



(12) **DEMANDE DE BREVET CANADIEN**
CANADIAN PATENT APPLICATION

(13) **A1**

(22) Date de dépôt/Filing Date: 2019/04/10

(41) Mise à la disp. pub./Open to Public Insp.: 2020/10/10

(51) Cl.Int./Int.Cl. *B09C 1/00* (2006.01),
B02C 17/00 (2006.01)

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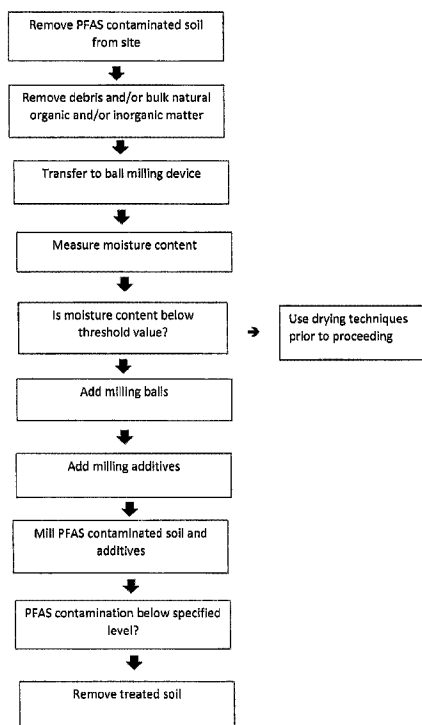
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(54) Titre : METHODE POUR ASSAINIR LE SOL CONTAMINE AU POLYFLUOROCARBURE

(54) Title: METHOD FOR REMEDIATING POLYFLUOROCARBON-CONTAMINATED SOIL



(57) Abrégé/Abstract:

A method for remediating PFAS-contaminated soil comprises measuring the initial moisture content of the PFAS-contaminated soil, optionally drying the PFAS-contaminated soil, and ball milling the PFAS-contaminated soil with or without the use of milling additives.

ABSTRACT

A method for remediating PFAS-contaminated soil comprises measuring the initial moisture content of the PFAS-contaminated soil, optionally drying the PFAS-contaminated soil, and ball milling the PFAS-contaminated soil with or without the use of milling additives.

METHOD FOR REMEDIATING POLYFLUOROCARBON-CONTAMINATED SOIL

FIELD

The invention relates to remediation of contaminated soil. More specifically, the invention relates to remediation of soil contaminated with persistent, manufactured, fluorocarbon compounds, such as per- and/or poly-fluoroalkyl substances.

BACKGROUND

Per- and poly-fluoroalkyl substances (PFAS) represent a group of manufactured fluorinated organic compounds that have been used in industrial applications and consumer products since the 1950s. Their excellent surface-active properties, including hydrophobicity, lipophobicity and hydrophilicity have made PFAS compounds ideal for use in a number of oil and water repellent products for application in the surface treatment of textiles, leathers, fibres and carpets; in food packaging and cooking ware materials; as additives to photographic films, hydraulic fluids, electronics, surfactants, and acid mist suppressants; and in fire-fighting foams such as aqueous film-forming foams (AFFF).

AFFF are the fire suppressants to combat severe fuel fires, such as the 2013 Lac-Mégantic crude oil train derailment disaster. Airports and firefighting training areas have used AFFF for decades to extinguish fires and to perform training drills. PFAS compounds are highly stable and persistent in the environment, resultantly, the soils of many airports and firefighting training facilities are contaminated with PFAS. Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are two of the most commonly detected, long chain ($C \geq 8$) PFAS found in AFFF contaminated soils. PFOS and PFOA have been identified as emerging contaminants of concern by the United States Environmental Protection Agency and PFOS is listed in Annex B of persistent organic pollutants by the Stockholm Convention. PFOS and PFOA are recalcitrant and resistant to conventional remediation strategies due to the strength of the carbon-fluorine bond and shielding size of fluorine atoms. Fluorinated surfactants adsorb to soils, via both hydrophobic attraction to organic carbon and electrostatic interactions from the anionic head group.

There is evidence that exposure to PFAS leads to adverse health outcomes in humans. Studies indicate that PFOA and PFOS can cause reproductive and developmental problems, liver and kidney

damage, and immunological effects in laboratory animals. Both chemicals have caused tumours in animals. The most consistent findings are increased cholesterol levels among exposed populations, with more limited findings related to low infant birth weights, immune system effects, cancer (in the case of PFOA), and thyroid hormone disruption (in the case of PFOS). Significant health effects have been detected and include carcinogenic potential, endocrine disrupting properties, and neonatal immunosuppressant effects. PFAS bind to proteins so they build up in the liver and kidneys. Since these compounds are lipophobic, they do not enter fatty-tissues the way many other organic contaminants may.

PFAS impacted soils are a continuous source of contamination to groundwater, which threatens supplies of drinking water as well as ecosystems. Unfortunately, options for treating or remediating PFAS-contaminated sites are limited. Currently, practical and large-scale remedial strategies available for PFAS-contaminated soil include encapsulation, excavation to landfill (where permissible), and excavation for incineration. Encapsulation methods only act to reduce risk of exposure. Of these, only incineration actually destroys PFAS (together with the soil it is bound to), but this method risks emitting fluorinated greenhouse gases into the atmosphere. Neither encapsulation nor incineration are cost effective and both impose significant logistical and safety concerns. Consequently, there is a need for a low-risk, effective, and economically viable remediation technology to reduce the risk of PFAS-contaminated soils to communities, wildlife, and the environment.

SUMMARY

In one aspect, the invention provides a method for remediating PFAS-contaminated soil, comprising disposing PFAS-contaminated soil into a ball mill, and operating the ball mill until soil that is substantially free of PFAS contaminants is obtained. In one embodiment, the method is conducted in the absence of base (e.g., KOH, NaOH). In one embodiment, the method further comprises adding drying agents to the ball mill, and rotating the ball mill until the hydration level of the PFAS-contaminated soil is in a selected range. In certain embodiments, the ball mill is a horizontal ball mill or a long roll ball mill. In one embodiment, the method further comprises disposing a plurality of milling balls in the ball mill prior to rotating the ball mill. In one embodiment, the method further comprises disposing a gas into the ball mill. In one embodiment, the gas is continuously disposed into the ball mill while the ball mill is rotating. In one embodiment, the gas is air, argon, nitrogen, helium, or a combination thereof. In one embodiment, the disposing of a plurality of milling balls occurs once the PFAS-contaminated soil has a selected hydration level. In one embodiment, the method further

comprises disposing a milling additive in the ball mill. In one embodiment, the milling additive comprises a defluorination agent, a processing additive, a drying additive, or a combination thereof. In one embodiment, the defluorination agent comprises potassium hydroxide, sodium hydroxide, calcium oxide, silicon dioxide, sand or a combination thereof. In one embodiment, the processing additive comprises a tribomaterial. In one embodiment, the tribomaterial is sand, granite, quartz porphyries, feldspar, talc, aluminum oxide, KOH, NaOH, SiO₂, porphyries, or a combination thereof. In one embodiment, the drying additive comprises sodium chloride, calcium chloride, sodium hydroxide, copper sulphate, phosphorus pentoxide, potassium hydroxide, silica gel, lithium bromide, lithium chloride, or a combination thereof. In one embodiment, the method further comprises removing debris and bulk natural organic and inorganic matter from the PFAS-contaminated soil prior to transferring the PFAS-contaminated soil to the ball mill. In one embodiment, the defluorination additive is added in a ratio of defluorination additive to PFAS-contaminated soil of about 0:1 to about 1:1. In one embodiment, the milling balls are added in a mass ratio of milling balls to PFAS-contaminated soil of about 20:1. In one embodiment, the PFAS-contaminated soil comprises perfluoroalkyl substances.

In one embodiment, the PFAS-contaminated soil comprises polyfluoroalkyl substances. In one embodiment, the PFAS-contaminated soil comprises perfluorooctanesulfonic acid (PFOS), perfluorooctanoic acid (PFOA), perfluorooctanesulfonamide (PFOSA), perfluorohexanoic acid (PFHxA), perfluoro-n-pentanoic acid (PFPeA), pentafluorobenzoic acid (PFBA), perfluorohexanesulfonic acid (PFHxS), or any combination thereof. In one embodiment, the PFAS-contaminated soil comprises PFAS in an amount that is about 5 ppm. In one embodiment, the remediation is conducted with no added KOH nor NaOH.

BRIEF DESCRIPTION OF THE DRAWINGS

For a better understanding of the invention and to show more clearly how it may be carried into effect, reference will now be made, by way of example, to the accompanying drawings, wherein:

Fig. 1 shows a flowchart outlining embodiments of the invention.

Fig. 2A shows normalized degradation profiles for 15g of dry contaminated sand having no KOH additive, where the contamination is PFOS (▲), or PFOA (●).

Fig. 2B shows normalized degradation profiles for 40g of dry contaminated sand having no KOH additive, where the contamination is PFOS (▲), or PFOA (●).

Fig. 2C shows normalized degradation profiles for 15g of water-saturated contaminated sand having no KOH additive, where the contamination is PFOS (▲), or PFOA (●).

Fig. 2D shows normalized degradation profiles for 40g of water-saturated contaminated sand having no KOH additive, where the contamination is PFOS (▲), or PFOA (●).

Fig. 2E shows normalized degradation profiles for 15g of dry contaminated sand having KOH additive (10 g), where the contamination is PFOS (▲), or PFOA (●).

Fig. 2F shows normalized degradation profiles for 40g of dry contaminated sand having KOH additive (10 g), where the contamination is PFOS (▲), or PFOA (●).

Fig. 2G shows normalized degradation profiles for 15g of water-saturated contaminated sand having KOH additive (10 g), where the contamination is PFOS (▲), or PFOA (●).

Fig. 2H shows normalized degradation profiles for 40g of water-saturated contaminated sand having KOH additive (10 g), where the contamination is PFOS (▲), or PFOA (●).

Fig. 3 shows a geometric view of the 23 factorial experimental design, presenting the mass of sand (g), mass of KOH (g) and hydration level (%) on the x, y and z axes, respectively.

Fig. 4 shows a graph of concentration of various PFAS compounds vs. milling time for 15 g dry spiked sand in the presence of 10 g KOH.

Figs. 5A and 5B show destruction profiles for (A) AFFF impacted sands (B) AFFF impacted clays.

Fig. 6 shows a plot of percentage PFOS destruction versus treatment parameters for FFTA sand using a long roll ball mill (ball mill parameters included sand, a grinding ball size of 2.86 cm, a charge ratio of 10:1, a reagent ratio of 4:1 (sand:KOH), and a speed of 47 RPM).

Fig. 7A shows a plot of concentration PFOS versus ball milling time in FFTA sand using a unitized ball mill.

Fig. 7B shows a plot of concentration PFOS versus ball milling time in FFTA clay using a unitized ball mill.

DETAILED DESCRIPTION OF EMBODIMENTS

Definitions

As used herein, the term “AFFF” refers to foams used in firefighting that are often called aqueous film-forming foams.

As used herein, the term “bulk natural inorganic matter” refers to matter that is not derived from animal or plant origins found within natural terrestrial environments, such as boulders, rocks, stones, etc.

As used herein, the term “bulk natural organic matter” refers to matter derived from animal or plant origins found within natural terrestrial environments, such as trees, plants, grasses, root materials, humus, etc.

As used herein, the term “defluorination agent” refers to a reagent that can assist with defluorination of fluorinated compounds such as PFAS compounds, examples of defluorination agents include, but are not limited to, potassium hydroxide (KOH), sodium hydroxide (NaOH), and calcium oxide (CaO).

As used herein, the term “FFTA” refers to fire-fighting training areas.

As used herein, the term “hygroscopic substance” refers to a substance that readily attracts water from its surroundings, through either absorption or adsorption.

As used herein, the term “PFAS” refers to per- and poly-fluoroalkyl substances.

As used herein, the term “PFAS-contaminated soil” refers to soil that has been contaminated with per- and/or poly-fluoroalkyl substances.

As used herein, the term “PFAS-contaminated site” refers to an area of land that has per- and/or poly-fluoroalkyl substances in its surface and subsurface soils, sediments, aquifer materials, and/or groundwater.

As used herein, the term “perfluoroalkyl substance” refers to a class of manufactured fluorinated hydrocarbon chemicals that are fully fluorinated.

As used herein, the term “PFBA” refers to pentafluorobenzoic acid.

As used herein, the term “PFHxA” refers to perfluorohexanoic acid.

As used herein, the term “PFHxS” refers to perfluorohexanesulphonic acid.

As used herein, the term “PFOA” refers to perfluorooctanoic acid or ammonium octanoate salt.

As used herein, the term “PFOS” refers to perfluorooctanesulfonic acid or a salt thereof.

As used herein, the term “PFOSA” refers to perfluorooctanesulfonamide.

As used herein, the term “PFPeA” refers to perfluoroheptanoic acid.

As used herein, the term “polyfluoroalkyl substance” refers to a class of manufactured fluorinated hydrocarbon chemicals that are not fully fluorinated.

As used herein, the term “processing additive” refers to an additive that assists or promotes the treatment or remediation of the PFAS-contaminated soil.

As used herein, the term “QL” refers to quantification limit.

As used herein, the term “treated soil” refers to PFAS-contaminated soil that has been treated or remediated such that the level of PFAS contamination in the soil is less than it was prior to being treated or remediated.

As used herein, the term “tribomaterial” refers to a material that forms surface plasmas upon the breakage of certain intramolecular bonds. Examples include sand, granite, quartz porphyries, feldspar, talc, aluminum oxide, KOH, NaOH, SiO₂, porphyries, or a combination thereof.

Embodiments

Methods for remediating soil that is contaminated with PFAS are described herein. Embodiments degrade, destroy, and/or alter PFAS in the soil such that resulting treated soil is has substantially no PFAS and conforms with local guidelines for PFAS contamination. As used herein, the term “PFAS” is used as a general term to represent perfluoroalkyl or polyfluoroalkyl substances. Such substances include perfluorooctanesulfonic acid (PFOS), perfluorooctanoic acid (PFOA), perfluorooctanesulfonamide (PFOSA), perfluorohexanoic acid (PFHxA), perfluoro-n-pentanoic acid (PFPeA), pentafluorobenzoic acid (PFBA), perfluorohexanesulfonic acid (PFHxS), or combinations thereof. In one embodiment, the PFAS substances are present in the PFAS-contaminated soil in an amount of about five parts per million (ppm).

Results described herein show that the methods are effective for a variety of soil types (sand and clay) and for a range of contamination levels and types of PFAS. As described in the Examples, PFAS-spiked soil samples as well as samples of soils that were retrieved from a site known to be contaminated with AFFF were remediated using the methods and resulted in significant reductions in the levels of PFAS-contamination in the soils being treated.

PFAS-contaminated soil was removed from a PFAS-contaminated site using soil removal techniques such as manual shoveling, excavation using a machine (i.e., backhoe, excavator, bulldozer), hydro excavation, etc. Debris and/or bulk natural organic and/or inorganic matter, such as trees, plants, grasses, root material, humus, boulders, rocks, stones, etc., that was present in the PFAS-contaminated soil was removed. Removal techniques included manual extraction, sifting, filtering, etc. After removal of such debris, the PFAS-contaminated soil was transferred into a ball milling device.

In one embodiment, PFAS-contaminated soil is tested to determine its moisture content. Techniques for determining moisture content include gravimetric measurement, frequency domain reflectometry, time domain transmission, time domain reflectometry, soil resistivity, neutron moisture gauges, and galvanic cells. For soil that has a high hydration level, drying the soil to a lower hydration level has been shown to improve the efficiency of the subsequent remediation process. In one embodiment, the soil is disposed in a ball mill, and then the hydration level is determined. Once the hydration level is determined, if the hydration level is quite high, then the hydration level is lowered by drying the soil either partially or fully.

There are several techniques to dry soil that can be used, alone or in combination. These include adding drying agents to the ball mill, and rotating the ball mill until the hydration level of the soil is reduced, flowing a gas through the ball mill as it is rotated, and heating the soil as it is rotated in the ball mill. Examples of drying agents include: sodium chloride, calcium chloride, sodium hydroxide, copper sulphate, phosphorus pentoxide, potassium hydroxide, silica gel, lithium bromide, lithium chloride, or any combination thereof. In one embodiment, soil is allowed to air dry.

If the hydration level is above a threshold level, the PFAS-contaminated soil is first dried in the ball milling device. Drying can be done by milling the PFAS-contaminated soil (in the absence of milling balls) for a specified period of time or until the moisture content of the PFAS-contaminated soil falls below the threshold level. Optionally, a gas is introduced into the ball milling device to accelerate the rate of drying. Examples of suitable gases include, but are not limited to, air, nitrogen, argon, and

helium. The gas can be heated if even faster drying rates are desired. Once the moisture level of the PFAS-contaminated soil is below the threshold level, the milling process proceeds until a specified PFAS contamination target level is achieved.

In one embodiment, a drying additive is added to the ball milling process. As shown in Figs. 2a-h, the addition of a hygroscopic substance (e.g., potassium hydroxide (KOH)) has a significant impact on the effectiveness of ball milling on remediating PFAS-contaminated soil that has an initial moisture content above the threshold level. In this embodiment, there is no separate drying step (although such a step is optional), rather, the drying additive is added to the PFAS-contaminated soil prior to and/or during the ball milling process and acts to reduce the moisture content of the PFAS-contaminated soil through hygroscopy. Examples of suitable drying agents include, but are not limited to, sodium chloride, calcium chloride, sodium hydroxide, copper sulphate, phosphorus pentoxide, potassium hydroxide, silica gel, lithium bromide, and lithium chloride.

As shown in Figs. 2a to 2h, the effectiveness of ball milling on treating or remediating PFAS-contaminated soil is affected by the initial moisture content of the PFAS-contaminated soil. Consequently, in one embodiment, a moisture content of the PFAS-contaminated soil is determined prior to remediation as this will inform subsequent processing conditions. When the initial moisture content of the PFAS-contaminated soil is below a certain threshold level, remediation by ball milling can proceed without any additional steps or additives.

Following an optional drying step, a remediation step is performed wherein the ball mill is operated until the PFAS-contaminated soil becomes treated soil that has substantially no PFAS-contamination (e.g., 99% or greater reduction from initial levels). Thus, as used herein, remediation refers to a reduction of amount of PFAS in a sample to a level that meets or exceeds local guidelines (see, e.g., Table 1 of Milley, S.A., et al., *Journal of Environmental Management* 222:122-131, 2018). Ball milling devices include horizontal ball mill, planetary ball mill, high-energy ball mill, and industrial ball mill devices. In one embodiment, the ball mill is a horizontal ball mill. In one embodiment, remediation is conducted by rotating the soil in the absence of milling balls, until the soil is remediated. In another embodiment, a plurality of milling balls is added to the ball mill and then the ball mill is rotated. In one embodiment, milling balls are added to the ball milling device so that a ratio of mass of milling balls to mass of PFAS-contaminated soil, which may include milling additives, was about 20:1. A suggested charge ratio (i.e., mass of milling balls to mass of PFAS-contaminated soil, which includes any milling additives) is about 30:1, preferably about 20:1. Once rotation of the ball mill starts, it proceeds for a

specified period of time or until testing of the PFAS-contaminated soil demonstrates a reduced level of PFAS contamination. Once a target low level of contamination is reached the remediated soil is removed from the ball mill. The treated soil is then removed from the ball mill and, if drying agent was used, optionally the drying agent is separated from the treated soil.

Although not wishing to be bound by theory, the inventors suggest that ball milling breaks up PFAS compounds and forms compounds, atoms, and/or ions that are less hazardous. HPLC-MS/MS (e.g., triple quadrupole MS) is used to prove the absence of PFAS compounds in remediated soil. Fluoride and other ions have been shown to be present in the remediated soil.

In another embodiment, a processing additive is added to the PFAS-contaminated soil prior to or during the ball milling process to promote remediation of the PFAS-contaminated soil. Without wishing to be bound by theory, it is believed that a mechanism of PFAS destruction involves the mechanical cracking of high energy intramolecular bonds which generate reactive surface plasmas that react with the C–F bonds of the PFAS compound, initiating a decomposition reaction that results in defluorination. Consequently, remediation of PFAS-contaminated soil can be accelerated by promoting this destruction mechanism. This acceleration can be accomplished by adding to the ball milling device certain surface plasma forming additives known as tribomaterials. Examples of suitable tribomaterials include, but are not limited to, sand, granite, quartz porphyries, feldspar, talc, KOH, NaOH, and aluminum oxides. In this embodiment, the milling process proceeds until a specified PFAS-contamination target level is achieved. The treated soil is then removed from the ball mill and, optionally, the processing additive is separated from the treated soil.

In another embodiment, a defluorination agent is added to the PFAS-contaminated soil prior to and/or during the ball milling process to assist or promote the treatment or remediation of the PFAS-contaminated soil. Without wishing to be bound by theory, it is believed that a mechanism of PFAS destruction involves defluorination through nucleophilic attack by hydroxides. Consequently, the treatment or remediation of PFAS-contaminated soil can be accelerated by promoting this destruction mechanism. This can be accomplished by adding to the ball milling device certain defluorination agents. In one embodiment, a ratio of the mass of defluorination additive to mass of PFAS-contaminated soil, which may include milling additives, is between 0:1 and 1:1. Examples of suitable defluorination agents include, but are not limited to, potassium hydroxide, calcium oxide, silicon dioxide, sodium hydroxide, and iron oxides. To avoid high pH levels in the remediated soil, which could turn the treated soil itself into a hazardous material and preclude its future use, the ratio between the mass of the defluorination

agent and the mass of the PFAS-contaminated soil should be about 1:1, preferably about 0.5:1. Milling proceeds until a specified PFAS-contamination target level is achieved. The treated soil is then removed from the ball mill and, optionally, the defluorination agent is separated from the treated soil.

Referring to Fig. 1, a flowchart is shown depicting steps of an embodiment of the remediation method described herein.

Figs. 2a-h show profiles for samples (15 g or 40 g) of PFOS- or PFOA-contaminated sand that is either dry or water-saturated and that are in the absence or presence of 10 g of KOH additive. All samples had a starting concentration of 5 mg/kg either PFOS or PFOA. It is noted that in Fig. 2f, the amount of PFAS remaining after four hours of milling time was below the detection limit of 0.001 mg/kg.

Referring to Fig. 3, a geometric view is shown of a 23 factorial experimental design, presenting the mass of sand (g), mass of KOH (g) and hydration level (%) on the x, y and z axes, respectively.

Referring to Fig. 4, a graph is shown to compare results of the absence and presence of KOH as a co-milling reagent. It was evaluated at a low level of 0 g (no added KOH pellets) and a high level of 10 g KOH pellets. KOH pellets (available from J.T. Baker 87.5%) were used at a KOH:PFAS mass ratio of > 20:1, assuming the initial concentration of spiked sand was 5 mg/kg. Water saturation studies were conducted to investigate the impact of fluid filled pore space. Dry (0% deionized water content) and fully saturated (100% deionized water content), were selected as the low and high levels, respectively.

Referring to Figs. 5A and 5B, destruction profiles are shown for (A) AFFF impacted sands and (B) AFFF impacted clays (see Table 2 for details).

Referring to Fig. 6, a plot is shown of percentage PFOS destruction versus treatment parameters for FFTA sand using a long roll ball mill (ball mill parameters included sand, a grinding ball size of 2.86 cm, a charge ratio of 10:1, a reagent ratio of 4:1 (sand:KOH), and a speed of 47 RPM).

Referring to Figs. 7A and 7B, plots are shown of concentration PFOS versus ball milling time in FFTA sand and clay using a unitized ball mill. The majority of PFOS destruction occurred within the first hour and was reduced below Canadian human health soil screening guidelines for agriculture/residential/parkland land use (3,200 ng/g).

The following working examples further illustrate the invention and are not intended to be limiting in any respect.

WORKING EXAMPLES

Example 1. Remediation of PFAS-contaminated soil

PFOS and PFOA destruction was evaluated using a 2³ factorial design to permit the analysis of main factor and interaction effects. Milling experiments for eight treatment configurations were performed in duplicate and sampled in duplicate for each of PFOS and PFOA separately. Milling trials were carried out at 275 rpm for 4 hours in a bench top planetary ball mill (Retsch PM 100 with a 250 mL stainless steel grinding jar and ninety 10 mm and ten 15 mm stainless steel grinding balls (total mass 495 g). Samples were collected every 15 minutes within the first hour, and then sampled hourly for the remainder of milling.

Charge ratios of approximately 20:1 (for 15 g spiked sand samples) and 10:1 (for 40 g spiked sand samples) were selected. Sand types were not varied, however, the nature of the sand chosen mimics an environmentally relevant material with a diverse mineralogy. Potassium hydroxide (KOH) as a milling additive was evaluated at a low level of 0 g (no added KOH pellets) and a high level of 10 g KOH pellets. KOH pellets (J.T. Baker 87.5%, CAS# 1310-58-3) were used at a KOH:PFAS mass ratio of > 20:1, assuming the initial concentration of spiked sand was 5 mg/kg.

A dry scenario with 0% deionized water content and fully saturated scenario with 100% deionized water content, were selected as the low and high levels, respectively.

Nepheline syenite (20/40) (Unimin Canada Ltd. CAS# 37244-96-5, Al₂KNaO₈Si₂, porosity 0.43, dry bulk density 1.46 g/cc) was acid washed following procedures used by (Van De Ven and Mumford 2018; Yee, Fein, and Daughney 2000) to remove impurities and fines. The clean sand was dried at 60°C for 48 hours. Sand was spiked to approximately 5 mg/kg PFOS or PFOA using solutions made from reagent grade PFOS (97%, CAS# 1763-23-1) and PFOA (98%, CAS# 335-67-1) purchased from Synquest Laboratories. Results are shown in Table 1.

Example 2. Remediation of AFFF soil samples

AFFF impacted soils were obtained from an unlined (i.e., absence of a liner) firefighting training area (FFTA) where fuel based fires had been extinguished for over 50 years. PFOS was the highest concentration PFAS detected in the FFTA soils. Aside from PFOS, the FFTA was known to have been impacted by other perfluorocarboxylic acids (PFCAs), perfluorosulfonic acids (PFSA), fluorotelomer sulfonates, fluorotelomer alcohols, and petroleum hydrocarbons.

Three sands and three clays of a predicted low, moderate and high concentration, from a FFTA were examined. FFTA sands identified as S1, S2, and S3 were retrieved directly from storage without drying, and had approximately 20% water saturation level. These samples provided examples of environmentally relevant, site-like conditions. FFTA clays, identified as C1, C2, and C3 were dried in a fume hood for two days to eliminate residual moisture to reduce predicted caking. Milling conditions were the same as reported in Example 1. Results are shown in Tables 2 and 3.

Example 3. Remediation using a long roll jar mill

A long roll jar mill (model 803DVM, Norstone, Inc., Bridgeport, Pennsylvania) was used. The 803DVM is a 3-tier model, with each roll measuring 121.92 cm in length. The overall length of the mill is 144.15 cm, the overall width is 41.91 cm, and the overall height is 153.67 cm.

Grinding media (purchased from Norstone) were 52100 chrome steel, in the following sizes: 1/8" (3.175 mm), 1/4" (6.35 mm), 3/8" (9.525 mm), 1/2" (12.7 mm), 3/4" (19.05 mm), and 1-1/8" (28.575 mm).

Unlined stainless steel (Type 304) grinding jars with internal lifter bars (model 611L, from US Stoneware, East Palestine, Ohio) were used. The jar size is classified as "6"; these jars have a 36.20 cm diameter, a 26.67 cm height (34.29 overall height including the locking mechanism), and a 20.32 cm opening. The corresponding internal volume is 25 L +/- 5 %. The weight of each jar is 10.89 kg.

PFAS-contaminated soil samples as described above were remediated using the long roll jar mill. Figs. 6 and 7A, 7B show the results.

Example 4. Analytical Methods

Solid sample extraction

Sand and sediment samples were extracted in basic (0.1% NaOH) high performance liquid chromatography (HPLC) grade methanol (CAS 67-56-1). Every 10 samples were spiked with 0.02 uL mass-labelled surrogate. Samples were vortexed for 10 seconds and agitated on an end-over-end shaker at 65 rpm for 30 minutes. Samples remained in solvent overnight. After sitting overnight, samples were vortexed for 30 seconds. Samples were then centrifuged at 4,000 rpm for 10 minutes to settle suspended soils and left to sit for a minimum of 5 minutes. Samples were filtered through a Whatman 0.45 um glass microfiber filter into a sterile, pre-weighed 15 mL centrifuge tube. Sample pH was measured with litmus paper and adjusted to pH 10-12 with 10% sulfuric acid, when required. A 750 uL aliquot of the sample was transferred to a pre-weighed HPLC vial. Each vial was then spiked with 10 uL of either PFDoA (for the spiked sand experiments) or mass-labelled surrogate (for the FFTA soil experiments) as an internal standard to track HPLC-mass spectrometer (MS) drift.

Sample analysis

Samples were analyzed directly (without cleanup) via LC-MS/MS utilizing multiple-reaction-monitoring (MRM) mode. The MRM method used analyzed the samples for PFBA (perfluorobutanoic acid), PFBS (per-fluorobutanesulfonic acid), PFDA (perfluorodecanoic acid), PFDoA (perfluorododecanoic acid), PFHpA (per-fluoroheptanoic acid), PFHxA (perfluorohexanoic acid), PFHxS (perfluorohexanesulfonic acid), PFNA (perfluorononanoic acid), PFOA (perfluorooctanoic acid), PFOS (perfluorooctanesulfonic acid), PFOSA (perfluorooctanesulfonamide), PFPeA (perfluoropentanoic acid), PFUnA (perfluoroundecanoic acid). Calibration standards for PFOS/PFOA were prepared using basic methanol.

LC-MS/MS analysis

Liquid chromatography was performed on an Agilent 1260 Infinity Series Bio-Inert HPLC system using two mobile phases, HPLC-grade water with ammonium acetate (2 mM) and methanol with ammonium acetate (2 mM), with gradient delivered at a flow rate of 0.4 mL/min. A 10 uL injection volume was used. A Zorbax Eclipse Plus C18 Column was used in conjunction with a paired guard

column. Initial eluent conditions were 94% water and 6% methanol. The percent methanol was ramped up to 100% until 6 minutes, held at 100% until 8 minutes, ramped down until 11 minutes, and the system was given 4 minutes post-run to re-equilibrate the mobile phase and pressure flow.

An Agilent 6460 Triple Quadrupole Mass Spectrometer operating in negative electrospray ionization mode using a multiple reaction monitoring (MRM) method was employed for sample analysis. Two MRM transitions were acquired for all possible analytes, but some analytes only had single transitions available. The dwell time for each transition was 120 ms. The monitored transitions were analyte dependent and were the same or similar to those used previously for the aforementioned suite of 13 PFAS.

Optimal instrumental source parameters were determined and are as follows: ion spray voltage, 4,000*V; curtain gas flow, 35 arbitrary units (au); nebulizer gas flow, 50 au; turbo gas flow, 50 au; medium collision gas flow; and source temperature, 650°C. Nitrogen provided by a NitroFlow Gas Generator System was used for the nebulizer and drier gas, and a nitrogen tank was used as the curtain and collision gas.

Quantitation was performed using Masshunter Quantitation Software with calibration curves generally having r^2 values greater than 0.99. Limits of quantitation were analyte, matrix, and run-dependent but were approximately 1 ng/g in soil and 0.4 ng/L in aqueous samples.

EQUIVALENTS

It will be understood by those skilled in the art that this description is made with reference to certain embodiments and that it is possible to make other embodiments employing the principles of the invention which fall within its spirit and scope.

Table 1A. Destruction percentages for all treatments of 2³ factorial design in PFOS and PFOA spiked sand samples at 4 hours of milling

Treatment combination	PFOS	PFOA
15 g dry sand with KOH	81% ± 11%	96% ± 4%
15 g dry sand, no KOH	98% ± 0.4%	99% ± 0.2%
15 g saturated sand with KOH	54% ± 13%	83% ± 8
15 g saturated sand no KOH	Negligible	38% ± 9%
40 g dry sand with KOH	99% ± 0.5%	99%*
40 g dry sand, no KOH	92% ± 6%	88% ± 1%
40 g saturated sand with KOH	87% ± 13	89% ± 2
40 g saturated sand, no KOH	Negligible	Negligible
* <QL by 4 hr of milling		

Table 1B. Destruction percentages for all treatments of 2³ factorial design in PFOS and PFOA spiked sand samples at 15 min, 1 hr and 4 hrs of milling

Milling Time	15 minutes		1 hour		4 hours	
Treatment combination	PFOS	PFOA	PFOS	PFOA	PFOS	PFOA
15 g dry sand <i>with</i> KOH	45% ± 10%	82% ± 1%	73% ± 6%	90% ± 5%	81% ± 11%	96% ± 4%
15 g dry sand, <i>no</i> KOH	70% ± 18%	59% ± 8%	88% ± 9%	83% ± 16%	98% ± 0.4%	99% ± 0.3%
15 g saturated sand <i>with</i> KOH	22% ± 15%	74% ± 2%	39% ± 7%	74% ± 10%	54% ± 13%	83% ± 8
15 g saturated sand <i>no</i> KOH	Negligible	29% ± 13%	Negligible	34% ± 5%	Negligible	38% ± 9%
40 g dry sand <i>with</i> KOH	90% ± 6%	94% ± 1%	97% ± 10%	97% ± 5%	99% ± 0.5%	99%*
40 g dry sand, <i>no</i> KOH	59% ± 4%	65% ± 27%	76% ± 4%	70% ± 7%	92% ± 6%	88% ± 1%
40 g saturated sand <i>with</i> KOH	97% ± 15%	88% ± 2%	99% ± 24%	88% ± 11%	99% ± 13	92% ± 2
40 g saturated sand, <i>no</i> KOH	Negligible	Negligible	Negligible	Negligible	Negligible	Negligible
* <QL by 4 hours of milling						

Table 2. Properties of FFTA sands and clays

ID	Soil type	Depth below ground surface (m)	Initial PFOS concentration (ng/g)	PFOS concentration at specified no. hours of milling (ng/g)
S1	sand	0 - 0.4	228 ± 10	132 ± 43 ^a
S2	sand	0.1 - 0.5	1538 ± 49	673 ± 14 ^b
S3	sand	0.6 - 1.0	2070 ± 177	633 ± 75 ^b
C1	clay	1.2 - 1.5	639 ± 192	100 ± 30 ^b
C2	clay	1.0 - 2.2	1670 ± 501	65 ± 20 ^b
C3	clay	1.5 - 2.2	639 ± 573	245 ± 11 ^b

^a5 hours of milling

^b6 hours of milling

Table 3. Destruction percentages for FFTA sands and clays after 6 hours of milling

Media	PFOS	PFOSA	PFHxA	PFPeA	PFBA	PFHxS
S1	42% ± 30%	NO DESTRUCTION	<QL by 1 hr	<QL by 1 hr	x	x
S2	56% ± 2%	NO DESTRUCTION	<QL by 1 hr	x	<QL by 1 hr	63% ± 17%
S3	69% ± 12%	x	x	x	x	x
C1	84% ± 5%	x	<QL by 1 hr	x	x	NO DESTRUCTION
C2	96% ± 1%	x	<QL by 4 hr	<QL by 1 hr	<QL by 1 hr	<QL by 6 hr
C3	69% ± 1%	x	x	<QL by 1 hr	x	x

x – Not detected in sample.

CLAIMS

1. A method for remediating PFAS-contaminated soil, comprising:

disposing PFAS-contaminated soil into a ball mill;

operating the ball mill until the PFAS-contaminated soil becomes soil that is substantially free of PFAS contaminants.
2. The method of claim 1, further comprising adding drying agents to the ball mill, and operating the ball mill until the hydration level of the PFAS-contaminated soil is in a selected range.
3. The method of claim 1 or 2, wherein the ball mill is a horizontal ball mill or a long roll ball mill.
4. The method of any one of claims 1 to 3, further comprising disposing a plurality of milling balls in the ball mill prior to rotating the ball mill.
5. The method of any one of claims 1 to 4, further comprising disposing a gas into the ball mill.
6. The method of claim 5, wherein the gas is continuously disposed into the ball mill while the ball mill is operating.
7. The method of claim 5 or 6, wherein the gas is air, argon, nitrogen, helium, or a combination of two or more thereof.
8. The method of claim 4, wherein the disposing a plurality of milling balls occurs when the PFAS-contaminated soil has attained a selected hydration level.

9. The method of any one of claims 1 to 8, further comprising disposing a milling additive in the ball mill.
10. The method of claim 9, wherein the milling additive comprises a defluorination agent, a processing additive, a drying additive, or a combination of two or more thereof.
11. The method of claim 10, wherein the defluorination agent comprises potassium hydroxide, sodium hydroxide, calcium oxide, silicon dioxide, sand, or a combination of two or more thereof.
12. The method of claim 10, wherein the processing additive comprises a tribomaterial.
13. The method of claim 12, wherein the tribomaterial is sand, granite, quartz porphyries, feldspar, talc, aluminum oxide, KOH, NaOH, SiO₂, porphyries, or a combination of two or more thereof.
14. The method of claim 10, wherein the drying additive comprises sodium chloride, calcium chloride, sodium hydroxide, copper sulphate, phosphorus pentoxide, potassium hydroxide, silica gel, lithium bromide, lithium chloride, or a combination of two or more thereof.
15. The method of any one of claims 1 to 12, further comprising removing debris and bulk natural organic and inorganic matter from the PFAS-contaminated soil prior to transferring the PFAS-contaminated soil to the ball mill.
16. The method of claim 10, wherein the defluorination additive is added in a ratio of defluorination additive to PFAS-contaminated soil of about 0:1 to about 1:1.

17. The method of claim 4, wherein the milling balls are added in a mass ratio of milling balls to PFAS-contaminated soil of about 20:1.
18. The method of any one of claims 1 to 17, wherein the PFAS-contaminated soil comprises perfluoroalkyl substances.
19. The method of any one of claims 1 to 17, wherein the PFAS-contaminated soil comprises polyfluoroalkyl substances.
20. The method of any one of claims 1 to 17, wherein PFAS-contaminated soil comprises perfluorooctanesulfonic acid (PFOS), perfluorooctanoic acid (PFOA), perfluorooctanesulfonamide (PFOSA), perfluorohexanoic acid (PFHxA), perfluoro-n-pentanoic acid (PFPeA), pentafluorobenzoic acid (PFBA), perfluorohexanesulfonic acid (PFHxS), or any combination thereof.
21. The method of any one of claims 1 to 20 wherein the PFAS-contaminated soil comprises PFAS in an amount that is about 5 ppm.
22. The method of claim 1, wherein the remediation is conducted in the absence of base selected from KOH, NaOH, or a combination thereof.

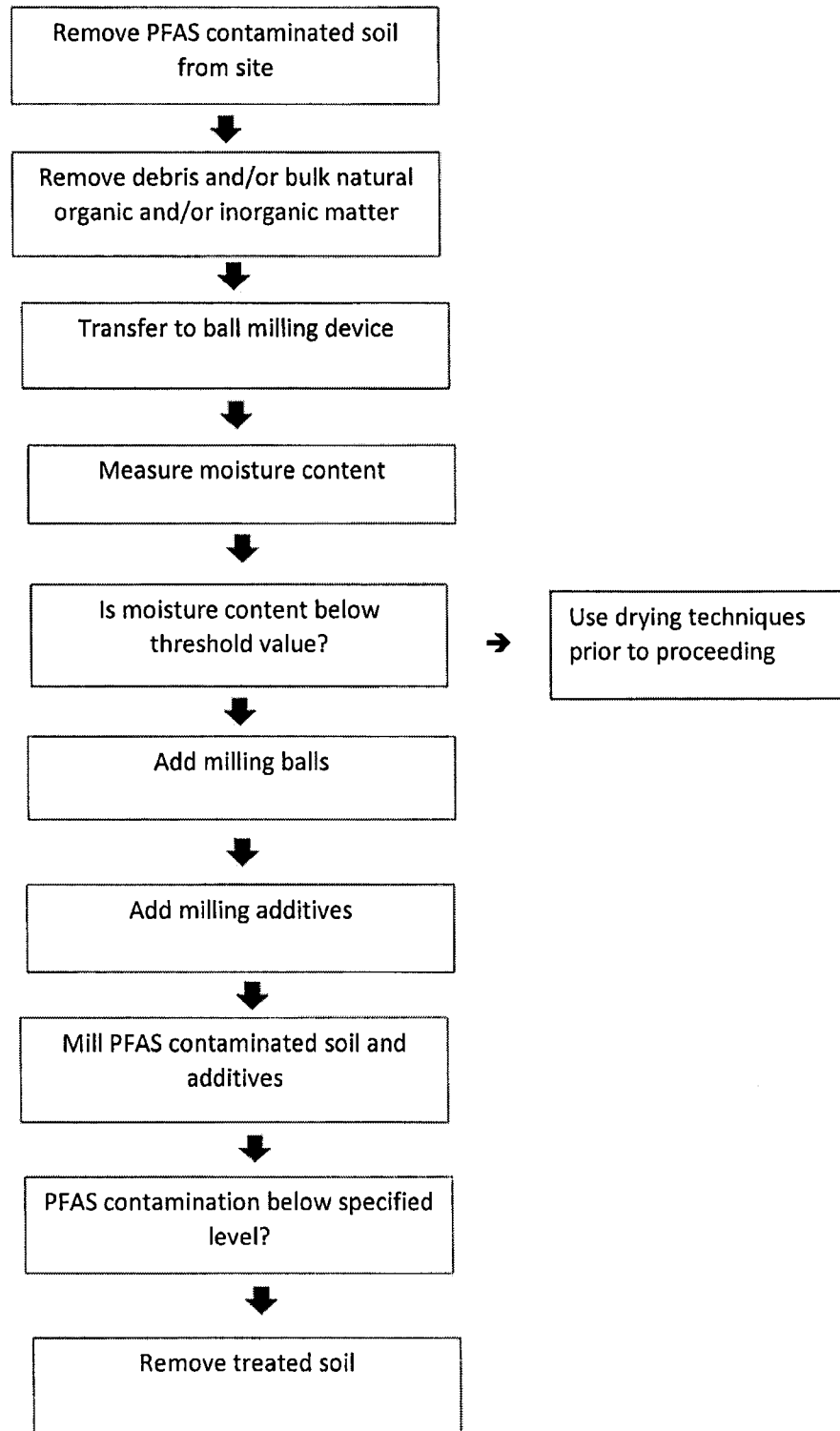


Fig. 1

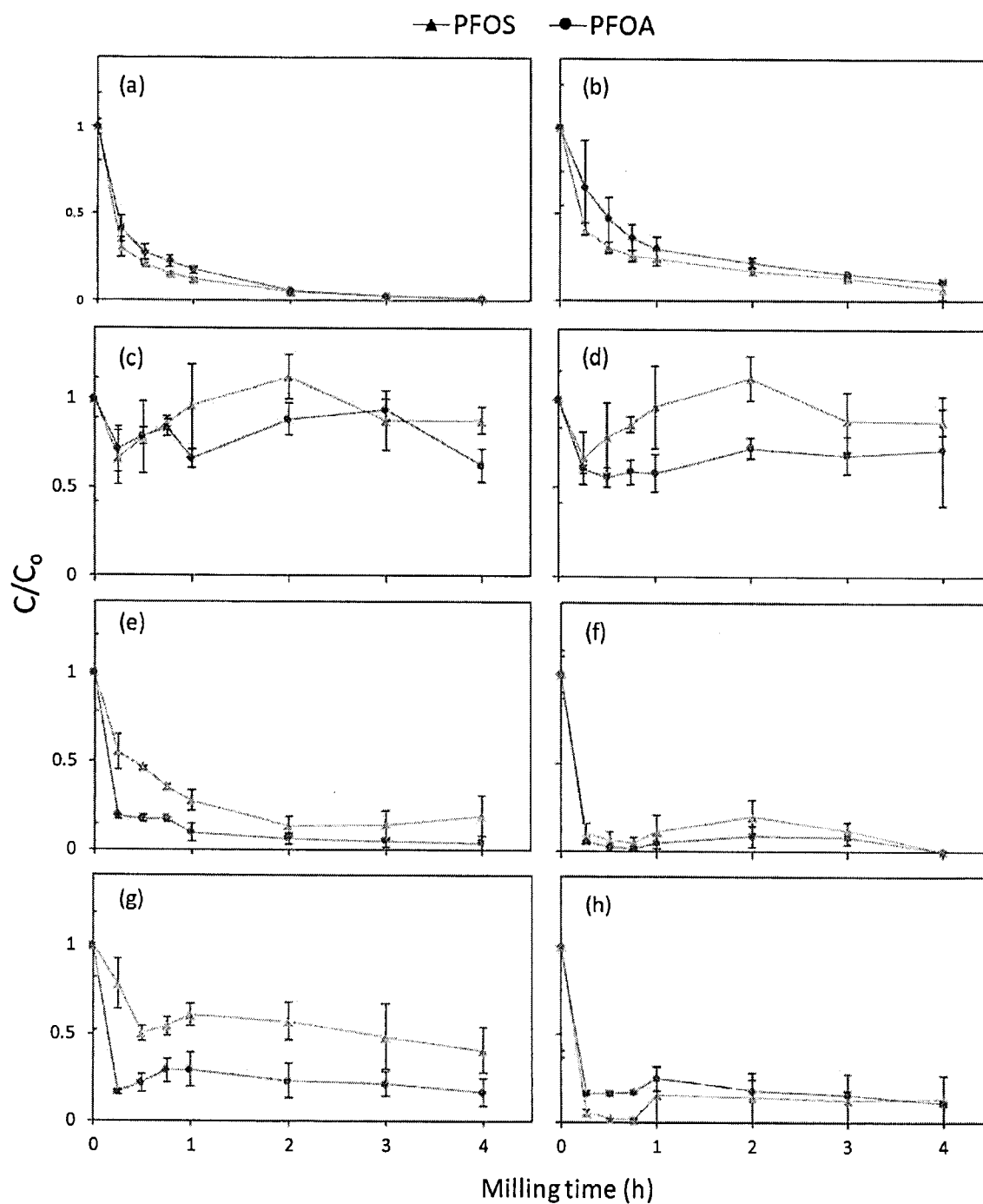


Fig. 2a-h

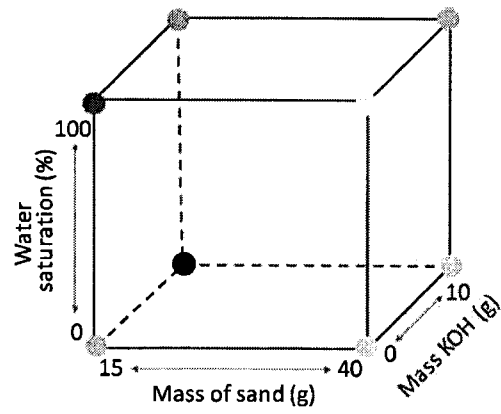


Fig. 3

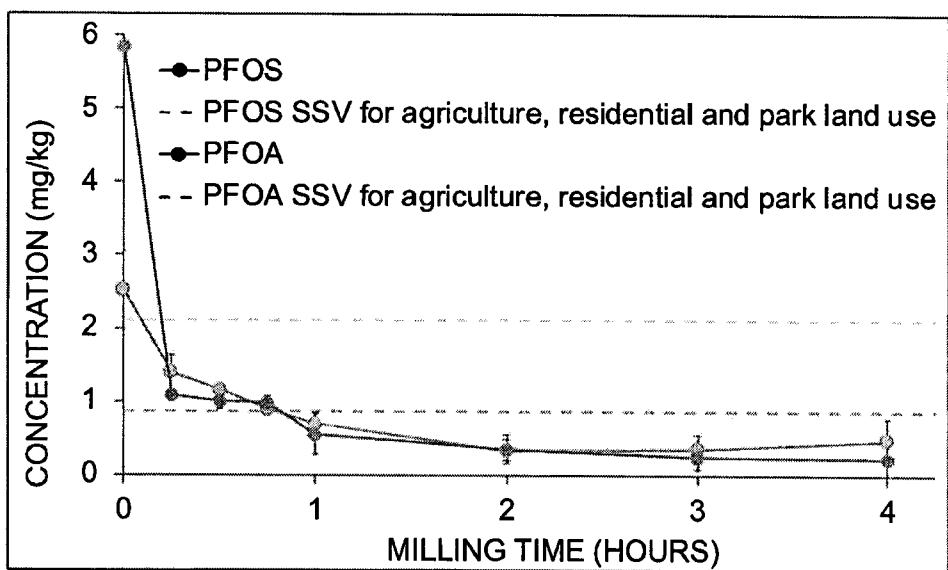


Fig. 4

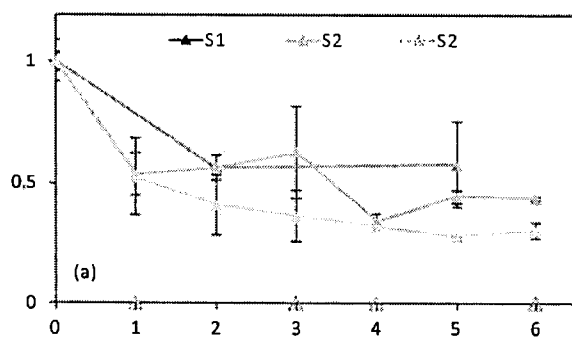


Fig. 5A

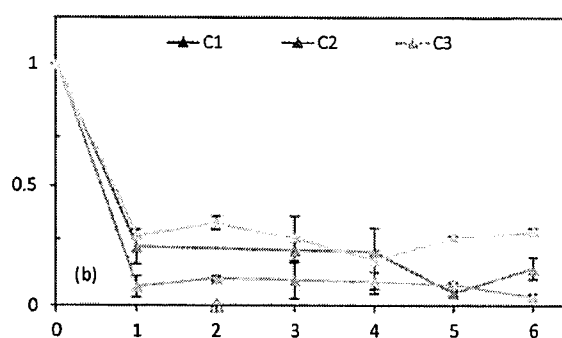


Fig. 5B

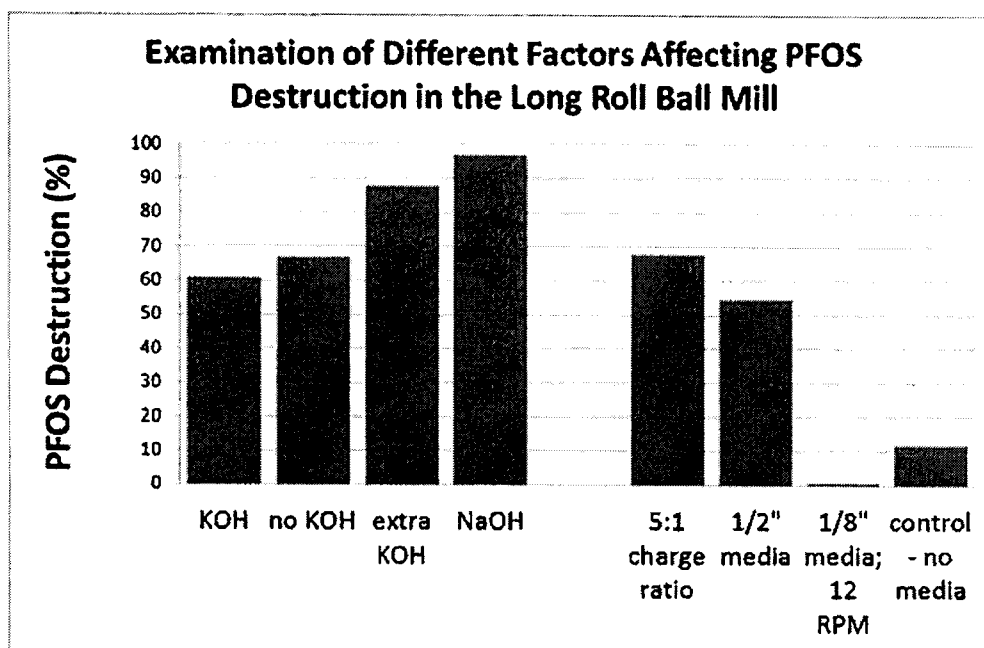


Fig. 6

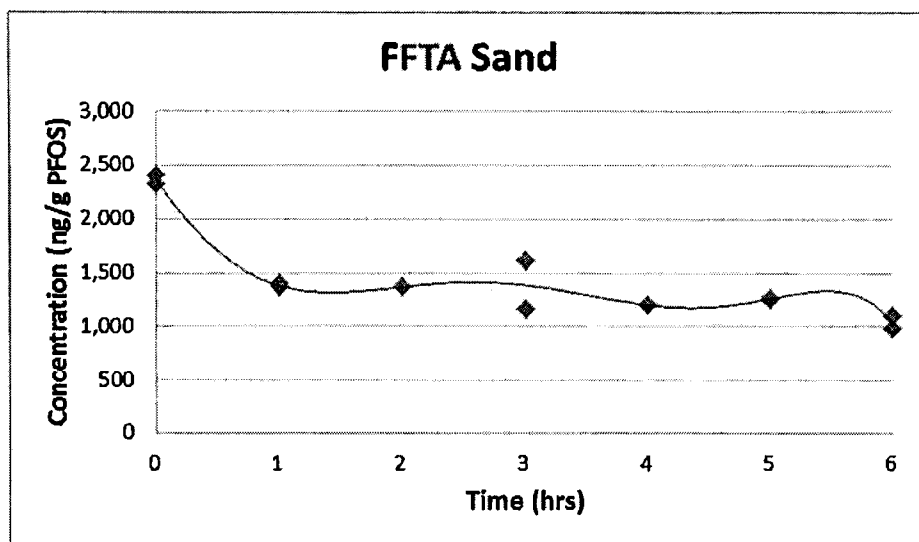


Fig. 7A

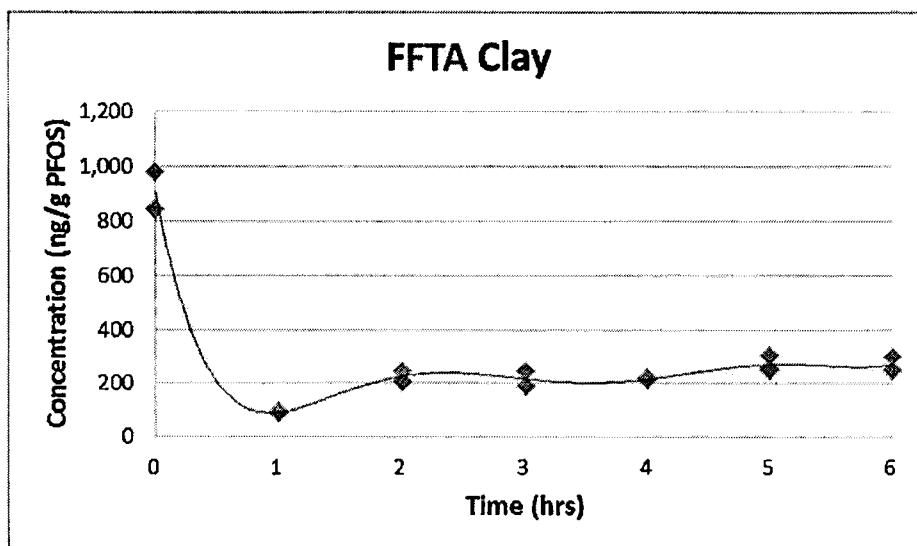


Fig. 7B

