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**United States Patent** [19]

Mouk et al.

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[54] **METHODS OF DECONTAMINATING  
SUBSTATES WITH IN-SITU GENERATED  
CYANIDES**

5,110,364 5/1992 Mazur et al. .... 134/2  
5,411,574 5/1995 Turney et al. .... 75/743  
5,414,200 5/1995 Mouk et al. .... 588/205

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**Related U.S. Application Data**

[63] **Continuation-in-part of Ser. No. 507,126, Aug. 23, 1995,**  
**Pat. No. 5,613,238, which is a continuation-in-part of Ser.**  
**No. 304,791, Sep. 12, 1994, Pat. No. 5,495,062.**

[51] **Int. Cl.<sup>6</sup>** ..... **G21F 9/00**

[52] **U.S. Cl.** ..... **588/1; 588/18; 588/236;**  
**134/2; 210/753**

[58] **Field of Search** ..... **588/1, 18, 236;**  
**210/753; 134/2**

[56] **References Cited**

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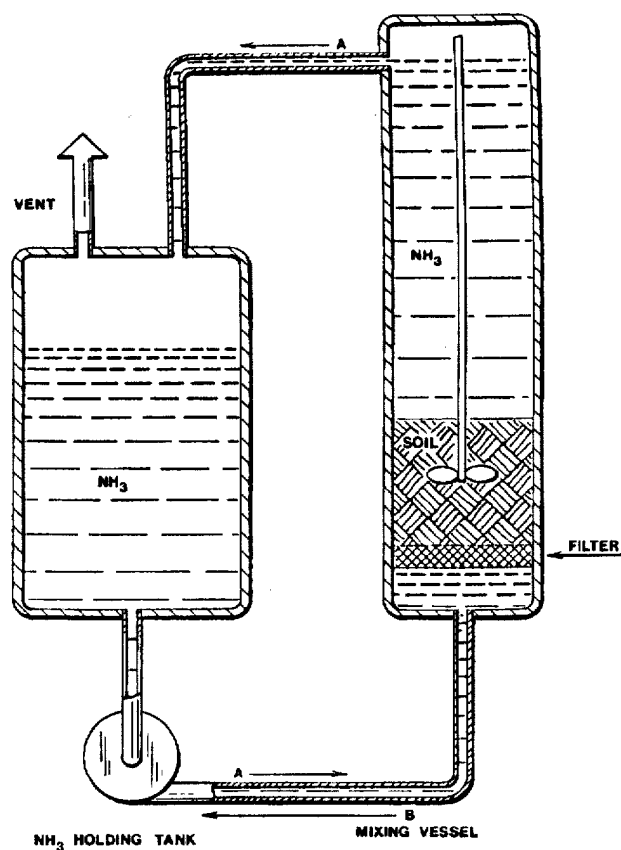
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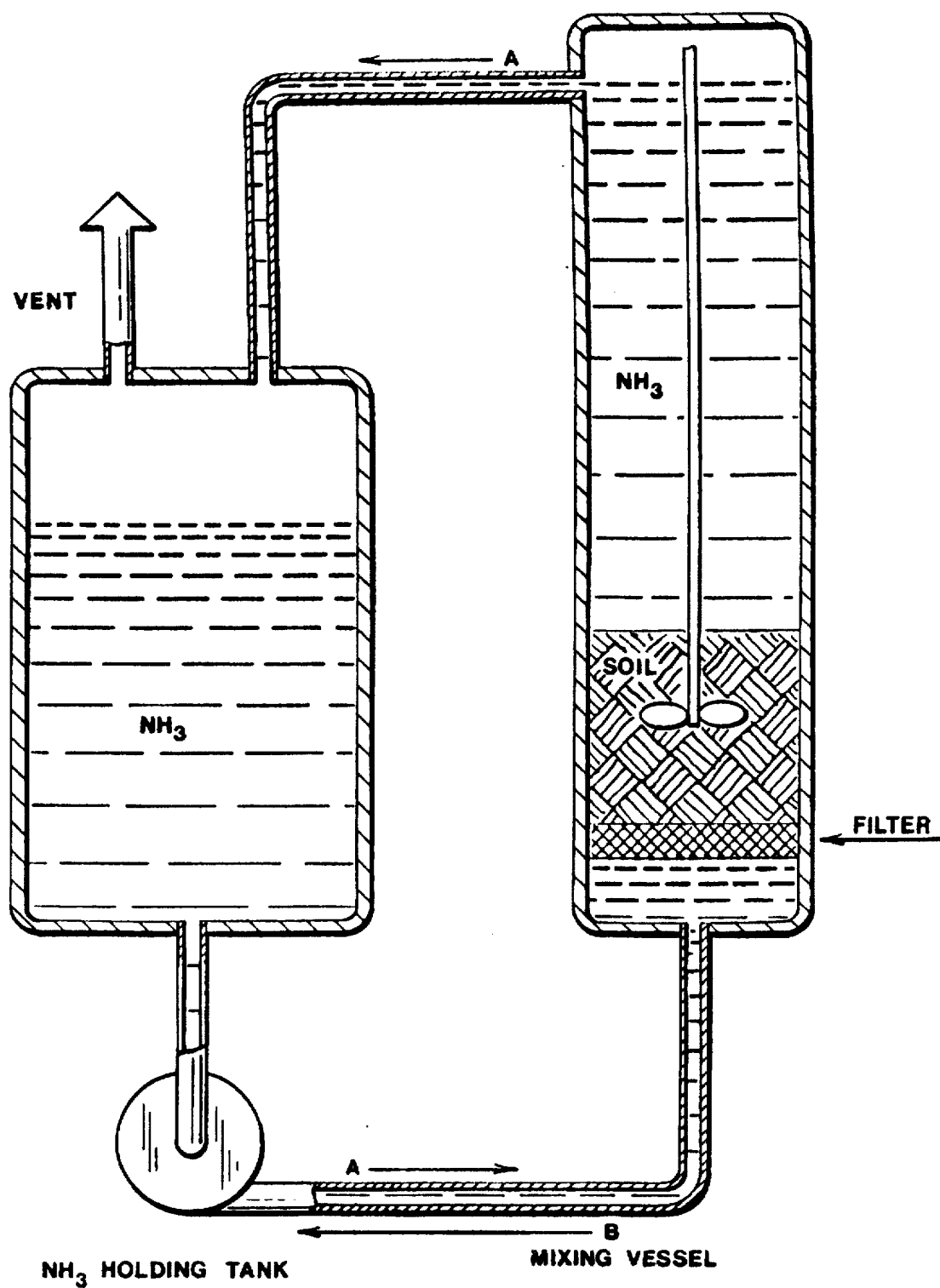
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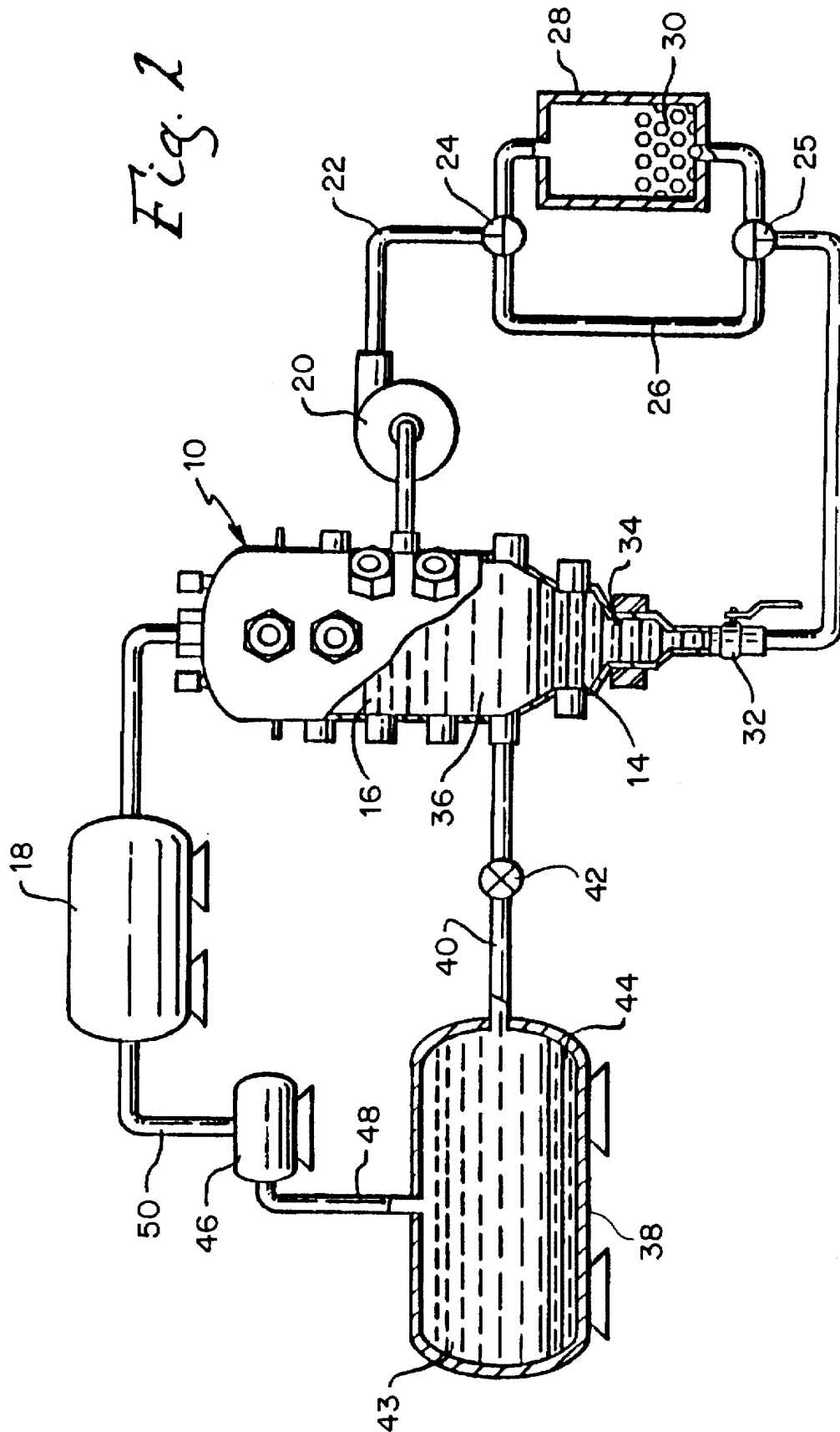
[57] **ABSTRACT**

Solid and liquid substrates, such as soil and solvents having radioactive metals or hazardous non-radioactive metals are decontaminated with the aid of cyanide ion generated in-situ to form co-ordination compounds with the unwanted metal contaminants. Cyanides are prepared by introducing into an ammoniacal liquid-containing slurry of a contaminated soil, or other solid or liquid substrate, a refrigerant compound, such as a hydrochlorofluorocarbon which produces ammonium cyanide, which in-turn forms a complex with the hazardous metal contaminant for separation with the ammoniacal liquid. The process may also utilize solvated electrons to at least partially dehalogenate a perhalogenated refrigerant like diclorodifluoromethane (R-12). Process avoids exposure to potentially hazardous cyanides through in-situ generation, while simultaneously destroying unwanted refrigerants which are potentially harmful to Earth's ozone layer.

**40 Claims, 2 Drawing Sheets**



*Fig. 1*



# METHODS OF DECONTAMINATING SUBSTRATES WITH IN-SITU GENERATED CYANIDES

## CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of Ser. No. 08/507,126 filed Aug. 23, 1995, now U.S. Pat. No. 5,613,238, which is a continuation-in-part of Ser. No. 08/304,791, filed Sep. 12, 1994, now U.S. Pat. No. 5,495,062.

## TECHNICAL FIELD

The present invention relates to methods of decontaminating solid and liquid substrates, including nuclear waste-containing soils, soils contaminated with ions of hazardous nonradioactive metals or metalloids and soils contaminated with mixed wastes by methods which also permit the reclamation of residual soil products.

## BACKGROUND OF THE INVENTION

As a result of military testing programs involving the detonation of nuclear devices, both in the United States and abroad, the environment, and particularly vast areas of soil in testing zones have become contaminated with nuclear waste materials. In some instances, for example, detonation of a nuclear device failed to achieve the needed critical mass of the radioactive components, resulting in substantial quantities of enriched uranium and plutonium being scattered over wide areas of desert testing grounds. In addition to nuclear testing programs, contamination of soil with radioactive materials has occurred at nuclear weapon manufacturing sites, such as at Hanford, Wash.; Rocky Flats, Colo.; Savannah River, Ga.; Oak Ridge, Tenn., and elsewhere through spills or releases into the environment.

Efforts to successfully decontaminate these sites have proven difficult and extremely costly due to massive amounts of soil requiring treatment and/or storage. Cleanup has usually meant a slow and costly process where the contaminated soil is excavated and transferred to a different location for storage. Abandoned salt mines and mountain repositories have been proposed as storage facilities for nuclear wastes, but too often rejected later on for technical and/or political reasons. Because of a finite amount of space available for storage of nuclear waste materials progress in the reclamation of contaminated sites has been slow.

In an effort to mitigate the nuclear waste storage crisis systems for reducing bulk quantities of contaminated soil requiring storage have been proposed wherein the radioactive components are concentrated in a soil fraction. One system, for example, employs an aqueous washing process requiring the use of soil scrubbing chemicals, multiple separation steps, water treatment, and so on. Although quite effective in concentrating radioactive components in silt and clay fractions of soil, capital and operating costs per ton of soil treated are viewed as economically unattractive. Consequently, most methods proposed for concentrating nuclear waste have not received wide acceptance.

Like nuclear wastes, environmental contamination by metal ions, especially when present in soil or groundwater, poses serious threats to human, animal and plant life. Metals such as lead, chromium, cadmium and arsenic have been released into the environment in quantities which make large-scale remediation projects necessary in order to protect the health of the general public. Such metals represent some of the more difficult environmental contaminants to treat

because they form salts or oxides, which in turn dissociate into ionized species facilitating their introduction into the food and biological chain.

While the inventors have discovered new and useful means for enhancing the removal of radioactive metals, hazardous non-radioactive metals and "mixed wastes" from soils through decontamination processes which include inter-alia the introduction of ligand complexing agents like ammonium cyanide, sodium cyanide, etc., to form co-ordination compounds, their use may not always be desirable. Regulatory laws, for example, provide for special safety precautions in transportation, storage and handling cyanides. This is because cyanides are highly toxic substances which need not be ingested to cause a fatality. They are also capable of acting through the lungs or skin. Salts of HCN, such as sodium cyanide and calcium cyanide are toxic by ingestion, skin contact or inhalation of their dust. Cyanide salts can absorb moisture from the air and evolve HCN, and therefore, must be kept scrupulously dry.

Accordingly, there is need for an innovative, cost-effective process for decontaminating solid and liquid substrates, such as soils, polar and non-polar solvents. Soils containing nuclear waste materials, such as those generated at sites of nuclear weapon plants, nuclear testing sites, and wherever treatment calls for managing substantial volumes of soil contaminated with radioactive materials. The process should enable reduction of space otherwise required for storage of untreated soils by concentrating in a small fraction of the soil while also permitting reclamation of these sites. Likewise, a cost effective process is needed for decontaminating soils containing ions of hazardous nonradioactive metals and metalloids, such as mercury, arsenic, selenium, chromium, lead, etc., and mixed wastes-containing such hazardous ions together with nuclear wastes like radionuclides of the actinide series, and/or organic compounds like PCBs. Finally, there is also a need for improved processes of decontaminating soils and other substrates which allows for a safer and less hazardous use of cyanides by eliminating the need for either handling, storing or transporting cyanide-containing chemicals to the work site.

## SUMMARY OF THE INVENTION

It is a principal object of the invention to provide improved, more economic methods for separating radioactive and non-radioactive components from contaminated soil wherein the treated soil is made sufficiently free of the potentially toxic components, i.e., metals and metalloids as to permit reclamation of the soil. The expression "sufficiently free" is intended to mean soil treated according to the present invention so it (i) is practically devoid of all unwanted radioisotopes (radionuclides), or (ii) contains residual amounts of low-level radioisotopes allowing treated soil to be reclaimed as is, or (iii) contains amounts of low-level radioisotopes which can be diluted sufficiently with an inert material to reduce its activity to an acceptable level.

Expressions, such as "nuclear waste" and "radioactive waste" as recited in the specification and claims are intended to refer to soils contaminated with isotopic forms of elements having unstable nuclei which disintegrate and emit energy most commonly as alpha particles, beta particles and gamma rays. They include mainly products or by-products of nuclear fission or unreacted products of a nuclear device. Representative examples include such radionuclides as Cs<sup>137</sup>; CO<sup>60</sup>; K<sup>40</sup>; Pu<sup>236</sup>; U<sup>235</sup>; U<sup>238</sup>; RU<sup>103</sup>; Te; Sr<sup>90</sup>; Rb; Y; Re; Rh; Pd; Tc; Np and Am.

Methods of the invention provide for the recovery of nuclear waste materials in soil fractions, particularly in small, high surface area particles, such as soil fines and silt fractions of clay for subsequent storage or further treatment. By concentrating nuclear waste materials in soil fines and clay silt, for example, storage space requirements per ton of soil treated are significantly reduced, perhaps by as much as 90 percent over storage space requirements otherwise required for untreated soils.

Methods of the invention comprise the steps of:

- (a) mixing a liquid ammonia or ammoniacal liquid with a soil contaminated with nuclear waste in a closed vessel to form an ammonia-nuclear waste containing soil dispersion or slurry;
- (b) allowing soil particles to selectively precipitate from the slurry or dispersion of step (a) to form a lower solid phase of soil particulates while forming an upper liquid-solid phase comprising soil fines dispersed in the liquid ammonia;
- (c) separating the upper liquid-solid phase from the lower solid phase of soil particulates, the fines of the upper liquid-solid phase having the majority of the radionuclide contaminant(s), or in other words, the lower solid phase is sufficiently free of the nuclear waste materials for reclamation of the soil particulates, and
- (d) separating the ammoniacal liquid from the soil fines containing the nuclear waste material for disposal or further treatment of the fines.

The term "disposal" is intended to include storage of the nuclear waste-containing soil fines. The expression "further treatment" is intended to include any procedure which will modify the potentially toxic properties of the radionuclide material to substances of reduced toxicity and impact on the environment, or to materials which can be recovered as useful by-products. It will be understood, methods of disposal and further treatment of the concentrated nuclear waste material by themselves do not constitute part of this invention.

Mazur et al in U.S. Pat. No. 5,110,364 disclose ammonia as a pretreatment in desorbing organic compounds, and particularly halogenated organic compounds like PCBs from soil, followed by chemical destruction of the compound by dehalogenation through a chemical reduction mechanism with solvated electrons. Mazur et al, however, fail to teach or suggest utilizing ammonia as a means of separating soil into fractions wherein the larger, lower surface area particulates are allowed to separate out from the less dense liquid ammonia-solid phase containing the smaller, higher surface area soil fines. In contradistinction, the methods of Mazur et al provide for treating "whole" soil in the reduction of the halogenated carbon compound contaminants without isolating soil particles or soil fractions from ammonia/soil slurries by allowing phase separation to occur and performing various separation steps.

Serendipitously, it was found that radionuclides appear to have a preferential affinity for the smaller, higher surface area fines and silts of soils, clays and sand. Hence, by isolating the fines and silt particulates, especially the smaller particles having higher surface areas relative to the particles precipitating out of ammonia-soil dispersions one, in effect, is selectively concentrating the nuclear waste material in the smallest volume of natural solid carrier material to effectively lessen the tonnage volume of material requiring storage or further treatment. Accordingly, it is a primary objective of the invention to provide an improved more economic method for concentrating a substantial portion of

the nuclear waste material in a reduced soil fraction for more efficient management of soil cleanup projects involving large volumes of soil, so as to permit reclamation of major volumes of previously contaminated soil.

It is still a further object of the invention to optionally include the step of recovering and recycling for reuse in the foregoing process ammonia from step (d), the recovery and recycling being performed by methods already known in the art.

For purposes of this invention, the expressions "liquid ammonia" and "ammoniacal liquid" as used herein are generally intended to include nitrogen-containing solvents, such as anhydrous liquid ammonia. This would also include solutions of ammonia comprising small amounts of water. However, when used in dissolving metal reactions in forming solvated electrons, as will be discussed in greater detail below, the ammoniacal liquid is preferably non-aqueous. In addition to liquid ammonia, other nitrogen-containing solvents and co-solvents can be employed which are inert in the presence of solvated electrons. Representative classes include primary amines, secondary amines, tertiary amines, and mixtures of such amines. Examples of such amines include alkyl amines, like methyl amine, ethyl amine, dimethyl amine, triethyl amine, n-propyl amine, isopropyl amine, pyrrolidine, and other nitrogen-containing solvents and co-solvents which are suitably inert in the presence of electrons.

It is still a further object to provide an additional embodiment of the invention for decontaminating soil containing nuclear waste by the steps of:

- (a) mixing a liquid ammonia or ammoniacal liquid with soil contaminated with nuclear waste in a closed vessel to form an ammonia-nuclear waste-containing soil dispersion or slurry;
- (b) treating the dispersion or slurry of step (a) with solvated electrons by contacting with a reactive metal;
- (c) allowing soil particles to selectively precipitate from the dispersion or slurry of step (b) to form a lower phase of soil particulates while forming an upper liquid-solid phase comprising soil fines suspended in the liquid ammonia;
- (d) separating the upper liquid-solid phase from the lower phase of soil particulates, the lower phase of soil particulates being sufficiently free of nuclear waste, and
- (e) separating the ammonia from the soil fines for disposal or further treatment of the fines.

While it has been observed that ammonia has a unique ability to form very fine slurries when mixed with soils, it was observed that dispersions of soil appear to be further altered by some mechanism not fully understood, when in the presence of solvated electrons formed in dissolving metal reactions with ammonia. That is, by contacting the ammoniated soil dispersion with either an alkali or alkaline earth metal, solvated electrons are formed in the mixture, in-situ. The solvated electrons appear in some instances to optimize separation of smaller soil fines. In some instances where particle size cross-section is larger than desired, electrons solvated in liquid ammonia, for example, appear to provide more optimal demarcation and separation of the smaller fines containing nuclear waste materials from other particles of the slurry.

As in the first embodiment of the invention, the foregoing second embodiment of the invention contemplates the step of recovering and recycling the ammonia from step (e) for reuse. Similarly, the precipitated residual solid soil particles of step (d) are sufficiently free of radioisotopes to permit reclamation of large bulk volumes of soil.

In accordance with the invention, it was also discovered the foregoing process with ammoniacal solutions, etc., is also useful in decontaminating soils containing hazardous, but nonradioactive metals by the steps of:

- (a) mixing in a closed vessel an ammoniacal liquid with a soil contaminated with at least one ion of a hazardous metal or metalloid to form a dispersion or slurry;
- (b) separating an ammoniacal liquid-containing product from the dispersion or slurry of step (a) to yield a soil residue sufficiently free of ions of the hazardous metal or metalloid to permit reclamation, and
- (c) separating the ammoniacal liquid from the ammoniacal liquid-containing product of step (b) to yield a hazardous metal or metalloid-containing residue for disposal or further treatment.

While not wishing to be held to any specific mechanism of action involved in separating ions of hazardous metals and metalloids from soils it has been observed the target material is frequently soluble in the ammoniacal liquid. In this regard, co-ordination compounds may form in the soil washing process with ammonia, and possibly form metal-ammonia ligand complexes. Representative metals of such coordination compounds and complexes may include those from the group of arsenic, antimony, selenium, cadmium, cobalt, mercury, chromium, lead and mixtures thereof.

Co-ordination compounds can also be prepared by introducing other ligand complexing agents into the ammonia-soil slurry-containing hazardous metals. Such metals can be removed by forming, for example, ammonia soluble metal cyanide ligand complexes by adding a source of cyanide ions, e.g., sodium cyanide, ammonia cyanide, etc., to the slurry. Removal of the ammoniacal liquid results in the elimination of the hazardous metal from the soil fraction.

As a further embodiment of the invention soils containing hazardous nonradioactive metals may be decontaminated by the steps of:

- (a) mixing in a closed vessel an ammoniacal liquid with a soil contaminated with at least one ion of a hazardous metal or metalloid to form a dispersion or slurry;
- (b) allowing soil particles to selectively precipitate from the dispersion or slurry of step (a) to provide a lower phase comprising a precipitate of soil particulates while forming an upper liquid-solid phase comprising soil fines dispersed in the ammoniacal liquid;
- (c) separating the upper liquid-solid phase from the lower phase, the precipitate of soil particulates of the lower phase being sufficiently free of ions of the hazardous metal or metalloid to permit reclamation of the soil particulates, and
- (d) separating the ammoniacal liquid of the upper liquid-solid phase to yield a residue comprising the hazardous metal or metalloid for disposal or further treatment.

It is yet a further aspect of the invention to provide a method of treating soils contaminated with mixed wastes, wherein the waste may be comprised of an ion of a hazardous non-radioactive metal or metalloid and a nuclear waste, for example. Typically, the nuclear waste is comprised of a radionuclide or radioactive isotopic metal. They are generally intended to include metals of the actinide series, such as uranium, plutonium, thorium and mixtures of the same.

As a further embodiment of the invention, soil contaminated with hazardous nonradioactive metals may be decontaminated with ammoniacal liquids and solvated electrons by the steps of:

- (a) mixing in a closed vessel an ammoniacal liquid with a soil contaminated with at least one ion of a hazardous metal or metalloid to form a dispersion or slurry;

- (b) treating the dispersion or slurry of step (a) with solvated electrons by contacting with a reactive metal selected from the group consisting of an alkali metal, alkaline earth metal and aluminum;

- (c) separating an ammoniacal liquid-containing product from the dispersion or slurry of step (b) to yield a soil residue sufficiently free of ions of the hazardous metal or metalloid to permit reclamation of the soil, and

- (d) separating the ammoniacal liquid from the ammoniacal liquid-containing product of step (c) to yield a hazardous metal or metalloid-containing residue for disposal or further treatment.

The method of step (b) may be performed by circulating at least a portion of the ammoniacal liquid through a by-pass containing the reactive metal. The solution of solvated electrons is recirculated back to the closed vessel for treating the contaminated soil.

This aspect of the invention also contemplates treatment of soils contaminated with mixed wastes, i.e., an ion of a hazardous nonradioactive metal or metalloid and a nuclear waste, for example. Typically, the nuclear waste comprises a radionuclide or a radioactive isotopic metal of the actinide series, such as uranium, plutonium, thorium and mixtures of the same.

The invention is also intended to include mixed wastes comprising an ion of a hazardous non-radioactive metal or metalloid and an organic compound, and more particularly, a halogenated organic compound, such as PCBs, dioxins and pesticides.

This invention broadly involves in-situ reactions comprising ammoniacal liquids with halocarbon refrigerants like CFCs and HCFCs, such as Freon® 12 and Freon 22, hereinafter known as R-12 and R-22, to produce cyanide compounds contemporaneously with the decontamination of substrates, such as soils. When the reaction is conducted in the presence of soils that are contaminated with metals or nuclear wastes, cyanides formed in-situ react with the metallic contaminants to form co-ordination complexes. These complexes are removed from the soil so the soil can be reclaimed.

The invention is especially advantageous in allowing for safer use of cyanide ligand complexing agents through in-situ methods of cyanide synthesis. In addition, however, the invention provides an important new means for eliminating unwanted or outlawed CFCs and HCFCs which are potentially destructive to the earth's ozone layer.

Reaction of the cyanide compounds with other substrates are also contemplated. Thus, a variety of processes and products are contemplated in this invention.

This invention further involves the safe preparation and use of cyanide compounds by forming such compounds at their point of use, such as, but not limited to, their formation and use in the presence of metal contaminated soil and nuclear waste. Methods are taught for metal recovery and solid remediation employing field generated cyanide compounds to selectively remove a variety of metals, metal compounds and certain radioisotopes.

One aspect of the invention involves a method of decontaminating soil containing a hazardous metal, which comprises the steps of:

- (a) mixing in a closed vessel an ammoniacal liquid with a soil contaminated with at least one ion of a hazardous metal or metalloid to form a soil-containing dispersion or slurry;

- (b) introducing into the soil-containing dispersion or slurry of step (a) a refrigerant comprising a hydrohalocarbon compound for reacting with the ammoniacal

liquid, such as anhydrous liquid ammonia to form  $\text{CN}^-$  ions in-situ and a soil-containing dispersion or slurry comprising CN complexes of the hazardous metal or metalloid, and

- (c) separating the soil from soil-containing dispersion or slurry of step (b) to yield a soil residue essentially free of the hazardous metal or metalloid.

A further aspect of the invention involves a method of decontaminating soil containing a hazardous metal with solvated electrons and halofluorocarbon, e.g., chlorofluorocarbon or CFC refrigerants, for example, which comprise the steps of:

- (a) mixing in a closed vessel an ammoniacal liquid with a soil contaminated with at least one ion of a hazardous metal or metalloid to form a soil-containing dispersion or slurry;
- (b) treating the soil-containing dispersion or slurry of step (a) with solvated electrons by contacting with a reactive metal selected from the group consisting of an alkali metal, alkaline earth metal and aluminum;
- (c) introducing into the closed vessel of step (b) a refrigerant compound, typically a CFC or a HCFC, to react with the solvated electrons and ammoniacal liquid of the soil-containing dispersion or slurry to form  $\text{CN}^-$  ions in-situ and a soil-containing dispersion or slurry comprising CN complexes of the hazardous metal or metalloid;
- (d) separating the soil from the soil-containing dispersion or slurry of step (c) to yield a soil residue essentially free of the hazardous metal or metalloid.

The processes of the invention are inherently safer for transport and handling because formation of  $\text{CN}^-$  ions cannot occur until the ammoniacal liquid and/or solvated electrons and refrigerant are brought together in the reactor because each contributes a critical component required to generate the  $\text{CN}^-$  ion. The order of addition is not important. However, since the vapor pressure of liquid ammonia exceeds that of most halomethanes, it is generally useful to add the components in the order of increasing vapor pressure.

In the method of the invention, these safer, less hazardous reactant materials are brought together at the point of use in the same vessel used in the decontamination process, to form  $\text{CN}^-$  ions in-situ. Although numerous applications will be apparent to those skilled in the art and are not intended to be excluded from the scope of our invention, specific application for the present invention will be directed principally to the separation of metals from soil surfaces.

Application of the process is intended for the removal of certain metal contaminants from soils, and other solid and liquid substrates. This includes the removal of isotopic metallic contaminants and other hazardous, but non-radioactive metals from soils, and even recovery of certain metals from soil for subsequent commercial use.

In addition to methods for the in-situ generation of  $\text{CN}^-$  ion for treatment of soils, this embodiment of the invention also encompasses methods for treating other solid substrates contaminated with hazardous metals, such as sands, gravels, aggregates, clays, sludges, sediments, and all other soil-like matrices.

If desired, cosolvents may be employed in the reaction of the halomethane and ammonia.

These reactants may be only a minor fraction of the materials in the reaction vessel. However, their amount must be sufficient to generate the desired quantity of  $\text{CN}^-$  ions required.

An alternative method for providing the ammonia required for the reaction would be to generate it in-situ from ammonia salts (ammonium chloride) and a base such as sodium hydroxide. Excess sodium hydroxide is useful as a mechanism for capturing and holding any HCN which might be formed and forcing the reaction pathway to NaCN.

In the present invention, the slurry-forming, particle-dispersive qualities of anhydrous ammonia are coupled with the mechanism for the in-situ formation of cyanide ions in the ammonia slurry as a mechanism for extracting metal ions from soil and other contaminated matrices.

Hence, an important objective of this invention is to provide a useful method for generating  $\text{CN}^-$  ions within a reaction vessel so they can be generated and consumed in one operation. Importantly, by our process there are no  $\text{CN}^-$  ions outside the reaction vessel before or after the reaction sequence. Accordingly, the methods of the invention minimize the potential hazards heretofore associated with the use of cyanides in chemical processes.

The invention is further directed to methods for the decontamination of substrates in general. That is, additional substrates can be treated according to the processes of the invention. Representative substrates include liquid substrates, such as contaminated polar and non-polar organic solvents, fluids such as dielectric fluids, hydraulic fluids, cutting fluids, used motor oils, used anti-freeze all of which may be contaminated with hazardous metallic ions. The methods of the invention may be used alone in removing metals from the foregoing substrates or used in tandem as part of a total purification process, e.g. in recycling used motor oils for reuse.

The process generally comprises the steps of:

- (a) mixing in a closed vessel an ammoniacal liquid with a substrate contaminated with at least one ion of a hazardous metal or metalloid;
- (b) introducing into the closed vessel of step (a) a refrigerant comprising a fluorohydrocarbon compound for reacting with the ammoniacal liquid of step (a) to form  $\text{CN}^-$  ions in-situ and a substrate comprising CN complexes of the hazardous metal or metalloid, and
- (c) separating the substrate from the ammoniacal liquid of step (b) to yield a substrate essentially free of the hazardous metal or metalloid.

A further embodiment of the invention involves a method of decontaminating a substrate containing a hazardous metal, which comprises the steps of:

- (a) mixing in a closed vessel an ammoniacal liquid with a substrate contaminated with at least one ion of a hazardous metal or metalloid;
- (b) treating the mixture of step (a) with solvated electrons by contacting with a reactive metal selected from the group consisting of an alkali metal, alkaline earth metal and aluminum;
- (c) introducing into the closed vessel of step (b) a refrigerant compound to react with the solvated electrons and ammoniacal liquid to form  $\text{CN}^-$  ions in-situ and a substrate comprising CN complexes of the hazardous metal or metalloid, and
- (d) separating the ammoniacal liquid of step (c) to yield a substrate essentially free of the hazardous metal or metalloid. Hazardous metals or metalloids include such representative examples as arsenic, antimony, selenium, cadmium, cobalt, mercury, chromium, lead and mixtures thereof.

#### BRIEF DESCRIPTION OF THE DRAWINGS

For a further understanding of the invention and its characterizing features reference should now be made to the accompanying drawings wherein:

FIG. 1 is a diagrammatic view of a system for decontaminating soil containing hazardous metals by filtration;

FIG. 2 is a diagrammatic view of a system for separating radionuclides in contaminated soil and concentrating in a reduced soil fraction using solvated electrons as an option.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention relates to improved methods for separating from solid substrates, e.g., soil and liquid substrates, e.g., solvents, unwanted nuclear waste material and hazardous metals, particularly radionuclides and ionized forms of potentially toxic nonradioactive metals and metalloids, such as arsenic, antimony and selenium, by concentrating in some instances in very small particles or fines of soil or clay. The concentrated radionuclide and nonradioactive metallic ion-containing fines, for example, are thus in a state which permits more efficient disposal, such as by storage, or for further treatment to modify the hazardous substances to less toxic and more environmentally benign substances.

The methods are based on the observation that liquid ammonia possesses the unique ability to break up soils into very fine particles. It was also found that suspensions of what appear to be extremely fine particles of these can be prepared by mixing with ammonia. Radionuclide-contaminated soils and soils contaminated with ions of hazardous nonradioactive metals and metalloids, or soils contaminated with both are mixed, preferably with anhydrous liquid ammonia, to form finely-dispersed suspensions or slurries. Because of the lower density of ammonia relative to water, significantly smaller soil particles remain suspended in the liquid, and particles which would otherwise be suspended in water readily precipitate from the dispersion because of the lower density and viscosity of ammonia. The greater bulk fraction of the soil consisting of larger precipitated particles are sufficiently free of the radionuclide or ions of the hazardous nonradioactive metal or metalloid contaminants as to permit reclaiming large volumes of the treated soil.

It was observed, for instance, that washing soils in ammoniacal solutions, and particularly anhydrous liquid ammonia results in significant reduction in concentrations of certain metal ions even when no particulates are visible in the ammonia following treatment. Accordingly, liquid ammonia was found to be effective in both physically and chemically enhancing decontamination in breaking down even tightly bound clays into fine slurries of platelets coupled with a metal transporting mechanism for maximizing extraction and exposure of metal contaminants, while possibly also performing as a ligand in binding the contaminating metals in complexing or chelating type reactions.

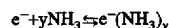
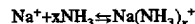
The ammoniacal liquid is preferably anhydrous liquid ammonia, but solutions of at least 50 percent-by-weight of ammonia in water can also be employed when using ammonia exclusively.

Solids, such as soils, and liquids contaminated with ions of hazardous nonradioactive metals and metalloids, such as arsenic and chromium (VI), or contaminated with mixed wastes, such as radioactive isotopic metals, like uranium, plutonium and thorium along with hazardous nonradioactive metal ions can also be effectively treated by forming dispersions or slurries with anhydrous liquid ammonia or other nitrogen-containing bases, which in-turn can be treated with solvated electrons by contacting the ammoniacal liquid-soil slurry with a reactive metal, particularly a more electropositive metal, like sodium, potassium, barium and calcium.

When a metal like sodium dissolves in the liquid ammonia, it becomes a cation by losing its valence electron as illustrated in the following equation:



The ammonia molecules then solvate these ions and electrons reversibly according to the equations:



This "ammoniated electron" is responsible for the strong reducing properties exhibited by such solutions. In this regard, the methods of the invention are suited for treating soils contaminated with hazardous chromium (VI) wherein the solvated electrons are useful in reducing metal ions having multiple oxidation states from the hazardous higher oxidation state, e.g., chromium (VI) to less hazardous chromium (III), for example.

The methods as described herein are especially well suited for the selective removal of lead from soils, and other substrates, particularly when treated with solvated electrons.

Solvated electrons are also useful in decontaminating soils and other non-solid substrates having mixed waste, like ions of a hazardous non-radioactive metal or metalloids or even radioactive metals along with polyhalogenated organic compounds, such as polychlorinated biphenyls (PCBs), as well as dioxins, e.g., 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin, and any of the several other members of the family of chlorinated dioxins, and various pesticides. The term "pesticide" is intended to denote any substance, organic or inorganic, used to destroy or inhibit the action of plant or animal pests. Thus, pesticides would include insecticides, herbicides, rodenticides, miticides, etc. Accordingly, this aspect of the invention is particularly effective in treating soils, for example, contaminated with mixed wastes by separating and complexing hazardous metal ions through the action of the ammonia, forming dispersions while simultaneously reducing halogenated compounds, e.g. pesticides, dioxins, and the like to compounds of lesser toxicity and impact on the environment. Methods for the destruction of halogenated organic compounds are disclosed in U.S. Pat. No. 5,110,364 (Mazur et al).

A general method of decontaminating soils containing hazardous metals or metalloids with ammoniacal solutions according to the present invention is illustrated by FIG. 1. Soil can be first added to the mixing vessel of FIG. 1. Anhydrous liquid ammonia, for example, is circulated from the ammonia holding tank and used to fluidize the soil resulting in the formation of a fine slurry of soil suspended in the ammonia. Agitation of the suspension can be provided by circulating the ammonia (A) between the mixing vessel and ammonia holding tank by pump means, although other mixing methods may be used. After the slurry has been sufficiently mixed the liquid phase ammonia can be separated from the soil by decanting, pressure filtration (B), or by other known methods. The ammonia in the holding tank contains metal ions which are recovered by evaporating the ammonia through the vent, where it is captured for reuse by conventional ammonia collection methods.

Methods of the invention may also be performed on soils which are predominantly sand, and which are practically free of clay and organic constituents. In this embodiment, clays possessing ion exchange properties, such as atapulgite, montmorillonite, kaolinite are added to the ammoniacal reaction mixture wherein the hazardous ions are adsorbed by the clay, and the clay-metal dispersion decanted from the sand.



As a further embodiment, the ammoniacal solutions can also employ known chelating agents, such as EDTA which enhance dissolving of the metal ions in the solvent for removing hazardous metals from the ammonia slurries.

As previously disclosed, the invention also contemplates the formation of co-ordination compounds, usually complexes, with contaminating metals to aid in their removal by introducing at least one ligand complexing agent into the closed reaction vessel, such as a source of cyanide ion. More preferably, however, the invention provides for the introduction of less hazardous reactants which allow for the generation of cyanide ion in-situ in the reaction vessel contemporaneously with the decontamination of substrates, e.g., soil. The contaminating metals are removed by forming, for instance, ammonia soluble metal cyanide ligand complexes by introducing into the closed reactor less toxic reactants for generating cyanides. The ammonia soluble metallic complexes are thus easily separated from the more dense precipitating soil particulates. This aspect of the invention is especially unique because it provides for inherently safer methods for transporting and handling chemical reactants for in-situ generation of cyanides thereby eliminating outside of the reactor cyanides per se. Cyanide ions are not generated outside the reactor and are not generated until the reactants are brought together at the point of use in the same reaction vessel used in the decontamination process.

This embodiment of the invention is also especially unique in that in addition to providing for a potentially less hazardous means for utilizing cyanides in the decontamination of substrates, it also provides for the utilization of refrigerants, e.g., chlorofluorocarbons (CFC) and hydrochlorofluorocarbons (HCFC) as key reactants in the in-situ generation of cyanide ion. In this regard, refrigerant halofluorocarbons, and more particularly CFCs, are synthetic chemical compounds widely used in refrigeration and air conditioning equipment; as aerosol propellants and solvents; in forming foams, including those used in fast-food packaging; in rigid insulation, and so on.

Scientists now view these synthetic chemicals as the main threat to Earth's protective ozone layer. Because refrigerants are immune to destruction in the troposphere, and because they eventually float upwardly, their manufacture and release have lead to the accumulation of large amounts in the stratosphere. In the stratosphere, CFCs, for example, are broken down by sunlight into chlorine, which has a catalytic and destructive effect on ozone. The result has been a significant decline in the global ozone shield and an increase in the amount of harmful ultraviolet radiation reaching the surface of Earth.

As a result, the destruction of CFCs and other related refrigerant compounds has become a vital component of the national and global strategies for protection of the earth's ozone layer. There are still, however, sizable reserves of refrigerants on hand which must be destroyed or converted to environmentally benign substances. Accordingly, the present invention provides a useful application for new, previously used refrigerants recovered from air conditioning and refrigeration equipment, or refrigerants which have become contaminated and are no longer suitable for conventional uses normally associated with such compounds. We discovered that ammoniacal liquids alone or in combination with solutions of solvated electrons are capable of reacting with refrigerants to provide a useful source of in-situ generated cyanide ions in chemical reactions requiring their use. Hence, the methods of the present invention provide for an important means for eliminating environmen-

tally harmful refrigerants by employing them as reactants in less hazardous processes calling for cyanides.

The term "refrigerant" as used throughout the specification and claims is a term intended to mean low boiling fluorocarbon compounds as a class of chemicals which are suitable principally for use in refrigeration and air conditioning equipment, but may have other applications. The term "refrigerant" embraces halofluorocarbons and halofluorohydrocarbons, such as chlorofluorocarbons (CFCs), bromofluorocarbons, chlorofluorohydrocarbons (HCFCs), and so on. Likewise, the term is also intended to include those fluorocarbon refrigerants which are useful as aerosol propellants, in manufacturing synthetic foams, packaging, insulation and retardant compounds for fire extinguishers.

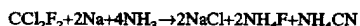
Refrigerants include perhalogenated compounds which are short chain carbon compounds fully substituted with halogens, like fluorine, chlorine and bromine, and comprise classes of compounds, such as chlorofluorocarbons and bromofluorocarbons. A specific representative example includes dichlorodifluoromethane, also known as R-12. Other refrigerants useful in the generation of cyanides include halofluorohydrocarbon refrigerant compounds like chlorofluorohydrocarbons and bromofluorohydrocarbons, such as the fluoromethane types like chlorodifluoromethane, fluorodichloromethane, chlorofluoromethane, bromofluoromethane, bromodifluoromethane, and mixtures thereof. For purposes of this invention, refrigerants are also intended to encompass azeotropic mixtures, or combinations of refrigerants, such as dichlorodifluoromethane and chlorodifluoromethane, as well as refrigerants containing contaminating amounts of other refrigerants.

Surprisingly, we discovered in U.S. Pat. No. 5,414,200 (Mouk et al) that a weak base like anhydrous liquid ammonia is a sufficiently strong that it can react with and totally dehalogenate HCFC type refrigerants, such as chlorodifluoromethane (Freon® 22). We recently also discovered that in the process of dehalogenating such refrigerants cyanides can be formed according to the following reaction:



In particular, it was found that a fluoromethane refrigerant having at least one hydrogen atom in the absence of a dissolving metal reactant, such as an alkali metal or alkaline earth metal, that the ammoniacal liquid alone as a weak base is capable reacting with and completely dehalogenating and destroying the refrigerant. In the process, however, ammonium cyanide is produced according the above reaction.

It was also discovered that perhalogenated refrigerants, such as the widely known CFCs, like dichlorodifluoromethane (Freon 12), which can adversely effect the ozone layer when released into the atmosphere, can also be destroyed with solvated electrons. However, the inventors also found when solvated electrons are formed in dissolving metal reactions using substoichiometric amounts of alkali or alkaline earth metals, cyanides are also produced according to the following reaction:



The generation of cyanides in the destruction of refrigerants in the presence of ammoniacal liquids was first disclosed as a potential problem in copending application Ser. No. 08/435,781, filed May 5, 1995. This co-pending application discloses methods for the elimination of cyanide by-products generated in the destruction of refrigerants.

Accordingly, this embodiment of the invention provides for the in-situ generation of cyanide ions as ligand com-

plexing agents for sequestering contaminating metals by forming co-ordination complexes for separation and removal from various solid and liquid substrates. The process is performed by the introduction of practically any refrigerant compound into the reaction vessel for reacting with either the ammoniacal liquid alone or reacting at least initially with solvated electrons.

As previously disclosed, ammoniacal liquids alone, according to one embodiment of this aspect of the invention, are capable of reacting with certain refrigerants in the formation of cyanide ions in-situ. Especially useful refrigerants for reaction with the ammoniacal liquids are the fluoroalkane refrigerants which includes the fluoromethanes and fluoroethane types. More specifically, they are hydrogen-containing refrigerants, such as chlorodifluoromethane (R-22); bromodichloromethane; fluorodichloromethane (R-21); chlorofluoromethane (R-31); 1,1,2,2-tetrachloro-2-fluoroethane (R-122), to name but a few.

Ammoniacal liquids suitable for use include mainly weak nitrogen-containing bases, such as anhydrous liquid ammonia and liquid ammonia especially having minor amounts of water, e.g. 3 percent. Other suitable nitrogen-containing bases in addition to ammonia which may be employed include primary amines, secondary amines, tertiary amines, cyclic amines, heterocyclic alkyl mono and polyamines and mixtures thereof. Representative examples include methyl amine, ethyl amine, dimethyl amine, diethyl amine, triethyl amine, n-propyl amine, piperidine, morpholine and ethylenediamine.

The foregoing nitrogen-containing bases are generally weak bases, which for purposes of this invention are intended to encompass mainly nitrogen-containing bases having a  $pK_b$  in the range of 2 to 5.

Alternatively, the in-situ generation of cyanide ion may be carried out by reacting the solvated electrons with refrigerants, either the previously described hydrogen-containing refrigerants or perhalogenated refrigerants which are free of hydrogen. Representative perhalogenated refrigerants include dichlorodifluoromethane (R-12); chlorotrifluoromethane (R-13); fluorotrichloromethane (R-11); 1,2-difluoro-1,1,2,2-tetrachloroethane (R-112), etc., all of which are free of hydrogen. This embodiment may also be performed with mixtures of refrigerants, either commercially produced azeotrope mixtures or with refrigerants, used or otherwise which have become contaminated with other refrigerants and cannot be re-used without prior purification.

The solvated electrons are formed in dissolving metal reactions by introducing a reactive metal, typically an alkali metal, such as sodium, potassium or lithium metal or an alkaline earth metal, such as calcium into the reaction vessel for dissolution in the ammoniacal liquid or by circulating the ammoniacal liquid from the reactor through a closed circulation loop which includes a solvator containing a bed of the reactive metal. In this latter embodiment, the solution of solvated electrons is then recirculated back to the reactor. In each instance, solvated electrons are formed according to the reactions disclosed above.

However, in one preferred embodiment of the invention fluorocarbon refrigerant, and particularly types which are not readily dehalogenated with weak bases, such as dichlorodifluoromethane, chlorotrifluoromethane, bromotrifluoromethane, and other perhalogenated fluorocarbon refrigerants can be partially dehalogenated initially through a reduction reaction with the above solutions of solvated electrons. It was found this partial dehalogenation of fluorocarbon refrigerants requires as little as one fourth of the reactive metal ordinarily employed in processes, such as

disclosed by U.S. Pat. No. 5,110,364 (Mazur et al) and Japanese unexamined application 59-10329 (1984). Such prior methods provide for removal of all halogen atoms from the perhalomethane refrigerants with stoichiometric amounts of the reactive metals, such as sodium in the formation of solvated electrons with ammonia or other nitrogen-containing base.

Unlike earlier methods, the in-situ generation of cyanide ion can be readily performed using substoichiometric amounts of reactive metal, e.g., calcium, for removing as little as a single halogen atom from the perhalogenated refrigerant compound, thereby requiring but a fraction of the metal reactant normally used. With the removal of as little as a single halogen atom from the perhalogenated refrigerant compound using reduced amounts of metal than required to fully dehalogenate the refrigerant, further dehalogenation of the refrigerant can be achieved with the ammonia or other nitrogen-containing base in the reaction mixture.

Reduction of the fluorocarbon refrigerant with solvated electrons to form the desired cyanide ion in-situ is carried out in the closed pressure vessel at temperatures sufficiently low as to inhibit reactions which might otherwise occur between by-products of the reduction reaction and the solvated electrons or nitrogen-containing base. Typically, in this embodiment of the invention reactions would be conducted at about 0° C. or lower. Subsequently the reaction vessel is allowed to warm to ambient temperatures which will in-turn initiate further dehalogenation of the partially dehalogenated fluorocarbon and to generate additional cyanide ions.

The following specific examples demonstrate the various embodiments of the invention, however, it is to be understood they are for illustrative purposes only and do not purport to be wholly definitive as to conditions and scope.

#### EXAMPLE I

Methods of the invention can be carried out by means of a system, such as that illustrated by FIG. 2. A closed reactor 10 is utilized as a mixing vessel for nuclear waste contaminated soil 14 positioned at the bottom of the vessel. The term "soil" is intended to have its ordinary understood meaning, and includes one or more components in varying proportions, such as of clay, stone, disintegrated rock particles or sand, organic matter, along with varying amounts of water and the like. Obviously, soil compositions will vary widely depending on source and location. For instance, soils from desert or other arid locations are mainly sandy compositions with little organic material or clay components. One representative soil from the State of Ohio known as Ohio Loam was found to have an analysis of 35% sand, 32% silt, 33% clay and 4.1% organic matter and have a pH 7.7. By contrast soil from Oak Ridge, Tenn. was found to contain only 1% sand, 26% silt, 73% clay, no organic matter, and have a pH of 5.2. In sum, the term "soil" for purposes of this invention is intended to have a broad compositional makeup, including varying ranges of clay, disintegrated rock/sand particulates, organic matter, silt-fines, moisture and so on. This would include soils which are mainly clay or sand.

Anhydrous liquid ammonia 16 or a solution of liquid ammonia containing up to a small amount of water is introduced to closed reactor 10 from ammonia storage vessel 18. Once filled, liquid ammonia is withdrawn from reactor 10 from below the surface of the liquid by circulating pump 20 positioned in outlet line 22. The flow of ammonia is directed by means of 3-way diverter valves 24-25 to either by-pass line 26 or to solvator 28 containing a bed of reactive metal 30, such as alkali or alkaline earth metals or mixtures

15

of the same. Suitable representative metals include sodium, potassium, lithium, calcium and magnesium. Aluminum would also be a suitable reactive metal. By circulating ammonia 16 through a bed of metal in reactor 28 solvated electrons are formed in-line. This avoids the problems associated with injecting metal rods or other metal sources directly to reaction vessel 10. Accordingly, methods of the present invention contemplate the option of enhanced particle size demarcation and separation of radioactive components in fines of soil and clay with ammonia and electrons solvated in the ammonia.

Whether ammonia circulates through by-pass line 26 or through solvator 28 the solution is recirculated to the bottom of reactor 10 through valve 32, setting up a fluidized flow pattern in the reactor. This produces a mixing action of the soil and ammonia solution and/or solvated electrons to form a slurry. Once the soil has been uniformly dispersed in the ammonia, pump 20 is deactivated to allow the dispersion to undergo phase separation, i.e. a lower solid phase and an upper liquid-solid phase. Large particulates of the dispersion precipitate out as solid phase 34 in the bottom of reactor 10, and are sufficiently free of radionuclide contaminants, the latter being concentrated in a smaller soil fraction consisting of fines or silt dispersed in the ammonia solution as upper liquid-solid phase 36.

The slurry of suspended particle fines forming the upper liquid-solid phase 36 is withdrawn from reactor vessel 10 to evaporator tank 38 via line 40 by opening valve 42. Ammonia 43 is evaporated to separate it from radioactive fines 44. Optionally, the ammonia can be transferred via line 48 to compressor 46 for reliquification if it is desired to recycle the ammonia for further use in the decontamination process. The liquified ammonia is then transferred to ammonia storage tank 18 through line 50.

#### EXAMPLE II

##### PART A

The decontamination of soil with ammoniacal liquid was demonstrated by the following experiment:

A two-kilo batch of common Ohio loam was doped with low levels of cobalt nitrate. The doped soil was analyzed and found to contain 4.5 ppm cobalt. A 10 gram sample of the doped soil was mixed with approximately 80 grams of anhydrous liquid ammonia and shaken until well mixed. The soil was then filtered from the ammonia and sent for analysis. The ammonia was allowed to evaporate from the residue. Analysis of the soil revealed the cobalt content had dropped from 4.5 ppm to 1.1 ppm.

##### PART B

In order to improve on the removal of  $\text{Co}^{+2}$  ions from soil which removal is not as efficient as  $\text{Co}^{+3}$ , two methods may be employed:

In the first method, 1.50 equivalents ethylenediaminetetraacetic acid (EDTA) per  $\text{Co}^{+2}$  ion is mixed with soil and anhydrous liquid ammonia. The soluble  $\text{Co-EDTA}$  complex is easily filtered from the soil matrix to lower the  $\text{Co}^{+2}$  concentration in the soil to an acceptable level.

In a second method, ammonium nitrate (10 grams/100 grams of soil) is added to a soil sample and the mixture is agitated with anhydrous liquid ammonia. The solubilized  $\text{Co}^{+2}$  ions are removed along with the ammonia solvent upon filtration. The toxic impurity and excess ammonium nitrate is isolated by evaporating the solvent and disposed of by methods known in the art.

#### EXAMPLE III

A 150 gram sample of soil contaminated both with 150 ppm  $\text{Sr}^{90}$  and 500 ppm polychlorinated biphenyls (PCBs) is

16

placed in reactor 10 (FIG. 2). The reactor is then charged with 1.5 L of liquid ammonia (anhydrous) and pumped through the recirculation loop described in Example I for agitating the soil. After a suitable period, the ammonia is allowed to flow through solvator 28 to generate a solution of solvated electrons by contact and dissolution of 10 grams of calcium metal 30. Solvated electron generation can be a one-time event in which the metal is completely consumed in a continuous flow of ammonia. Alternatively, bypass 26 can be employed at intervals to interrupt the flow of solvated electron solution, and thus cause the introduction of reactant to be a sequence of pulses.

When a sufficient quantity of reactant has been added, the ammonia circulation pump 20 is stopped and the soil slurry allowed to settle briefly to delineate a bottom phase of larger soil particles and a supernatant suspension of ammonia/soil fines/metal particles. This suspension is transferred to tank 38 from whence the ammonia may be separated by vaporization leaving the greatly reduced volume of soil fines/metal material for final disposition in accordance with established local, state and Federal Regulations.

The bulk of the original soil sample charged to the reactor remains therein. The concentration of both radionuclide and PCBs is low enough to permit the treated soil to be returned as landfill as permitted by accepted practices in the remediation field.

#### EXAMPLE IV

A soil having a higher clay content than that used in Example I, or a soil having a clay fraction with a higher cation exchange capacity than that used in Example I is doped with an arsenic compound. The soil is treated with ammonia as in Example I except no solvated electron solution is introduced. After agitation and separation of the soil fines, the larger particles soil fraction is sufficiently free from the toxic metalloid as to permit its return to a suitable landfill or to the original site of excavation. The clay fines containing the arsenic impurity are of greatly reduced volume and can be stored in less volume of space than otherwise required.

#### EXAMPLE V

A Soil contaminated with hazardous chromium VI ions is mixed with a liquid ammonia in a closed reactor and agitated to thoroughly disperse the soil particles. About 0.5 gallon of liquid ammonia per pound of soil is employed. A solution of solvated electrons is formed from the reaction of the liquid ammonia with calcium metal introduced to the reactor. The addition of the metal may be in a one-time injection or by serial mode of addition. When the blue color typical of solvated electrons persists, the addition of further metal is terminated. After a few minutes to assure complete reaction, the solvated electron solution is quenched. The ammonia is allowed to evaporate and is recovered for further use. The soil has all the chromium ions now with an oxidation number of less than VI, e.g., chromium III ions, in suitable form for reclamation without further remediation.

#### EXAMPLE VI

A 500 gram sample of sand contaminated with plutonium compounds is slurried with 1.0 l of anhydrous liquid ammonia in a reaction apparatus such as that illustrated in FIG. 1. Agitation is stopped and the sand quickly settles to reveal a clear ammonia layer due to the lack of any fined-sized particles. The ammonia is decanted and is found to contain very little dissolved plutonium compounds, demonstrating

little change has occurred in the level of plutonium compounds in the sand.

For purposes of comparison, 25 gram of montmorillonite clay is added to the reactor and the clay and sand mixture is resuspended in 1.0 l of anhydrous liquid ammonia. Agitation is continued for a time previously shown to permit the clay to adsorb the plutonium ions. Agitation is stopped and the sand quickly settles leaving a clay/ammonia suspension above it. The suspension is removed by decantation.

Since some of the clay/ammonia suspension remains in the reactor, additional ammonia is added and the sequence of agitation, settling and decantation is repeated until the amount of plutonium laden clay is lowered to the desired extent.

The treated sand is removed for appropriate disposal. The clay is freed from the ammonia by vaporizing the liquid. The clay solids are disposed of in a manner prescribed for plutonium contaminated materials. Because of the reduced volume of waste, handling and disposition are more efficient.

#### EXAMPLE VII

150 grams of soil containing cadmium salts (144 ppm  $\text{Cd}^{+2}$ ) is treated with 1.5 liters of anhydrous liquid ammonia in a 3 liter pressure bomb. 8.5 grams of sodium cyanide is added and the mixture stirred for 1 or 2 hours at room temperature. The mixture is filtered. The largest bulk portion of the soil remains on the filter and the small soil fines pass through. Both soil batches are freed from ammonia by evaporation in open vessels. The larger soil particles on the filter (19.5 gram filter cake) are found to have only 38 ppm  $\text{Cd}^{+2}$  ions. This accounts for 90 percent of the original amount of cadmium in the soil.

This example demonstrates the ability of an ammoniacal liquid and cyanide ion in removing and concentrating hazardous metal ions in small particle fractions of soil.

Thus, the methods of the disclosed invention provide the advantages of separating nuclear waste and/or ions of hazardous nonradioactive metals or metalloids by means of smaller particles than relied on using aqueous based systems; permits recycling of ammonia not otherwise achieved with systems relying on more costly scrubbing chemicals; provides means for readily separating fines from liquid ammonia; eliminates transport and storage of water to desert locations, and provides additional means for controlling particles sizes within a predetermined range with solvated electrons.

#### EXAMPLE VIII

150 grams of soil containing cadmium salts (144 ppm  $\text{Cd}^{+2}$ ) is treated with 1.5 liters of anhydrous liquid ammonia in a 3 liter pressure bomb. 1.0 gram of chlorodifluoromethane refrigerant (R-22) is added to the slurry. A slight exothermic reaction is indicated by a rise in temperature and pressure. The mixture is stirred for 1 or 2 hours at room temperature. During this period a small aliquot is withdrawn and tested for the presence of cyanide ion. The test proves positive. As in the previous examples, the mixture is filtered. Analysis shows that the larger soil particles remaining on the filter are found to have greatly diminished levels of cadmium. The filtrate can be analyzed for the presence of cadmium cyanide complex using U.V. spectroscopy.

#### EXAMPLE IX

150 grams of soil containing cadmium salts (144 ppm  $\text{Cd}^{+2}$ ) is treated with 1.5 liters of anhydrous liquid ammonia

in a 3 liter pressure bomb. 1.0 gram of sodium metal is added to the reactor through a metal addition port and the mixture stirred until the blue solution typical of solvated electron solutions permeates the solvent/soil slurry. 1.5 grams of dichlorodifluoromethane refrigerant (R-12) is added to the slurry. A slight exothermic reaction is indicated by a rise in temperature and pressure. The mixture is stirred for 1 or 2 hours at room temperature during which time the blue solvated electron color fades. During this period a small aliquot can be withdrawn and analyzed for the presence of cyanide ion. As in the previous examples, the mixture is filtered. The filtrate can be analyzed for the presence of cadmium cyanide complex using U.V. spectroscopy. Analysis shows that the larger soil particles remaining on the filter have greatly diminished levels of cadmium.

While the invention has been described in conjunction with various embodiments, they are illustrative only. Accordingly, many alternatives, modifications and variations will be apparent to persons skilled in the art in light of the foregoing detailed description, and it is therefore intended to embrace all such alternatives and variations as to fall within the spirit and broad scope of the appended claim.

We claim:

1. A method of decontaminating a solid substrate containing a hazardous metal, which comprises the steps of:

- (a) mixing in a closed vessel an ammoniacal liquid with a solid substrate contaminated with at least one ion of a hazardous metal or metalloid to form a solid substrate-containing dispersion or slurry;
- (b) introducing into the closed vessel of step (a) a refrigerant comprising a fluorohydrocarbon compound for reacting with the ammoniacal liquid of the solid substrate-containing dispersion or slurry to form  $\text{CN}^-$  ions in-situ and a solid substrate-containing dispersion or slurry comprising CN complexes of the hazardous metal or metalloid, and
- (c) separating the solid substrate from the solid substrate-containing dispersion or slurry of step (b) to yield a solid substrate residue essentially free of the hazardous metal or metalloid.

2. The method of claim 1 wherein the solid substrate is a member selected from the group consisting of soil, sand, gravel, aggregates, sludge, sediment and mixtures thereof.

3. The method of claim 1, including the step of separating an ammoniacal liquid remaining after separation of the solid substrate residue of step (c) to yield a residue comprising the CN complexed metal or metalloid.

4. The method of claim 1 wherein the refrigerant comprising the fluorohydrocarbon compound of step (b) is a chlorofluorohydrocarbon or a bromofluorohydrocarbon.

5. The method of claim 4 wherein the fluorohydrocarbon compound is a member selected from the group consisting of chlorodifluoromethane, fluorodichloromethane, chlorofluoromethane, bromofluoromethane, bromodifluoromethane and mixtures thereof.

6. The method of claim 4 wherein the ion of said hazardous metal or metalloid is a member selected from the group consisting of radioactive metals, hazardous nonradioactive metals and mixtures thereof.

7. The method of claim 4 wherein the ion of said hazardous metal or metalloid is a member selected from the group consisting of arsenic, antimony, selenium, cadmium, cobalt, mercury, chromium, lead and mixtures thereof.

8. The method of claim 1 wherein the ammoniacal liquid is anhydrous liquid ammonia or an ammonia-containing solution.

9. A method of decontaminating solid substrate containing a hazardous metal, which comprises the steps of:

- (a) mixing in a closed vessel an ammoniacal liquid with a solid substrate contaminated with at least one ion of a hazardous metal or metalloid to form a solid substrate-containing dispersion or slurry;
- (b) forming solvated electrons in the solid substrate-containing dispersion or slurry of step (a) by contacting with a reactive metal selected from the group consisting of an alkali metal, alkaline earth metal and aluminum;
- (c) introducing into the closed vessel of step (b) a refrigerant compound to react with the solvated electrons in the solid substrate-containing dispersion or slurry to form  $CN^-$  ions in-situ and a solid substrate-containing dispersion or slurry comprising CN complexes of said hazardous metal or metalloids, and
- (d) separating the solid substrate from the solid substrate-containing dispersion or slurry of step (c) to yield a solid substrate residue essentially free of said hazardous metal or metalloid.

10. The method of claim 9 wherein the solid substrate is a member selected from the group consisting of soil, sand, gravel, aggregates, sludge, sediment and mixtures thereof.

11. The method of claim 9 wherein the solvated electrons are formed by utilizing less than an amount of reactive metal needed to fully dehalogenate the refrigerant compound of step (c).

12. The method of claim 9, including the step of separating an ammoniacal liquid remaining after separation of the solid substrate residue of step (c) to yield a residue comprising the CN complexed metal or metalloid.

13. The method of claim 9 wherein the refrigerant of step (c) comprises a halofluorocarbon or a halofluorohydrocarbon compound.

14. The method of claim 9 wherein the refrigerant of step (c) comprises at least one member selected from the group consisting of chlorofluorocarbon, bromofluorocarbon, chlorofluorohydrocarbon, bromofluorohydrocarbon and mixtures thereof.

15. The method of claim 9 wherein the refrigerant comprises dichlorodifluoromethane.

16. The method of claim 9 wherein the refrigerant comprises dichlorodifluoromethane and chlorodifluoromethane.

17. The method of claim 9 wherein the ammoniacal liquid is anhydrous liquid ammonia or ammonia-containing solution.

18. The method of claim 17 wherein the ion of the hazardous metal or metalloid is a member selected from the group consisting of radioactive metals, nonradioactive metals and mixtures thereof.

19. The method of claim 17 wherein the ion of said hazardous metal or metalloid is nonradioactive and is a member selected from the group consisting of arsenic, antimony, selenium, cadmium, cobalt, mercury, chromium, lead and mixtures thereof.

20. The method of claim 17 wherein the solid substrate is soil which is contaminated with chromium VI, and is reduced by the solvated electrons.

21. The method of claim 17 wherein the solid substrate is soil which comprises a member selected from the group consisting of clay, disintegrated rock, sand, organic matter and mixtures thereof.

22. The method of claim 17 wherein the solid substrate is soil which is mainly sand and step (a) includes the addition of a clay to the vessel.

23. The method of claim 17 wherein the solid substrate is soil and comprises a mixed waste.

24. The method of claim 23 wherein the mixed waste comprises an ion of a hazardous nonradioactive metal or metalloid and a nuclear waste.

25. The method of claim 23 wherein the mixed waste comprises an ion of a hazardous nonradioactive metal or metalloid and an ion of a radioactive isotopic metal.

26. The method of claim 9 wherein the solid substrate comprises at least one radionuclide.

27. The method of claim 26 wherein the radionuclide is a member of the actinide series.

28. The method of claim 25 wherein the radioactive isotopic metal is a member selected from the group consisting of uranium, plutonium, thorium and mixtures thereof.

29. A method of decontaminating a substrate containing a hazardous metal, which comprises steps of:

(a) mixing in a closed vessel an ammoniacal liquid with a liquid substrate contaminated with at least one ion of a hazardous metal or metalloid;

(b) introducing into the closed vessel of step (a) a refrigerant comprising a fluorohydrocarbon compound for reacting with the ammoniacal liquid of step (a) to form  $CN^-$  ions in-situ and a substrate comprising CN complexes of said hazardous metal or metalloid, and

(c) separating the substrate from the ammoniacal liquid of step (b) to yield a substrate essentially free of said hazardous metal or metalloid.

30. The method of claim 29, including the step of separating an ammoniacal liquid remaining after separation of the substrate of step (c) to yield a residue comprising the CN complexed metal or metalloid.

31. The method of claim 29 wherein the substrate is a solvent, dielectric fluid, hydraulic fluid, used motor oil, or cutting fluid.

32. The method of claim 29 wherein the ion of said hazardous metal or metalloid is a member selected from the group consisting of radioactive metals, hazardous nonradioactive metals and mixtures thereof.

33. The method of claim 29 wherein the ion of said hazardous metal or metalloid is a member selected from the group consisting of arsenic, antimony, selenium, cadmium, cobalt, mercury, chromium, lead and mixtures thereof.

34. The method of claim 32 wherein the ammoniacal liquid is anhydrous liquid ammonia or an ammonia-containing solution.

35. A method of decontaminating a substrate containing a hazardous metal, which comprises the steps of:

(a) mixing in a closed vessel an ammoniacal liquid with a liquid substrate contaminated with at least one ion of a hazardous metal or metalloid;

(b) forming solvated electrons in the mixture of step (a) by contacting with a reactive metal selected from the group consisting of alkali metal, alkaline earth metal and aluminum;

(c) introducing into the closed vessel of step (b) a refrigerant compound to react with the solvated electrons and ammoniacal liquid to form  $CN^-$  ions in-situ and a substrate comprising CN complexes of said hazardous metal or metalloid, and

(d) separating the ammoniacal liquid of step (c) to yield a substrate essentially free of said hazardous metal or metalloids.

## 21

36. The method of claim 35, including the step of separating the ammoniacal liquid remaining after separation of the substrate of step (d) to yield a residue comprising the CN complexed metal or metalloid.

37. The method of claim 35 wherein the solvated electrons are formed by utilizing less than an amount of reactive metal needed to fully dehalogenate the refrigerant compound of step (c).

38. The method of claim 35 wherein the ammoniacal liquid is anhydrous liquid ammonia.

## 22

39. The method of claim 35 wherein the ion of said hazardous metal or metalloid is nonradioactive and is a member selected from the group consisting of arsenic, antimony, selenium, cadmium, cobalt, mercury, chromium, lead and mixtures thereof.

40. The method of claim 35 wherein the refrigerant of step (c) is a chlorofluorocarbon or a hydrochlorofluorocarbon.

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