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- (71) Applicant: **ADVANCED TECHNOLOGY MATERIALS, INC.** [US/US]; 7 Commerce Drive, Danbury, Connecticut 06810 (US).
- (72) Inventors: **KORZENSKI, Michael B.**; 110 Woodcrest Lane, Danbury, Connecticut 06810 (US). **CHEN, Tianniu**; 146 Sunset Ridge, Rocky Hill, Connecticut 06067 (US). **JIANG, Ping**; 10 South Street, Unit 56, Danbury, Connecticut 06810 (US).
- (74) Agent: **FUIERER, Tristan**; Moore & Van Allen PLLC, P.O. Box 13706, Research Triangle Park, North Carolina 27709 (US).

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(54) Title: REMOVAL OF LEAD FROM SOLID MATERIALS

(57) Abstract: A leaching composition that substantially removes lead from solid materials and a method of using said composition. Preferably, the concentration of lead in the solid materials following processing is low enough that the solid materials can be reused and/or disposed of at minimal cost to the processor. Preferably, the solid materials comprise glass, such as cathode ray tube glass.



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REMOVAL OF LEAD FROM SOLID MATERIALS

FIELD

[0001] The present invention relates generally to a composition that substantially removes lead from solid materials, and a method of using said composition.

DESCRIPTION OF THE RELATED ART

[0002] As the world transitions to flat panel televisions and flat panel computer monitors, more and more cathode ray tubes (CRTs) are being discarded. The safe disposal of CRTs present a serious environmental challenge since they contain leaded glass (primarily in the funnel, neck and frit) which may be readily leached from a landfill by acidic water. The lead content in the glass of a CRT can be as high as 20%, which means that a single 34" television might contain more than 1 kg of lead. Lead is toxic and is known to damage the body's nervous and reproductive systems and kidneys. It can also cause high blood pressure and anemia. Lead is especially harmful to the developing brains of fetuses and young children and to pregnant women. As a result, lead has been banned from fuel, paint, pipes and all new electronics.

[0003] Recycling glass is manually intensive and expensive. This is so because one vendor of glass may use different concentrations of lead or other metals in their glass products than another glass vendor. Waste disposal facilities receive glass waste that is not separated, and the waste disposal facilities have no effective techniques for automatically separating different glass wastes from one another. Because of the expense and time consuming nature associated with recycling glass waste, many waste disposal facilities have resorted to the illegal disposal of glass waste.

[0004] In the past, the most popular and legal technique for disposing of CRTs is a smelting technique, wherein the glass of the monitor is melted at an extremely high temperature and the lead extracted off the top of the liquid produced. A literature survey indicates that smelting recovers only 50% of the lead in the glass, produces toxic vapors and a contaminated toxic slag that is either landfilled (at high cost) or used as a low-value aggregate. Therefore, the EPA realizes that it cannot permit the smelting process to continue indefinitely and is actively pursuing and promoting research to replace the process. Currently, CRT waste is the number two contributor to hazardous lead waste in the United States.

[0005] Since no truly viable solution to this problem exists, millions of tons of waste glass are being stockpiled by electronics recyclers looking for a solution. Reuse is not a real option since relatively few new CRTs are being manufactured. This problem will only get worse as liquid crystal and/or

plasma screen technology is integrated into the industry and the at least 1.9 billion CRTs still in use worldwide are systematically disposed of.

[0006] Accordingly, there is a need for improved techniques to extract heavy metals from glass waste products and other materials comprising said heavy metals. The techniques should be environmentally safe, efficient, and practical so that the techniques are readily embraced and adopted by waste disposal facilities.

SUMMARY

[0007] The present invention generally relates to a composition that substantially removes lead from solid materials, and a method of using said composition. Preferably, the concentration of lead in the solid materials following processing is low enough that the solid materials can be reused and/or disposed of at minimal cost to the processor. Preferably, the solid materials comprise glass, such as cathode ray tube glass.

[0008] In one aspect, a method of leaching lead or other heavy metals from solid materials, said method comprising:

pulverizing the solid materials to size in a range from about 10 microns to about 3 mm;

introducing the pulverized solid materials into a chemical processing vessel comprising a leaching composition to form a slurry;

agitating the slurry to leach the lead or other heavy metals from the solid material into the leaching composition,

wherein the leaching composition comprises at least one oxidant, at least one solvent, optionally at least one metal chelator, optionally at least one accelerator/NO_x (nitrogen oxide) suppressor, and optionally at least one etchant.

[0009] In another aspect, a leaching composition is described, said leaching composition comprising at least one oxidant, at least one solvent, optionally at least one metal chelator, optionally at least one accelerator/NO_x (nitrogen oxide) suppressor, and optionally at least one etchant.

[0010] Other aspects, features and advantages of the invention will be more fully apparent from the ensuing disclosure and appended claims.

DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS THEREOF

[0011] The present invention generally relates to a composition that substantially removes lead from solid materials, and a method of using said composition to remediate lead from said solid materials. Preferably, the concentration of lead in the solid materials following processing is low enough that the solid materials can be reused and/or disposed of at minimal cost to the processor. Preferably, the solid materials comprise glass, such as cathode ray tube glass. It is also contemplated that the compositions described herein can be used to remove lead from soil, electronic equipment, solder sludge, and paint chips.

[0012] As defined herein, “substantially devoid” corresponds to less than about 2 wt. %, more preferably less than 1 wt. %, and most preferably less than 0.1 wt. % of the composition, based on the total weight of said composition.

[0013] “Substantially removed” is defined herein to mean that more than 95 wt. % of the heavy metal originally present is dissolved or otherwise solubilized, preferably more than 98 wt. %, more preferably more than 99 wt. %, and most preferably more than 99.9 wt. %.

[0014] As used herein, the term “leaches” corresponds to the complete removal or extraction of the lead or other metals from the material into the leaching composition or the partial removal or extraction of the lead or other metals from the material into the leaching composition. The lead or other metals is dissolved or otherwise solubilized in the leaching composition, preferably dissolved.

[0015] As defined herein, the “material” corresponds to any solid that requires lead or other metal remediation including, but not limited to, CRT glass waste, soil, paint chips, electronic waste, and solder sludge.

[0016] As has been discussed in detail above, glass waste, particularly glass waste associated with CRT monitors or televisions, includes unacceptable levels of lead, or other heavy metals (e.g., cadmium, mercury, selenium, arsenic, and the like), that need to be removed or decreased to acceptable levels before the glass waste can be disposed of in a landfill. Using the composition and method described herein, glass waste can economically and safely be disposed of well within the current EPA standards by safely and efficiently removing lead and other heavy metals from the glass waste. Alternatively, the glass can safely be recycled for reuse as glass or for incorporation into other products such as concrete or asphalt.

[0017] The material, such as CRT glass waste, soil, paint chips, electronic waste, and solder sludge, can be pulverized using means suitable for crushing or grinding said materials to variable particle sizes. For example, CRT glass waste can be fed to a grinding device such as a high-speed hammer mill, grinder, or any other size reduction means. Preferably, the material is pulverized to size in a range from about 10 microns to about 3 mm. As the material leaves the grinding means, preferably a separation device classifies the material particles by size. For example, the separation device can be configured to classify the material particles into sizes between less than 3 mm and sizes greater than approximately 10 microns. Material particles have a desired diameter size between about 10 microns

and about 3 mm or less, although it should be appreciated that diameters less than 10 microns and greater than 3 mm can be processed as well using the composition and method described herein.

[0018] The pulverized material particles are then introduced into a chemical processing vessel comprising a leaching composition, which will be described below. The chemical processing vessel can be a drum set-up, a tumbler system, a mixing apparatus, or an equivalent thereof. The leaching composition in combination with the pulverized material particles results in the formation of a slurry, which can be agitated by stirring, mixing, tumbling, shaking, etc., in the presence or absence of added heat. Preferably, the temperature of the slurry during agitation is about 30°C to about 150°C, preferably about 30°C to about 70°C. The slurry can alternatively be circulated using a pumping system. In still another alternative, a feed-and-bleed system is contemplated whereby some amount of the leaching composition is removed for processing and fresh or recycled leaching composition added to the chemical processing vessel.

[0019] The slurry can be agitated for time in a range from about 5 min to 6 hr, depending on the volume of leaching composition and the amount of pulverized material particles added. Upon completion of the leaching process, the leaching composition is removed from the vessel and/or the material particles are filtered from the leaching composition. Following filtration, the material particles are preferably rinsed with water to remove residual leaching composition from the material particles. Thereafter, the material particles can be filtered again. The leaching composition can be reused for another cycle of material particle treatment or treated for disposal.

[0020] With regards to additional cycles, the leaching composition can be reused until the leaching composition is saturated with lead and other metals and no longer efficiently solubilizes lead into the leaching composition. Ion-exchange resins selective to lead can be used in combination with the leaching composition to further extend the life of the bath. Moreover, as will be discussed below, the leaching composition can be recycled using diffusion dialysis and reused. With regards to disposal procedures, when no longer viable, the leaching composition can be rendered essentially non-toxic by electrowinning or precipitating the Pb and neutralizing the excess acidity.

[0021] At this point, particles consisting of glass (e.g., CRT glass) are substantially devoid of lead and other heavy metals on their surface due to the mixing cycles with the leaching composition. Moreover, any lead or heavy metal remaining within the filtered glass particles cannot be extracted from the filtered glass particles because of the size of the glass particle and the fact that the remaining heavy metals are sequestered in the core. Products, such as road materials and others, can include the filtered glass particles with assurance that lead or other heavy metals (e.g., cadmium, mercury, arsenic, selenium, and others) will not be released. Therefore, the particles consisting of glass can be used for other products such as foundations for roads, mixtures for concrete, etc.

[0022] Preferably, all of the lead is removed from the material. For example, when the material comprises soil or some other amorphous solid, the leaching composition can penetrate the entire

material and the lead can be substantially removed from the material. When the material comprises glass, only the lead on the surface of the glass is removed. This is advantageous because the lead in the core of the particle is sequestered and not easily removed if disposed of in a landfill. That said, it is theorized that if the leaching composition can solubilize the glass particle then substantial removal of the lead can be effectuated and substantially lead-free glass re-precipitated and sold for reuse. As defined herein, “substantially lead-free” corresponds to a concentration of lead in the material less than about 5 wt%, preferably less than about 2 wt%, and even more preferably less than 1 wt%, based on the total weight of the solid glass.

[0023] The leaching composition is formulated to oxidize and sequester the lead thereby removing same from the material. The leaching composition comprises, consists of, or consists essentially of at least one oxidant, at least one solvent, optionally at least one metal chelator, optionally at least one accelerator/NO_x (nitrogen oxide) suppressor, optionally at least one etchant. In one embodiment, the leaching composition comprises, consists of, or consists essentially of at least two oxidants, at least one solvent, and at least one accelerator/NO_x (nitrogen oxide) suppressor. In another embodiment, the leaching composition comprises, consists of, or consists essentially of at least one oxidant, at least one solvent, at least one metal chelator, and at least one accelerator/NO_x (nitrogen oxide) suppressor.

[0024] The components of the leaching composition comprising, consisting of, or consisting essentially of at least two oxidants, at least one solvent, and at least one accelerator/NO_x (nitrogen oxide) suppressor can be present in the following amounts, based on the total weight of the leaching composition:

Component	weight %
oxidizing agent(s)	about 6 wt% to about 85 wt%
accelerator/NO _x suppressor(s)	about 0.1 wt% to about 10 wt%
solvent(s)	about 5 wt% to about 93.9 wt%

[0025] The components of the leaching composition comprising, consisting of, or consisting essentially of at least one oxidant, at least one solvent, at least one metal chelator, and at least one accelerator/NO_x (nitrogen oxide) suppressor can be present in the following amounts, based on the total weight of the leaching composition:

Component	weight %
oxidizing agent(s)	about 5 wt% to about 20 wt%
metal chelator(s)	about 10 wt% to about 65 wt%
accelerator/NO _x suppressor(s)	about 0.2 wt% to about 10 wt%
solvent(s)	about 5 wt% to about 84.8 wt%

[0026] Oxidizing agents are included in the leaching composition to oxidize the metals to be removed into an ionic form and accumulate highly soluble salts of dissolved metals. Oxidizing agents contemplated herein include, but are not limited to, ozone, nitric acid (HNO₃), bubbled air,

cyclohexylaminosulfonic acid, , hydrogen peroxide (H_2O_2), oxone (potassium peroxymonosulfate, $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$), ammonium polyatomic salts (e.g., ammonium peroxomonosulfate, ammonium chlorite (NH_4ClO_2), ammonium chlorate (NH_4ClO_3), ammonium iodate (NH_4IO_3), ammonium perborate (NH_4BO_3), ammonium perchlorate (NH_4ClO_4), ammonium periodate (NH_4IO_3), ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$), ammonium hypochlorite (NH_4ClO)), sodium polyatomic salts (e.g., sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$), sodium hypochlorite (NaClO)), potassium polyatomic salts (e.g., potassium iodate (KIO_3), potassium permanganate (KMnO_4), potassium persulfate, potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), potassium hypochlorite (KClO)), tetramethylammonium polyatomic salts (e.g., tetramethylammonium chlorite ($(\text{N}(\text{CH}_3)_4\text{ClO}_2$), tetramethylammonium chlorate ($(\text{N}(\text{CH}_3)_4\text{ClO}_3$), tetramethylammonium iodate ($(\text{N}(\text{CH}_3)_4\text{IO}_3$), tetramethylammonium perborate ($(\text{N}(\text{CH}_3)_4\text{BO}_3$), tetramethylammonium perchlorate ($(\text{N}(\text{CH}_3)_4\text{ClO}_4$), tetramethylammonium periodate ($(\text{N}(\text{CH}_3)_4\text{IO}_4$), tetramethylammonium persulfate ($(\text{N}(\text{CH}_3)_4\text{S}_2\text{O}_8$)), tetrabutylammonium polyatomic salts (e.g., tetrabutylammonium peroxomonosulfate), peroxomonosulfuric acid, urea hydrogen peroxide ($(\text{CO}(\text{NH}_2)_2\text{H}_2\text{O}_2$), peracetic acid ($\text{CH}_3(\text{CO})\text{OOH}$), sodium nitrate, potassium nitrate, ammonium nitrate, sulfuric acid, and combinations thereof. Although not oxidizing agents per se, for the sake of the present disclosure, oxidizing agents further include alkanesulfonic acids (e.g., methanesulfonic acid (MSA), ethanesulfonic acid, 2-hydroxyethanesulfonic acid, n-propanesulfonic acid, isopropanesulfonic acid, isobutenesulfonic acid, n-butenesulfonic acid, and n-octanesulfonic acid). The oxidizing agents can include a combination of the any of the species defined herein as oxidizing agent. The oxidizing agent may be introduced to the first composition at the manufacturer, prior to introduction of the leaching composition to the particles, or alternatively *in situ*. Preferably, the oxidizing agent comprises methanesulfonic acid, nitric acid, or a combination of methanesulfonic acid and nitric acid.

[0027] When present, it is thought that an effective amount of nitric acid serves as an accelerator of the leaching process. Accordingly, in some embodiments, the oxidizing agent in the leaching composition preferably comprises an alkane sulfonic acid (e.g., MSA) and nitric acid, wherein the alkane sulfonic acid is present in an amount ranging from 0.1 to 85 wt%, more preferably from 5 to 45 wt%, and the nitric acid is present in an amount of about 0.1 to 80 wt%, preferably from about 1 to 40 wt%.

[0028] Metal chelators are included to complex the metal ions generated by the oxidizing agent. Metal chelators contemplated herein include, but are not limited to: β -diketonate compounds such as acetylacetonate, 1,1,1-trifluoro-2,4-pentanedione, and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione; carboxylates such as formate and acetate and other long chain carboxylates; and amides (and amines), such as bis(trimethylsilylamide) tetramer. Additional chelating agents include amines and amino acids (i.e. glycine, serine, proline, leucine, alanine, asparagine, aspartic acid, glutamine, valine, and lysine), citric acid, acetic acid, maleic acid, oxalic acid, malonic acid, succinic acid, phosphonic acid, phosphonic acid derivatives such as hydroxyethylidene diphosphonic acid (HEDP), 1-hydroxyethane-

1,1-diphosphonic acid, nitrilo-tris(methylenephosphonic acid), nitrilotriacetic acid, iminodiacetic acid, etidronic acid, ethylenediamine, ethylenediaminetetraacetic acid (EDTA), and (1,2-cyclohexylenedinitrilo)tetraacetic acid (CDTA), uric acid, tetraglyme, pentamethyldiethylenetriamine (PMDETA), 1,3,5-triazine-2,4,6-thithiol trisodium salt solution, 1,3,5-triazine-2,4,6-thithiol triammonium salt solution, sodium diethyldithiocarbamate, disubstituted dithiocarbamates ($R^1(CH_2CH_2O)_2NR^2CS_2Na$) with one alkyl group (R^2 = hexyl, octyl, deceyl or dodecyl) and one oligoether ($R^1(CH_2CH_2O)_2$, where R^1 = ethyl or butyl), ammonium sulfate, monoethanolamine (MEA), Dequest 2000, Dequest 2010, Dequest 2060s, diethylenetriamine pentaacetic acid, propylenediamine tetraacetic acid, 2-hydroxypyridine 1-oxide, ethylenediamine disuccinic acid (EDDS), N-(2-hydroxyethyl)iminodiacetic acid (HEIDA), sodium triphosphate penta basic, sodium and ammonium salts thereof, ammonium chloride, sodium chloride, lithium chloride, potassium chloride, ammonium sulfate, hydrochloric acid, sulfuric acid, and combinations thereof. Preferably, the metal chelator comprises ammonium chloride, sodium chloride, lithium chloride, potassium chloride, ammonium sulfate, hydrochloric acid, sulfuric acid, and combinations thereof, most preferably sodium chloride, sulfuric acid, or a combination of sodium chloride and sulfuric acid.

[0029] When nitric acid is included in the leaching composition, nitrogen oxides (NO_x) are generated. Accordingly, NO_x suppressors are preferably included when the leaching composition includes nitric acid. Surprisingly, however, the NO_x suppressors are also accelerators of the metal etch rates so they can be added even if the leaching composition does not include nitric acid. NO_x suppressors/accelerators contemplated include, but are not limited to, ascorbic acid, adenosine, L(+)-ascorbic acid, isoascorbic acid, ascorbic acid derivatives, citric acid, ethylenediamine, gallic acid, oxalic acid, tannic acid, ethylenediaminetetraacetic acid (EDTA), uric acid, 1,2,4-triazole (TAZ), triazole derivatives (e.g., benzotriazole (BTA), tolyltriazole, 5-phenyl-benzotriazole, 5-nitro-benzotriazole, 3-amino-5-mercapto-1,2,4-triazole, 1-amino-1,2,4-triazole, hydroxybenzotriazole, 2-(5-amino-pentyl)-benzotriazole, 1-amino-1,2,3-triazole, 1-amino-5-methyl-1,2,3-triazole, 3-amino-1,2,4-triazole, 3-mercapto-1,2,4-triazole, 3-isopropyl-1,2,4-triazole, 5-phenylthiol-benzotriazole, halo-benzotriazoles (halo = F, Cl, Br or I), naphthotriazole), 4-amino-1,2,4-triazole (ATAZ), 2-mercaptobenzimidazole (MBI), 2-mercaptobenzothiazole, 4-methyl-2-phenylimidazole, 2-mercaptothiazoline, 5-aminotetrazole (ATA), 5-amino-1,3,4-thiadiazole-2-thiol, 2,4-diamino-6-methyl-1,3,5-triazine, thiazole, triazine, methyltetrazole, 1,3-dimethyl-2-imidazolidinone, 1,5-pentamethylenetetrazole, 1-phenyl-5-mercaptotetrazole, diaminomethyltriazine, imidazoline thione, mercaptobenzimidazole, 4-methyl-4H-1,2,4-triazole-3-thiol, 5-amino-1,3,4-thiadiazole-2-thiol, benzothiazole, tritolyl phosphate, imidazole, indiazole, benzoic acid, boric acid, malonic acid, ammonium benzoate, catechol, pyrogallol, resorcinol, hydroquinone, cyanuric acid, barbituric acid and derivatives such as 1,2-dimethylbarbituric acid, alpha-keto acids such as pyruvic acid, adenine, purine, phosphonic acid and derivatives thereof, glycine/ascorbic acid, Dequest 2000, Dequest 7000, p-tolylthiourea, succinic acid, phosphonobutane tricarboxylic acid (PBTCA), sodium molybdate,

ammonium molybdate, salts of chromate (e.g., sodium, potassium, calcium, barium), sodium tungstate, salts of dichromate (e.g., sodium, potassium, ammonium), suberic acid, azaleic acid, sebacic acid, adipic acid, octamethylene dicarboxylic acid, pimelic acid, dodecane dicarboxylic acid, dimethyl malonic acid, 3,3-diethyl succinic acid, 2,2-dimethyl glutaric acid, 2-methyl adipic acid, trimethyl adipic acid, 1,3-cyclopentane dicarboxylic acid, 1,4-cyclohexane dicarboxylic acid, terephthalic acid, isophthalic acid, 2,6-naphthalene dicarboxylic acid, 2,7-naphthalene dicarboxylic acid, 1,4-naphthalene dicarboxylic acid, 1,4-phenylenedioxy diacetic acid, 1,3-phenylenedioxy diacetic acid, diphenic acid, 4,4'-biphenyl dicarboxylic acid, 4,4'-oxydibenzoic acid, diphenylmethane-4,4'-dicarboxylic acid, diphenylsulfone-4,4'-dicarboxylic acid, decamethylene dicarboxylic acid, undecamethylene dicarboxylic acid, dodecamethylene dicarboxylic acid, orthophthalic acid, naphthalenedicarboxylic acid, paraphenylenedicarboxylic acid, trimellitic acid, pyromellitic acid, sodium phosphates (e.g., sodium hexametaphosphate), sodium silicates, amino acids and their derivatives such as l-arginine, nucleoside and nucleobases such as adenosine and adenine, respectively, and combinations thereof. Most preferably, the NO_x suppressor/accelerator comprises ATAZ, TAZ, triazole derivatives, or combinations thereof, most preferably ATAZ.

[0030] Solvents contemplated herein include water, preferably deionized water, as well as organic solvent such as alcohols, glycol ethers, glycols, and carbonates, including, but not limited to, methanol, ethanol, isopropanol, butanol, and higher alcohols (including diols, triols, etc.), ethylene glycol, propylene glycol, butylene carbonate, ethylene carbonate, propylene carbonate, dipropylene glycol, diethylene glycol monomethyl ether, triethylene glycol monomethyl ether, diethylene glycol monoethyl ether, triethylene glycol monoethyl ether, ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, diethylene glycol monobutyl ether (i.e., butyl carbitol), triethylene glycol monobutyl ether, ethylene glycol monohexyl ether, diethylene glycol monohexyl ether, ethylene glycol phenyl ether, propylene glycol methyl ether, dipropylene glycol methyl ether (DPGME), tripropylene glycol methyl ether, dipropylene glycol dimethyl ether, dipropylene glycol ethyl ether, propylene glycol n-propyl ether, dipropylene glycol n-propyl ether (DPGPE), tripropylene glycol n-propyl ether, propylene glycol n-butyl ether, dipropylene glycol n-butyl ether, tripropylene glycol n-butyl ether, propylene glycol phenyl ether, and combinations thereof, and combinations thereof. Preferably, the solvent comprises water.

[0031] When present, the at least one etchant can include at least one carbonate species, at least one hydroxide species and/or at least one fluoride species. Carbonates include, but are not limited to, sodium carbonate, potassium carbonate, sodium hydrogen carbonate, and combinations thereof. Hydroxides contemplated include, but are not limited to, alkali hydroxides, alkaline earth metal hydroxides, metal ion-free hydroxides, and combinations thereof such as LiOH, NaOH, KOH, RbOH, CsOH, Mg(OH)₂, Ca(OH)₂, Sr(OH)₂, Ba(OH)₂, NR₄OH, wherein R can be the same as or different from one another and include H, C₁-C₆ alkyl (e.g., methyl, ethyl, propyl, butyl, pentyl, hexyl) or C₆-C₁₀ aryl (e.g., benzyl), and combinations thereof. The at least one fluoride species may comprise a

species selected from the group consisting of xenon difluoride; HF; pentamethyldiethylenetriammonium trifluoride; ammonium bifluoride; triethylaminogallate trihydrofluoride; alkyl hydrogen fluoride (NRH_3F), wherein each R is independently selected from hydrogen and $\text{C}_1\text{-C}_4$ alkyl (e.g., methyl, ethyl, propyl, butyl); dialkylammonium hydrogen fluoride ($\text{NR}_2\text{H}_2\text{F}$), wherein each R is independently selected from hydrogen and $\text{C}_1\text{-C}_4$ alkyl; trialkylammonium hydrogen fluoride (NR_3HF), wherein each R is independently selected from hydrogen and $\text{C}_1\text{-C}_4$ alkyl; trialkylammonium trihydrogen fluoride ($\text{NR}_3\text{:3HF}$), wherein each R is independently selected from hydrogen and $\text{C}_1\text{-C}_4$ alkyl; ammonium fluorides of the formula R_4NF , wherein each R is independently selected from hydrogen, $\text{C}_1\text{-C}_4$ alkyl, and $\text{C}_1\text{-C}_4$ alkanol (e.g., methanol, ethanol, propanol, butanol) such as ammonium fluoride, tetramethylammonium fluoride, triethanolammonium fluoride, tetraethylammonium fluoride; and combinations thereof. Preferably, the fluoride source comprises HF, ammonium fluoride, or combinations thereof. When present the amount of etchant is preferably in a range from about 0.01 wt% to about 10 wt%, based on the total weight of the composition.

[0032] It is also contemplated herein that the combination of low energy sonication or megasonics with leaching formulations also can accelerate lead removal from CRT glass.

[0033] Advantageously, an easily recyclable leaching composition can be employed in a closed-loop process generating minimal waste. For example, when the leaching composition includes MSA, the MSA is easily recycled using diffusion dialysis.

[0034] Most preferably, the leaching composition comprises, consists or consists essentially of MSA, nitric acid, and ATAZ. In another preferred embodiment, the leaching composition comprises, consists of, or consists essentially of MSA, sulfuric acid, ATAZ, and NaCl.

[0035] In another aspect, the leaching composition and the pulverized CRT glass can be placed into a high pressure autoclave for the leaching process. Water is known to have very strong oxidizing properties at hydrothermal ($>100^\circ\text{C}$ and >100 psi) conditions and near critical conditions ($>300^\circ\text{C}$ and >3000 psi). Accordingly, at these hydrothermal conditions, water alone may be strong enough to oxidize the lead so that the chelator can extract the lead. Suitable chelators include chloride, iodide, hydroxide, or sulfate salts (e.g., as described herein), wherein hydroxide or sulfate are preferred because they will not corrode steel vessels required for high pressure applications and they will readily precipitate from solution upon cooling and depressurizing of the vessel.

[0036] The resulting lead-free glass may be remelted for reuse (e.g., bricks, tiles, foam), mixed into, for example, asphalt or cement as a filler, or sent to a landfill for safe disposal. Lead can be removed from the solution in the form of an oxide or salt and may be resold. The system is closed so that no vapors escapes and all of the chemistry and the rinse water are recycled for reuse in the process. Small amounts of rinse water are discharged, but it is first neutralized and has less than part-per-million trace metals and no organics.

[0037] Although the invention has been variously disclosed herein with reference to illustrative embodiments and features, it will be appreciated that the embodiments and features described hereinabove are not intended to limit the invention, and that other variations, modifications and other embodiments will suggest themselves to those of ordinary skill in the art, based on the disclosure herein. The invention therefore is to be broadly construed, as encompassing all such variations, modifications and alternative embodiments within the spirit and scope of the claims hereafter set forth.

THE CLAIMS

What is claimed is:

1. A method of leaching lead or other heavy metals from solid materials, said method comprising:

pulverizing the solid materials to size in a range from about 10 microns to about 3 mm;

introducing the pulverized solid materials into a chemical processing vessel comprising a leaching composition to form a slurry;

agitating the slurry to leach the lead or other heavy metals from the solid material into the leaching composition,

wherein the leaching composition comprises at least one oxidant, at least one solvent, optionally at least one metal chelator, optionally at least one accelerator/NO_x (nitrogen oxide) suppressor, and optionally at least one etchant.

2. The method of claim 1, wherein the solid material comprises cathode ray tube glass, soil, paint chips, electronic waste, and solder sludge.

3. The method of claims 1 or 2, wherein the agitation occurs in the presence of added heat.

4. The method of any of the preceding claims, further comprising filtering the solid material from the leaching composition.

5. The method of claim 4, further comprising rinsing the solid material with a rinse composition to remove residual leaching composition therefrom.

6. The method of claim 4, further comprising processing the leaching composition to recapture the lead or other heavy metals.

7. The method of any of the preceding claims, wherein the material comprises glass and wherein the lead or other heavy metals on the surface of the pulverized solid material have been substantially removed.

8. The method of any of the preceding claims, wherein the at least one oxidant comprises ozone, nitric acid, bubbled air, cyclohexylaminosulfonic acid, , hydrogen peroxide, oxone, ammonium peroxomonosulfate, ammonium chlorite, ammonium chlorate, ammonium iodate, ammonium perborate, ammonium perchlorate, ammonium periodate, ammonium persulfate, ammonium hypochlorite, sodium persulfate, sodium hypochlorite, potassium iodate, potassium permanganate, potassium persulfate, potassium persulfate, potassium hypochlorite, tetramethylammonium chlorite, tetramethylammonium chlorate, tetramethylammonium iodate, tetramethylammonium perborate, tetramethylammonium perchlorate, tetramethylammonium periodate, tetramethylammonium persulfate, tetrabutylammonium peroxomonosulfate, peroxomonosulfuric acid, urea hydrogen peroxide, peracetic acid, sodium nitrate, potassium nitrate, ammonium nitrate, sulfuric acid, methanesulfonic acid (MSA), ethanesulfonic acid, 2-hydroxyethanesulfonic acid, n-propanesulfonic acid, isopropanesulfonic acid, isobutenesulfonic acid, n-butenesulfonic acid, and n-octanesulfonic acid, and combinations thereof.

9. The method of any of the preceding claims, wherein the at least one oxidant comprises methanesulfonic acid, nitric acid, or a combination of methanesulfonic acid and nitric acid.

10. The method of any of the preceding claims, wherein the leaching composition comprises the at least one metal chelator, wherein the at least one metal chelator comprises a species selected from the group consisting of acetylacetonate, 1,1,1-trifluoro-2,4-pentanedione, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, formates, acetates, bis(trimethylsilylamide) tetramer, glycine, serine, proline, leucine, alanine, asparagine, aspartic acid, glutamine, valine, and lysine, citric acid, acetic acid, maleic acid, oxalic acid, malonic acid, succinic acid, phosphonic acid, hydroxyethylidene diphosphonic acid (HEDP), 1-hydroxyethane-1,1-diphosphonic acid, nitrilo-tris(methylenephosphonic acid), nitrilotriacetic acid, iminodiacetic acid, etidronic acid, ethylenediamine, ethylenediaminetetraacetic acid (EDTA), (1,2-cyclohexylenedinitrilo)tetraacetic acid (CDTA), uric acid, tetraglyme, pentamethyldiethylenetriamine (PMDETA), 1,3,5-triazine-2,4,6-thithiol trisodium salt solution, 1,3,5-triazine-2,4,6-thithiol triammonium salt solution, sodium diethyldithiocarbamate, disubstituted dithiocarbamates, ammonium sulfate, monoethanolamine (MEA), Dequest 2000, Dequest 2010, Dequest 2060s, diethylenetriamine pentaacetic acid, propylenediamine tetraacetic acid, 2-hydroxypyridine 1-oxide, ethylenediamine disuccinic acid (EDDS), N-(2-hydroxyethyl)iminodiacetic acid (HEIDA), sodium triphosphate penta basic, ammonium chloride, sodium chloride, lithium chloride, potassium chloride, ammonium sulfate, hydrochloric acid, sulfuric acid, and combinations thereof.

11. The method of any of the preceding claims, wherein the leaching composition comprises the at least one metal chelator, wherein the at least one metal chelator comprises ammonium chloride,

sodium chloride, lithium chloride, potassium chloride, ammonium sulfate, hydrochloric acid, sulfuric acid, and combinations thereof.

12. The method of any of the preceding claims, wherein the leaching composition comprises the at least one accelerator/ NO_x (nitrogen oxide) suppressor, wherein the at least one accelerator/ NO_x suppressor comprises a species selected from the group consisting of ascorbic acid, adenosine, L(+)-ascorbic acid, isoascorbic acid, ascorbic acid derivatives, citric acid, ethylenediamine, gallic acid, oxalic acid, tannic acid, ethylenediaminetetraacetic acid (EDTA), uric acid, 1,2,4-triazole (TAZ), benzotriazole (BTA), tolyltriazole, 5-phenyl-benzotriazole, 5-nitro-benzotriazole, 3-amino-5-mercapto-1,2,4-triazole, 1-amino-1,2,4-triazole, hydroxybenzotriazole, 2-(5-amino-pentyl)-benzotriazole, 1-amino-1,2,3-triazole, 1-amino-5-methyl-1,2,3-triazole, 3-amino-1,2,4-triazole, 3-mercapto-1,2,4-triazole, 3-isopropyl-1,2,4-triazole, 5-phenylthiol-benzotriazole, halo-benzotriazoles (halo = F, Cl, Br or I), naphthotriazole), 4-amino-1,2,4-triazole (ATAZ), 2-mercaptobenzimidazole (MBI), 2-mercaptobenzothiazole, 4-methyl-2-phenylimidazole, 2-mercaptothiazoline, 5-aminotetrazole (ATA), 5-amino-1,3,4-thiadiazole-2-thiol, 2,4-diamino-6-methyl-1,3,5-triazine, thiazole, triazine, methyltetrazole, 1,3-dimethyl-2-imidazolidinone, 1,5-pentamethylenetetrazole, 1-phenyl-5-mercaptotetrazole, diaminomethyltriazine, imidazoline thione, mercaptobenzimidazole, 4-methyl-4H-1,2,4-triazole-3-thiol, 5-amino-1,3,4-thiadiazole-2-thiol, benzothiazole, tritolyl phosphate, imidazole, indiazole, benzoic acid, boric acid, malonic acid, ammonium benzoate, catechol, pyrogallol, resorcinol, hydroquinone, cyanuric acid, barbituric acid, 1,2-dimethylbarbituric acid, pyruvic acid, adenine, purine, phosphonic acid and derivatives thereof, glycine/ascorbic acid, Dequest 2000, Dequest 7000, p-tolylthiourea, succinic acid, phosphonobutane tricarboxylic acid (PBTCA), sodium molybdate, ammonium molybdate, salts of chromate (e.g., sodium, potassium, calcium, barium), sodium tungstate, salts of dichromate (e.g., sodium, potassium, ammonium), suberic acid, azaleic acid, sebacic acid, adipic acid, octamethylene dicarboxylic acid, pimelic acid, dodecane dicarboxylic acid, dimethyl malonic acid, 3,3-diethyl succinic acid, 2,2-dimethyl glutaric acid, 2-methyl adipic acid, trimethyl adipic acid, 1,3-cyclopentane dicarboxylic acid, 1,4-cyclohexane dicarboxylic acid, terephthalic acid, isophthalic acid, 2,6-naphthalene dicarboxylic acid, 2,7-naphthalene dicarboxylic acid, 1,4-naphthalene dicarboxylic acid, 1,4-phenylenedioxy diacetic acid, 1,3-phenylenedioxy diacetic acid, diphenic acid, 4,4'-biphenyl dicarboxylic acid, 4,4'-oxydibenzoic acid, diphenylmethane-4,4'-dicarboxylic acid, diphenylsulfone-4,4'-dicarboxylic acid, decamethylene dicarboxylic acid, undecamethylene dicarboxylic acid, dodecamethylene dicarboxylic acid, orthophthalic acid, naphthalenedicarboxylic acid, paraphenylenedicarboxylic acid, trimellitic acid, pyromellitic acid, sodium hexametaphosphate, sodium silicates, l-arginine, adenosine, adenine, and combinations thereof.

13. The method of any of the preceding claims, wherein the leaching composition comprises the at least one accelerator/ NO_x (nitrogen oxide) suppressor, wherein the at least one accelerator/ NO_x suppressor comprises ATAZ, TAZ, triazole derivatives, or combinations thereof.
14. The method of any of the preceding claims, wherein the solvent comprises water.
15. The method of any of the preceding claims, wherein the leaching composition comprises the at least one etchant, wherein the at least one etchant is selected from the group consisting of at least one carbonate species, at least one hydroxide species, at least one fluoride species, and any combination thereof.
16. The method of claim 15, wherein the at least one etchant comprises a species selected from the group consisting of sodium carbonate; potassium carbonate; sodium hydrogen carbonate; LiOH ; NaOH ; KOH ; RbOH ; CsOH ; $\text{Mg}(\text{OH})_2$; $\text{Ca}(\text{OH})_2$; $\text{Sr}(\text{OH})_2$; $\text{Ba}(\text{OH})_2$; NR_4OH , wherein R can be the same as or different from one another and include H, $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_6\text{-C}_{10}$ aryl, and combinations thereof; xenon difluoride; HF ; pentamethyldiethylenetriammonium trifluoride; ammonium bifluoride; triethylaminogallate trihydrofluoride; alkyl hydrogen fluoride (NRH_3F), wherein each R is independently selected from hydrogen and $\text{C}_1\text{-C}_4$ alkyl; dialkylammonium hydrogen fluoride ($\text{NR}_2\text{H}_2\text{F}$), wherein each R is independently selected from hydrogen and $\text{C}_1\text{-C}_4$ alkyl; trialkylammonium hydrogen fluoride (NR_3HF), wherein each R is independently selected from hydrogen and $\text{C}_1\text{-C}_4$ alkyl; trialkylammonium trihydrogen fluoride ($\text{NR}_3\text{:}3\text{HF}$), wherein each R is independently selected from hydrogen and $\text{C}_1\text{-C}_4$ alkyl; ammonium fluorides of the formula R_4NF , wherein each R is independently selected from hydrogen, $\text{C}_1\text{-C}_4$ alkyl, and $\text{C}_1\text{-C}_4$ alkanol; and combinations thereof.

A. CLASSIFICATION OF SUBJECT MATTER**B02C 23/08(2006.01)i, H01J 9/52(2006.01)i**

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B02C 23/08; C22B 7/00; C22B 3/04; C21B 15/00; C22B 3/06; C23F 1/44; B01D 11/02; H01J 9/52

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & keywords: CRT, lead, heavy metal, leach, pulverize, oxidant, solvent, chelator, etchant, accelerator

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6666904 B1 (LOUGH, LARRY LEE) 23 December 2003 See abstract; column 10-65, column 3 lines 33-67 and column 4 lines 1-49; claims 8 and 14-16.	1-3
Y	WO 2011-130622 A1 (ADVANCED TECHNOL. MATERIALS INC. et al.) 20 October 2011 See abstract; paragraphs [0002] and [0057]-[0065]; figs. 1 and 2.	1-3
A	WO 2012-019383 A1 (SHENZHEN GEM HIGH-TECH CO., LTD. et al.) 16 February 2012 See abstract; page 8 and 9; figs. 1 and 2; claims 1, 4 and 5.	1-3
A	US 2004-0083856 A1 (GREEN, FREDERICK H.) 06 May 2004 See abstract; paragraphs [0002], [0014] and [0050]-[0052].	1-3
A	JP 2004-162141 A (ENERGY KANKYO SEKKEI KK.) 10 June 2004 See abstract; paragraphs [0001], [0008] and [0023]-[0025]; figs. 1-3.	1-3



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

19 July 2013 (19.07.2013)

Date of mailing of the international search report

22 July 2013 (22.07.2013)

Name and mailing address of the ISA/KR


 Korean Intellectual Property Office
 189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City,
 302-701, Republic of Korea

Facsimile No. +82-42-472-7140

Authorized officer

CHANG Bong Ho

Telephone No. +82-42-481-3353



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/035379

Box No. II **Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 5,6,16
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claims 5, 6 and 16 are unclear because they refer to a multiple dependent claim which does not comply with PCT Rule 6.4(a).
3. ☒ Claims Nos.: 4,7-15
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2013/035379

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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JP 2004-162141 A	10/06/2004	None	