li_2O, Li_2O_2 and LiO_2.

51. The process as defined in any one of statements 45 to 49, wherein the activator is at least one selected from NaOH, Na_2O, Na_2O_2 and NaO_2.

52. The process as defined in any one of statements 45 to 49, wherein the activator is at least one selected from KOH, K_2O_2 and KO_2.

53. The process as defined in any one of statements 45 to 49, wherein the activator is at least one selected from CsOH (including hydrated forms), Cs_2O, Cs_2O_2, Cs_2O_3, CsO_2 and CsO_3.

54. The process as defined in any one of statements 45 to 49, wherein the activator is selected from NaOH, Na_2O, KOH, CsOH (e.g., $CsOH \cdot H_2O$), LiOH and Li_2O.

55. The process as defined in any one of statements 45 to 49, wherein the activator is NaOH or Na_2O.

56. The process as defined in any one of statements 45 to 49, wherein the activator is KOH.

57. The process as defined in any one of statements 45 to 49, wherein the activator is CsOH (e.g., $CsOH \cdot H_2O$).

58. The process as defined in any one of statements 45 to 49, wherein the activator is LiOH or Li_2O.

59. The process as defined in any one of statements 45 to 57, wherein the fluoride source is CaF_2 (e.g., fluorspar).

60. The process as defined in any one of statement 45 or 59, wherein a sequestrant is pulverised together with the fluoride source and the activator, wherein the sequestrant is at least one selected from TiO_2, MoO_3, WO_3, Pb_3O_4 and PbO_2.

61. The process as defined in statement 60, wherein the sequestrant is TiO_2.

62. The process as defined in any one of statements 45 to 61, wherein the fluorochemical is lithium fluoride, sodium fluoride, potassium fluoride, caesium fluoride and/or an alkali metal (i.e., Li, Na, K or Cs) metallate fluoride.

63. The process as defined in any one of statements 45 to 62, wherein the pulverising step results in the formation of a pulverised mixture comprising the fluorochemical, an oxide or hydroxide of Ca, Sr, Ba or Mg and optionally residual fluoride source.

64. The process as defined in any one of statements 45 to 63, wherein the pulverising step is conducted in the absence of aluminium oxide or in the absence of any aluminium-containing species.

65. The process as defined in any one of statements 45 to 64, wherein the pulverising step (and optionally any other steps forming the process) is conducted at a temperature lower than 300°C.

66. The process as defined in any one of statements 45 to 65, wherein the pulverising step (and optionally any other steps forming the process) is conducted in the absence of a mineral acid; and/or HF is not formed during the pulverising step (optionally nor is it formed during any other steps forming the process).

67. The process as defined in any one of statements 45 to 66, further comprising the step of isolating the fluorochemical resulting from the pulverising step by solvent extraction and/or filtration.

68. A pulverised mixture obtained, directly obtained or obtainable by the process as defined in any one of statements 45 to 66.

69. A mixture comprising:
at least one of lithium fluoride, sodium fluoride, potassium fluoride and caesium fluoride; and
an oxide or hydroxide of Ca, Sr, Ba or Mg.

70. The mixture as defined in statement 69, wherein the mixture is a solid mixture.

71. The mixture as defined in statement 69 or 70, further comprising an alkali metal (i.e., Li, Na, K or Cs) metallate fluoride.

72. The mixture as defined in statement 69, 70 or 71, further comprising a fluoride source, wherein the fluoride source is one or more selected from CaF_2, SrF_2, BaF_2 and MgF_2.

73. The mixture as defined in statement 72, wherein the fluoride source is CaF_2.

74. A process for the preparation of a fluorochemical, the process comprising the step of:
pulverising together a fluoride source and an activator,

wherein the fluoride source is MgF_2, and the activator is at least one selected from NaOH, Na_2O, Na_2O_2 and NaO_2.

75. The process as defined in statement 74, wherein the pulverising step is conducted in the absence of a solvent.

76. The process as defined in statement 74 or 75, wherein the pulverising step is a mechanochemical reaction.

77 The process as defined in statement 74, 75 or 76, wherein the pulverising step is conducted in a ball mill, a pestle and mortar or a twin-screw extruder.

78. The process as defined in any one of statements 74 to 77, wherein the pulverising step is conducted in a ball mill.

79. The process as defined in any one of statements 74 or 78, wherein a sequestrant is pulverised together with the fluoride source and the activator, wherein the sequestrant is at least one selected from TiO_2, MoO_3, WO_3, Pb_3O_4 and PbO_2.

80. The process as defined in statement 79, wherein the sequestrant is TiO_2.

81. The process as defined in any one of statements 74 to 80 wherein the fluorochemical is sodium fluoride.

82. The process as defined in any one of statements 74 to 81, wherein the pulverising step results in the formation of a pulverised mixture comprising the fluorochemical and at least one of MgO and $Mg(OH)_2$.

83. The process as defined in any one of statements 74 to 82, wherein the pulverising step is conducted in the absence of aluminium oxide or in the absence of any aluminium-containing species.

84. The process as defined in any one of statements 74 to 83, wherein the pulverising step (and optionally any other steps forming the process) is conducted at a temperature lower than 300°C.

85. The process as defined in any one of statements 74 to 84, wherein the pulverising step (and optionally any other steps forming the process) is conducted in the absence of a mineral acid; and/or HF is not formed during the pulverising step (optionally nor is it formed during any other steps forming the process).

86. The process as defined in any one of statements 74 to 85, further comprising the step of isolating the fluorochemical resulting from the pulverising step by solvent extraction and/or filtration.

87. A pulverised mixture obtained, directly obtained or obtainable by the process as defined in any one of statements 74 to 86.

88. A mixture comprising sodium fluoride and at least one of MgO and $Mg(OH)_2$.

89. The mixture as defined in statement 88, wherein the mixture is a solid mixture.

EXAMPLES

[00136] Examples of the invention will now be described, for the purpose of illustration only.

Example 1

[00137] To a 15 mL stainless steel milling jar was added a 7 g stainless-steel ball, acid grade fluorspar (328 mg, 1 equiv.), NaOH (336 mg, 2 equiv.), and TiO_2 (336 mg, 1 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. The product was found by powder X-ray analysis to contain NaF, $CaTiO_3$, and residual CaF_2.

Example 2

[00138] To a 15 mL stainless steel milling jar was added a 7 g stainless-steel ball, acid grade fluorspar (355 mg, 1 equiv.), Na_2O (282 mg, 1 equiv.), and TiO_2 (363 mg, 1 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and

collected. The product was found by powder X-ray analysis to contain NaF, $CaTiO_3$, and residual TiO_2.

Example 3

[00139] To a 15 mL stainless steel milling jar was added a 7 g stainless-steel ball, acid grade fluorspar (500 mg, 1 equiv.) and Na_2S (500 mg, 1 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. The product was found by powder X-ray analysis to contain NaF, CaS, and residual CaF_2 as well as Na_2S.

Example 4

[00140] To a 15 mL stainless steel milling jar was added a 7 g stainless-steel ball, acid grade fluorspar (620 mg, 1 equiv.) and LiOH (380 mg, 2 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. The product was found by powder X-ray analysis to contain LiF, $Ca(OH)_2$, and residual CaF_2.

Example 5

[00141] To a 15 mL stainless steel milling jar was added a 7 g stainless-steel ball, acid grade fluorspar (723 mg, 1 equiv.) and Li_2O (277 mg, 1 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. The product was found by powder X-ray analysis to contain LiF, CaO, and residual CaF_2.

Example 6

[00142] To a 15 mL stainless steel milling jar was added a 7 g stainless-steel ball, MgF_2 (501 mg, 1 equiv.) and Na_2O (499 mg, 1 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. The product was found by powder X-ray analysis to contain NaF and MgO.

Example 7

[00143] To a 15 mL stainless steel milling jar was added a 7 g stainless-steel ball, SrF_2 (470 mg, 1 equiv.), Na_2O (232 mg, 1 equiv.), and TiO_2 (299 mg, 1 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. The product was found by powder X-ray analysis to contain NaF and $SrTiO_3$.

Example 8

[00144] To a 15 mL stainless steel milling jar was added a 7 g stainless-steel ball, BaF_2 (553 mg, 1 equiv.), Na_2O (195 mg, 1 equiv.), and TiO_2 (252 mg, 1 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. The product was found by powder X-ray analysis to contain NaF and $BaTiO_3$.

Example 9

[00145] To a 15 mL stainless steel milling jar was added a 7 g stainless-steel ball, acid grade fluorspar (275 mg, 1 equiv.), Na_2O (218 mg, 1 equiv.), and MoO_3 (507 mg, 1 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. The product was found by powder X-ray analysis to contain $CaMoO_4$, Na_2MoO_4, Na_3MoO_4F, and residual CaF_2.

Example 10

[00146] To a 15 mL stainless steel milling jar was added a 7 g stainless-steel ball, acid grade fluorspar (210 mg, 1 equiv.), Na_2O (167 mg, 1 equiv.), and WO_3 (623 mg, 1 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. The product was found by powder X-ray analysis to contain $CaWO_4$, Na_2WO_4, and Na_3WO_4F.

Example 11

[00147] To a 15 mL stainless steel milling jar was added a 7 g stainless-steel ball, acid grade fluorspar (95 mg, 1 equiv.), Na_2O (75 mg, 1 equiv.), and Pb_3O_4 (830 mg, 1 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. The product was found by powder X-ray analysis to contain NaF, Ca_2PbO_4, and PbO.

Example 12

[00148] To a 15 mL stainless steel milling jar was added a 7 g stainless-steel ball, acid grade fluorspar (206 mg, 1 equiv.), Na_2O (163 mg, 1 equiv.), and PbO_2 (631 mg, 1 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. The product was found by powder X-ray analysis to contain NaF and Ca_2PbO_4.

Example 13

[00149] To a 15 mL stainless steel milling jar was added a 7 g stainless-steel ball, acid grade fluorspar (83 mg, 1 equiv.), Na_2O_2 (83 mg, 1 equiv.), and TiO_2 (85 mg, 1 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. The product was found by powder X-ray analysis to contain NaF and $CaTiO_3$.

Example 14

[00150] To a 15 mL stainless steel milling jar was added one 7 g stainless-steel ball, acid grade fluorspar (494 mg, 1 equiv.), and NaOH (506 mg, 2 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. To another 15 mL stainless steel milling jar was added one 7 g stainless-steel ball, the mixture obtained (497 mg, 1 equiv.), and TiO_2 (503 mg, 2 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. The product was found by quantitative ^{19}F-NMR spectroscopy (using NaOTf as internal standard) analysis to contain 50% of extractable fluoride.

Example 15

[00151] To a 15 mL stainless steel milling jar were added two 7 g stainless-steel balls, acid grade fluorspar (340 mg, 1 equiv.), NaOH (313 mg, 1.8 equiv.), and TiO_2 (347 mg, 1 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. The product was found by quantitative ^{19}F-NMR spectroscopy (using NaOTf as internal standard) analysis to contain 84% of extractable fluoride.

Example 16

[00152] To a 15 mL stainless steel milling jar were added two 7 g stainless-steel balls, acid grade fluorspar (365 mg, 1 equiv.), Na_2O (261 mg, 0.9 equiv.), and TiO_2 (374 mg, 1 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. The product was found by quantitative ^{19}F-NMR spectroscopy (using NaOTf as internal standard) analysis to contain 78% of extractable fluoride.

Example 17

[00153] To a 12 mL zirconium oxide milling jar were added six 10 mm zirconium oxide balls, acid grade fluorspar (328 mg, 1 equiv.), NaOH (336 mg, 2 equiv.), and TiO_2 (336 mg, 1 equiv.). The

jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 800 rpm. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. The product was found by quantitative ^{19}F-NMR spectroscopy (using NaOTf as internal standard) analysis to contain 62% of extractable fluoride.

Example 18

[00154] To six 15 mL stainless steel milling jars were added two 7 g stainless-steel balls, acid grade fluorspar (340 mg, 1 equiv.), NaOH (313 mg, 1.8 equiv.), and TiO_2 (347 mg, 1 equiv.) each. The jars were then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jars were opened and the solid residues were scratched out with a spatula and collected. An aliquot of 4.30 g of the mixture obtained was extracted with H_2O (45 mL), filtered and washed with H_2O (3 x 20 mL). The filtrate was evaporated to dryness and flame-dried in high vacuum to give 1.27 g NaF (90% yield). The purity was found by quantitative ^{19}F-NMR spectroscopy (using NaOTf as internal standard) analysis to be 99%.

Example 19

[00155] To a 15 mL stainless steel milling jar were added two 7 g stainless-steel balls, acid grade fluorspar (379 mg, 1 equiv.), LiOH (233 mg, 2 equiv.), and TiO_2 (388 mg, 1 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. The product was found by powder X-ray analysis to contain LiF, $CaTiO_3$, residual CaF_2 and residual TiO_2.

Example 20

[00156] To a 15 mL stainless steel milling jar were added two 7 g stainless-steel balls, acid grade fluorspar (416 mg, 1 equiv.), Li_2O (159 mg, 1 equiv.), and TiO_2 (425 mg, 1 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. The product was found by powder X-ray analysis to contain LiF, $CaTiO_3$, residual CaF_2 and residual TiO_2.

Example 21

[00157] To six 15 mL stainless steel milling jars were added two 7 g stainless-steel balls, acid grade fluorspar (416 mg, 1 equiv.), Li_2O (159 mg, 1 equiv.), and TiO_2 (425 mg, 1 equiv.) each. The jars were then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jars were opened and the solid residues were scratched out with a spatula and collected. An aliquot of 4.84 g of the mixture obtained was washed with H_2O (15 mL) before it was extracted with H_2O (3 x 500 mL), filtered and washed with H_2O (3 x 50 mL). The

filtrate was evaporated to dryness and the obtained solid was washed with H_2O (2 x 10 mL) and flame-dried in high vacuum to give 888 mg LiF (66% yield). The product was found by powder X-ray analysis to contain LiF only.

Example 22

[00158] To a 15 mL stainless steel milling jar were added two 7 g stainless-steel balls, acid grade fluorspar (289 mg, 1 equiv.), KOH (415 mg, 2 equiv.), and TiO_2 (296 mg, 1 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. The product was found by quantitative ^{19}F-NMR spectroscopy (using NaOTf as internal standard) analysis to contain 23% of extractable fluoride.

Example 23

[00159] To a 15 mL stainless steel milling jar were added two 7 g stainless-steel balls, acid grade fluorspar (410 mg, 1 equiv.), and KOH (590 mg, 2 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. The product was found by quantitative ^{19}F-NMR spectroscopy (using NaOTf as internal standard) analysis to contain 7% of extractable fluoride.

Example 24

[00160] To a 15 mL stainless steel milling jar were added two 7 g stainless-steel balls, acid grade fluorspar (158 mg, 1 equiv.), $CsOH{\cdot}H_2O$ (680 mg, 2 equiv.), and TiO_2 (162 mg, 1 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. The product was found by quantitative ^{19}F-NMR spectroscopy (using NaOTf as internal standard) analysis to contain 46% of extractable fluoride.

Example 25

[00161] To a 15 mL stainless steel milling jar were added two 7 g stainless-steel balls, acid grade fluorspar (189 mg, 1 equiv.), and $CsOH{\cdot}H_2O$ (811 mg, 2 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. The product was found by quantitative ^{19}F-NMR spectroscopy (using NaOTf as internal standard) analysis to contain 5% of extractable fluoride.

Example 26

[00162] To a 15 mL stainless steel milling jar were added two 7 g stainless-steel balls, acid grade fluorspar (494 mg, 1 equiv.), and NaOH (506 mg, 2 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. The product was found by quantitative ^{19}F-NMR spectroscopy (using NaOTf as internal standard) analysis to contain 8% of extractable fluoride.

Comparative example 1

[00163] Example 2 was repeated, except that TiO_2 was replaced with CeO_2, TiO, Ti_2O_3, ZrO_2, VO_2, V_2O_5, NbO_2, CrO_2, CrO_3, MoO_2, WO_2, MnO_2, Fe_2O_3, CuO, B_2O_3, Al_2O_3, GeO_2, SnO_2, PbO, Sb_2O_3, Sb_2O_5, Bi_2O_3, or SeO_2. For all of the aforementioned oxides, no Ca-containing, mixed metal oxide was detected by powder X-ray analysis of the product, suggesting that these oxides may not be able to act as a sequestrant.

Comparative example 2

[00164] To a 15 mL stainless steel milling jar were added two 7 g stainless-steel balls, acid grade fluorspar (371 mg, 1 equiv.), NaOH (343 mg, 1.8 equiv.), and SiO_2 (286 mg, 1 equiv.). The jar was then closed and securely fitted to the mill which was set for 3 h at the frequency of 35 Hz. After that time, the jar was opened and the solid residue was scratched out with a spatula and collected. The product was found by quantitative ^{19}F-NMR spectroscopy (using NaOTf as internal standard) analysis to contain 43% of extractable fluoride in the case of silica gel as sequestrant and 26% of extractable fluoride in the case of sand as sequestrant.

[00165] While specific embodiments of the invention have been described herein for the purpose of reference and illustration, various modifications will be apparent to a person skilled in the art without departing from the scope of the invention as defined by the appended claims.

[00166] The project leading to this application has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No 832994).

CLAIMS

1. A process for the preparation of a fluorochemical, the process comprising the step of: pulverising together a fluoride source, an activator and a sequestrant,
wherein the fluoride source is at least one selected from CaF_2, SrF_2 and BaF_2, the activator is at least one selected from NaOH, Na_2O, Na_2O_2 and NaO_2, and the sequestrant is at least one selected from TiO_2, MoO_3, WO_3, Pb_3O_4 and PbO_2.

2. The process as claimed in claim 1, wherein the pulverising step is conducted in the absence of a solvent.

3. The process as claimed in claim 1 or 2, wherein the pulverising step is a mechanochemical reaction.

4. The process as claimed in claim 1, 2 or 3, wherein the pulverising step is conducted in a ball mill, a pestle and mortar or a twin-screw extruder.

5. The process as claimed in any one of the preceding claims, wherein the pulverising step is conducted in a ball mill.

6. The process as claimed in any one of the preceding claims, wherein the fluoride source is CaF_2 (e.g., fluorspar).

7. The process as claimed in any one of the preceding claims, wherein the activator is NaOH or Na_2O.

8. The process as claimed in any one of the preceding claims, wherein the activator is Na_2O.

9. The process as claimed in any one of the preceding claims, wherein the sequestrant is TiO_2.

10. The process as claimed in any one of the preceding claims, wherein the fluorochemical is sodium fluoride or a sodium metallate fluoride.

11. The process as claimed in claim 10, wherein the sodium metallate fluoride is sodium tungstate fluoride or sodium molybdate fluoride.

12. The process as claimed in any one of the preceding claims, wherein the pulverising step results in the formation of a pulverised mixture comprising the fluorochemical, a mixed metal oxide and optionally at least one of residual fluoride source and residual sequestrant.

13. The process as claimed in claim 12, where the mixed metal oxide comprises a first metal selected from Ca, Sr and Ba, and a second metal selected from Ti, Mo, W and Pb.

14. The process as claimed in any one of the preceding claims, further comprising the step of isolating the fluorochemical resulting from the pulverising step by solvent extraction and/or filtration.

15. A pulverised mixture obtained, directly obtained or obtainable by the process as claimed in any one of claims 1 to 13.

16. A mixture comprising:
sodium fluoride or a sodium metallate fluoride, and
a mixed metal oxide.

17. The mixture as claimed in claim 16, wherein the mixture is a solid mixture.

18. The mixture as claimed in claim 16 or 17, wherein the mixed metal oxide comprises a first metal selected from Ca, Sr and Ba, and a second metal selected from Ti, Mo, W and Pb.

19. The mixture as claimed in any one of claims 16, 17 or 18, wherein the mixed metal oxide is $CaTiO_3$.

20. The mixture as claimed in any one of claims 16 to 19, further comprising at least one of a fluoride source and a sequestrant, wherein the fluoride source is one or more selected from CaF_2, SrF_2 and BaF_2, and the sequestrant is one or more selected from TiO_2, MoO_3, WO_3, Pb_3O_4 and PbO_2.

21. The mixture as claimed in claim 20, wherein the fluoride source is CaF_2.

22. The mixture as claimed in claim 20 or 21, wherein the sequestrant is TiO_2.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2024/051524

A. CLASSIFICATION OF SUBJECT MATTER

INV. C01D3/02 C01D15/04 C01F5/02 C01F11/00 C01F11/10
C01G21/06 C01G21/22 C01G23/00 C01G39/00 C01G41/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01D C01F C01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 105 883 856 B (UNIV WUHAN TECH) 29 September 2017 (2017-09-29) paragraphs [0022] - [0024]; examples 3, 5, 6	1-22
A	US 2 690 430 A (ANDERSON RAYMOND J) 28 September 1954 (1954-09-28) claims	1-22

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
13 September 2024	26/09/2024

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2024/051524

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 105883856 B	29-09-2017	NONE	
US 2690430 A	28-09-1954	NONE	