

ORIGINAL

11550 N. MERIDIAN STREET • SUITE 180 • CARMEL • INDIANA 46032 • PH 317.660.6868 • FX 317.569.0451

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December 17, 2008

DEC 18 2008

STATE OF ILLINOIS
Pollution Control Board

PC# 324

Royal Coulter, President
Peoria Disposal Company
4700 North Sterling Avenue
Peoria, Illinois 61615-3652

RE: **NOTICE OF EXCLUSIVE LICENSE**
United States Patents 6,191,068 and 6,313,368

Dear Mr. Coulter:

Terra Materials, LLC has recently become aware of your company's interest in using a magnesium sulfite/magnesium scrubber residue (MSR) in conjunction with your proposed "delisting permit" now pending before the Illinois Environmental Protection Agency (Case No. AS 2008-010 - In the Matter of: RCRA Delisting Adjusted Standard Petition of Peoria Disposal Company).

Terra Materials, LLC is not fully familiar with your company's proposed treatment regime, but has reviewed sworn testimony presented on your company's behalf at the August 18, 2008 hearing before the Illinois Pollution Control Board. Specifically, beginning on page 33 of the testimony, Dr. Ajit Chowdhury described the proposed treatment to be used by Peoria Disposal as:

"The new chemical treatment regimen PDC utilized for the trials incorporated addition of reagents involving sulfur oxy-anion compounds of alkaline-earth metals along with agents for pH control which included calcined and uncalcined lime. As necessary, the pH control agents which may be used include various phosphate and iron compounds. The additive mix ratio and dosage were controlled to provide a robust chemistry such that the potential for leaching of heavy metals of concern are minimized under various natural and induced leaching scenarios. During this treatment, the heavy metals are stabilized through a series of complex precipitation and adsorption-coprecipitation reactions in a pH regime of very low solubility of the metals. The material after stabilization is characterized by low potential for leaching of heavy metals as indicated by the TCLP (U.S. EPA Toxicity Characteristic Leaching Procedure) which is TCLP, analysis with using different 8 extraction fluids like acidic, neutral and a pH 11.0 solution and also the corresponding MEP tests which is a multiple extraction procedure of U.S.EPA."

After discussing this matter with our supplier of MSR and reviewing the public record of your proposed delisting permit, we concluded we should advise you that Terra Materials, LLC is the exclusive licensee of:

11550 N. MERIDIAN STREET · SUITE 180 · CARMEL · INDIANA 46032 · PH 317.660.6868 · FX 317.569.0451



United States Patent 6,191,068 relating to compositions comprising magnesium sulfite, triple super phosphate, and at least one of limestone and hydroboracite, methods for the treatment of heavy metal-containing matrices, methods for controlling the pH of matrices, and methods for removing acid gases from solid, semi-solid, liquid or gaseous matrices; and,

United States Patent 6,313,368 relating to methods of stabilizing heavy metal-containing matrices comprising mixing with such matrices an effective amount of sulfonated calcium aluminum magnesium phosphate to render such matrices inert, methods of stabilizing heavy metal-containing matrices comprising mixing with such matrices an effective amount of magnesium sulfite to render such matrices inert, and methods of stabilizing heavy metal-containing matrices comprising mixing with such matrices an effective amount of hydroboracite to render such matrices inert.

Copies of the referenced patents are attached for your convenience.

In addition to these exclusive licenses, Terra Materials, LLC has also filed patent applications for methods for the stabilization and/or fixation of leachable metals on its own behalf. These patent applications describe the use of magnesium-based scrubber byproducts and calcium-based products and byproducts either individually or in various combinations for the stabilization and/or fixation of heavy metal-containing matrices, other contaminants and chemicals matrices.

Terra Materials, LLC desires to maximize the use of the inventions disclosed and protected by these patents and applications through sale and use of products incorporating these technologies, as well as through sub-licensing, sales agreements, and other arrangements with others. It is in this spirit that we are notifying you and others of these matters.

We look forward to working with your company to achieve this goal. Please contact us so we can amicably reach a mutually profitable agreement.

Sincerely,

TERRA MATERIALS, LLC

A handwritten signature in black ink, appearing to read "Thomas P. McCullough". The signature is fluid and cursive, with the first name being the most prominent.

Thomas P. McCullough
Managing Partner

cc: Steve Thomas, Headwaters Resources, Inc.
Tom D'Annunzio, Exelon Supply Management
Dr. Ajit Chowdhury, Trishul Technologies, LLC
Clerk's Office, Illinois Pollution Control Board

Enclosures: US Patent Nos. 6,191,068 and 6,313,368



US006313368B1

(12) **United States Patent**
Bhat

(10) **Patent No.:** US 6,313,368 B1
(45) **Date of Patent:** *Nov. 6, 2001

(54) **METHOD AND COMPOSITIONS FOR STABILIZATION OF HEAVY METALS, ACID GAS REMOVAL AND PH CONTROL IN CONTAMINATED MATRICES**

(75) **Inventor:** Vasanth K. Bhat, 9 Belsaw Pl., Cincinnati, OH (US) 45220

(73) **Assignee:** Vasanth K. Bhat

(*) **Notice:** Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) **Appl. No.:** 09/404,531

(22) **Filed:** Sep. 24, 1999

Related U.S. Application Data

(60) Continuation of application No. 08/961,823, filed on Oct. 31, 1997, now Pat. No. 5,985,778, which is a division of application No. 08/790,700, filed on Jan. 29, 1997, now Pat. No. 5,719,099

(60) Provisional application No. 60/028,935, filed on Oct. 22, 1996.

(51) **Int. Cl.7** A62D 3/00

(52) **U.S. Cl.** 588/231; 588/236; 588/252

(58) **Field of Search** 502/3, 14, 414, 502/415, 521; 423/424.1; 501/48; 588/231, 236, 252, 257, 901

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Primary Examiner—Steven P. Griffin

Assistant Examiner—Eileen E. Nave

(57) **ABSTRACT**

A one-step method and compositions for stabilization of heavy metals, acid gas removal and pH control in hazardous and toxic solid, semi-solid, liquid and/or gaseous matrices using a mixture of reactive agents in a single product, for the broader purpose of enhancing environmental pollution control, prevention and remediation are described. The product contains sulfonated calcium aluminum magnesium phosphate. This material may be used alone or in combination with magnesium sulfite and/or hydroboracite.

3 Claims, No Drawings

US 6,313,368 B1

1

**METHOD AND COMPOSITIONS FOR
STABILIZATION OF HEAVY METALS, ACID
GAS REMOVAL AND PH CONTROL IN
CONTAMINATED MATRICES**

This application is a Continuation of application Ser. No. 08/961,823 filed on Oct. 31, 1997, now U.S. Pat. No. 5,985,778 which is a Divisional of application Ser. No. 08/790,700 filed Jan. 29, 1997, now U.S. Pat. No. 5,719,099. This application claims priority of provisional application Serial No. 60/028,935 filed Oct. 22, 1996.

TECHNICAL FIELD

This invention relates to the treatment of contaminated materials. Specifically, it relates to methods and compositions for rendering inert a broad spectrum of heavy metals that may be present in hazardous and/or toxic matrices, such as fly ash and slag from incinerators, process water from ink and paint manufacturing, process dust, water and sludge from ferrous and non-ferrous foundries, electric arc furnace dust, for example, from steel mills, hazardous waste, toxic waste, soils, sludges and sediments. Heavy metals like antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, mercury, molybdenum, nickel, selenium, silver, thallium, vanadium and zinc are reduced to a level of permanent stability meeting the glacial acetic acid leachate criteria set forth by the U.S. EPA in the Toxicity Characteristic Leaching Procedure (TCLP) and the water leach tests, for example, California or Indiana Water Leach Tests, simulating leaching due to rain as it actually occurs in the environment. The invention also relates to industrial processes that require acid gas removal from the contaminated matrix and pH control of the contaminated matrix.

BACKGROUND OF THE INVENTION

When biologically available, heavy metals leaching from soil, water or waste, as well as those released into the air, are detrimental to all living beings. Permissible levels of heavy metal pollution are regulated by the local, state and federal authorities. The important sets of federal regulations are the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), which governs the Superfund program. One of the earliest remediation methods, the removal and hauling of heavy metal contained waste and soil to a landfill, while still in use, is more frequently being viewed by the public as unacceptable. New regulations and continued desire to find better and/or inexpensive environmental pollution control, prevention and remediation techniques have driven potential hazardous and/or toxic waste generators toward new technologies. Encapsulation of heavy metal-containing waste in portland cement, for example, though meeting the letter of the environmental law, does not meet the spirit of the law when the encapsulated waste is exposed to rain. Under those circumstances, heavy metals go into solution and become biologically available. Permanent stabilization by forming geochemically stable compounds of heavy metals is by far the best solution to this challenge. Certain industrial processes may also release acid gases which need to be removed. Often pH control of the contaminated matrix is also required.

Numerous methods, mostly multi-step and sequential-step, have been utilized to prevent the leaching of hazardous heavy metals in solid, semi-solid, liquid and/or gaseous complex matrices so that the waste is rendered suitable for disposal in a sanitary landfill. There has, however, been no

2

suggestion to use sulfonated calcium aluminum magnesium phosphates, hydroboracite or scrubber magnesium product (magnesium sulfite) for the purpose of providing heavy metal stabilization, together with the additional benefits of acid gas removal and pH control, to contaminated or treated matrices in a one-step method or single-product composition. U.S. Pat. No. 4,671,882, Douglas et al., issued June, 1987, discloses a multi-step process for heavy metal stabilization. Douglas does not prefer to use limestone because he believes that the use of limestone results in the production of carbon dioxide gas when added to acid solution and such gas would adversely affect the pH increasing step essential to his multi-step heavy metal stabilization process. Both U.S. Pat. Nos. 4,889,640 and 5,037,479, Stanforth, suggest that limestone is not effective in the disclosed heavy metal stabilization processes because it is a non-reactive form of calcium and/or magnesium carbonate. The above-mentioned patents do not suggest any products or processes for acid gas removal.

SUMMARY OF THE INVENTION

It is the primary object of the present invention to provide a one-step method and single-product compositions that simultaneously stabilize heavy metals, remove acid gases and control pH in contaminated solid, semi-solid, liquid and/or gaseous complex matrices.

It is a further object of the present invention to provide a new method for the simultaneous treatment of a wide variety of matrices including in-process and waste materials contaminated with a broad range of heavy metals classified by the U.S. EPA as hazardous, such that geochemically stable, substantially non-leaching compounds of heavy metals are formed and the contaminated matrices are rendered inert.

It is another object of the present invention to provide a new family of compositions that achieve permanent stability of leachable heavy metals in complex matrices exposed to actual environmental conditions.

It is still another object of the present invention to provide a method and a general range of compositions that stabilize more heavy metals than those in the prior art using one-step treatment and using a single product which may contain one or more reactive agents.

It is yet another object of the present invention to provide a method and compositions that are more cost-effective than those of the prior art in stabilizing heavy metals in a wide variety of complex matrices.

In accordance with the present invention there is provided a method and compositions for the treatment of in-process hazardous materials and waste materials contaminated with hazardous heavy metals to levels of local, state and federal regulatory limits. Simultaneously, this invention provides a single-step method and single-product compositions for heavy metal stabilization, acid gas removal and pH control in contaminated complex matrices.

Specifically, the present invention encompasses a composition for the treatment of heavy metal-containing matrices comprising an effective amount of sulfonated calcium aluminum magnesium phosphate. The composition may optionally include magnesium sulfite and/or hydroboracite.

The invention also relates to a method for making a composition for the treatment of heavy metal-containing matrices comprising the steps of mixing the following materials:

- (a) a phosphate-containing material selected from the group consisting of phosphoric acid, rock phosphate,

US 6,313,368 B1

3

- apatite, triple super phosphate, calcium magnesium monohydrogen phosphate dihydrate, alkali phosphate, and mixtures thereof;
- (b) an aluminum-containing material selected from the group consisting of kaolinite, bauxite, alumina dihydrate, bentonite, zeolites, and mixtures thereof; and
- (c) an alkaline earth-containing material selected from the group consisting of dolomite, dolime, quicklime, fly ash, limestone, brucite, magnesite, periclase, dolomitic limestone, magnesia, magnesium hydroxide, hydroboracite, colemanite, and mixtures thereof; and sulfonating the product(s) of said mixing step.

DETAILED DESCRIPTION OF THE INVENTION

The goals set forth above are accomplished using a single product and a one-step application method, as opposed to using several different reagents and multi-step or sequential application method to:

- (1) stabilize a broad spectrum of heavy metals (Table I) listed by the U.S. EPA as hazardous;
 - (2) control acid gases found in complex matrices, including industrial processes and waste; and
 - (3) control pH of the contaminated and treated matrices.
- This invention relates to compositions and methods for accomplishing these goals, as well as to method for preparing those compositions.

Table I—U.S. EPA List of Hazardous Heavy Metals

Antimony, Arsenic, Barium, Beryllium, Cadmium, Chromium, Cobalt, Copper, Lead, Mercury, Molybdenum, Nickel, Selenium, Silver, Thallium, Vanadium, and Zinc.

In developing the heavy metal stabilizing product compositions of this invention, economic considerations were applied to the following technical conceptual basis: Ingredients that form salts of low solubility with the heavy metals in question will also produce permanently stable, pH independent, complex, non-leaching compounds that immobilize the heavy metals when they contain glass (non-crystalline) network forming cations (such as Si, B, P, Ge and mixtures thereof) and glass (non-crystalline) network forming anions (such as O, S, Se, Te and mixtures thereof). In conjunction with ingredients containing the glass (non-crystalline) network forming ions, those containing network dwellers (such as Al, Mg, Ga and mixtures thereof) and network modifiers (such as Ca, Mg and mixtures thereof) are also found to help in stabilizing heavy metals contained in contaminated matrices. It is not necessary that glass actually be formed as a result of the reaction between heavy metals and the heavy metal stabilizer, but rather that the ingredients used to prepare the heavy metal stabilizers be capable of forming glass. It is important that salts of low solubility are formed as a result of the reaction between these ions and the heavy metals.

Thus, the technical concept of this invention advances two essential conditions for the production of permanently stable, pH independent, complex, non-leaching compounds that immobilize the heavy metals: (1) in selecting the ingredients for heavy metal stabilizing product compositions, it is important that they are capable of forming glass (that is, they contain glass network forming, network dwelling or network modifying ions), and (2) that salts of low solubility be formed as a result of the reaction between these ions and the heavy metals in question.

4

Sulfonated Calcium Aluminum Magnesium Phosphate (SCAMP) is a product composition that fits the technical concept by itself, as well as in conjunction with other ingredients. SCAMP can be described by the general formula $x \cdot (C_{12}H_{25}(C_6H_4)SO_3Na) (Ca_2Al Mg_3(PO_4)_6 \cdot 9H_2O)$, wherein $x < 1$. It can also be described as a sulfonated phosphate or a sulfonated mixture of phosphates, with ingredients containing calcium, aluminum and magnesium ions. The sulfonate in this case is sodium dodecylbenzene sulfonate. The presence of SCAMP can be detected directly by the combination of powder x-ray diffraction technique for calcium aluminum magnesium phosphate and wet chemical analysis for the sulfonate. SCAMP prepared according to the present application is an effective stabilizer for a broad spectrum of heavy metals.

In water, the sulfonate behaves like soap in forming micelles, but has an advantage over soap in not forming precipitates with calcium ions. Additionally, the sulfonate being a surfactant, reduces the surface tension of the particles coated with it, accelerates reactions between acidic and basic ingredients in a given mixture to form complex salts, prevents caking, and improves flowability of the product. The sulfonate also promotes the formation of heavy metal complex salts of very low solubility by facilitating the sequestering and fixing of heavy metal leachates from a contaminated matrix. These practically insoluble complex salts confirm pH independent and permanent fixing of leachates in a landfill. Sulfonates useful in the present invention include any salt of the reaction product of sulfonic acid and hydrocarbons, such as long chain alkylbenzene sulfonates, with sodium dodecylbenzene sulfonate being preferred.

SCAMP can be prepared in a number of ways. As an example, to produce one mole of SCAMP, combine 1 ½ moles of dolomitic limestone or 3 moles of dolomitic lime; with ½ mole of either kaolinite, bauxite or alumina trihydrate; react the same with 5 moles of phosphoric acid and treat the reaction product with less than one mole of the sulfonate. As another example, to produce one mole of SCAMP, combine and react 1 ½ moles of dolomitic limestone or 3 moles of dolomitic lime; with ½ mole of either kaolinite, bauxite or alumina trihydrate; and with 2 ½ moles of either triple super phosphate or rock phosphate, along with an appropriate amount of water, if needed, and less than one mole of the sulfonate. The solid raw materials are ground or pulverized to fine powder to provide high surface area for the required reaction(s) to take place. It is sometimes helpful to add heat to the reaction, although frequently the increased temperatures caused by grinding and the heat of reaction between ingredients are sufficient to provide the desired end product.

In general, a SCAMP-containing single product composition for the treatment of heavy metal-containing matrices may be prepared by combining, mixing and reacting the following materials:

- (a) a phosphate-containing material selected from the group consisting of phosphoric acid, rock phosphate, apatite, triple super phosphate, calcium magnesium monohydrogen phosphate dihydrate, alkali phosphate, and mixtures thereof (preferably phosphoric acid, rock phosphate or triple super phosphate, and most preferably rock phosphate);
- (b) an aluminum-containing material selected from the group consisting of kaolinite, bauxite, alumina trihydrate, bentonite, zeolites, and mixtures thereof (preferably bauxite or kaolinite); and

US 6,313,368 B1

5

(c) an alkaline earth-containing material selected from the group consisting of dolomitic limestone (dolomite), dolomitic lime (dolime), quicklime, fly ash, limestone, brucite, magnesite, periclase, magnesia, magnesium hydroxide, hydroboracite, colemanite, and mixtures thereof (preferably dolomitic limestone, dolimitic lime or hydroboracite, and most preferably dolomitic limestone);

and sulfonating the product(s) of said combining, mixing and reacting steps.

The proportions of the individual reactions listed above may be varied depending on the properties required for the final product. For example, for optimal heavy metal stabilization, the amount of material(s) from group (a) above in proportion to groups (b) and (c) should be about 6:1:3. For optimal acid gas control, the ratio should be about 6:1:12. For optimal pH control of the contaminated and treated matrices, the ratio should be about 6:1:3. SCAMP is an essential active agent in the product composition of the invention that assures in a single step, simultaneous and effective stabilization of at least 8 of the 17 heavy metals listed in Table I (see Table II below), as well as acid gas and pH control. Materials from groups (a), (b) or (c) used in excess of that required stoichiometrically for the formation of SCAMP are essentially for fine tuning the heavy metal stabilization, acid gas control or pH control characteristics of the final product. For example, formulating a product such that it contains excess phosphate material provides extra benefits in terms of pH control and in the stabilization of heavy metals that form phosphates of low solubility. Excess aluminum-containing material helps in pH control and in the stabilization of heavy metals that form oxides or hydroxides of low solubility, while excess alkaline earth-containing material helps in pH control and acid gas control.

Stabilization of all 17 heavy metals listed as hazardous by the U.S. EPA can be accomplished in a single-step, along with acid gas and pH control, using a product composition that comprises SCAMP and sulfur-containing materials such as magnesium sulfite, calcium sulfite, magnesium sulfate, sodium metabisulfite, calcium magnesium sulfite, epsom salt, gypsum, and mixtures thereof. Preferred sulfur-containing materials include magnesium sulfate, calcium sulfate and calcium magnesium sulfite, and mixtures thereof, with magnesium sulfite being most preferred. An inexpensive source of magnesium sulfite that also contains minor amounts of magnesium sulfate is Scrubber Magnesium

6

Product (SMP). This material is a by-product of scrubbing acid gases, like sulfur dioxide and oxides of nitrogen, with magnesium-containing reagents, such as magnesia, magnesium hydroxide, calcium magnesium oxide (dolime), calcium magnesium borate (hydroboracite), and calcium magnesium carbonate (dolomite). The use of sulfur-containing material (for example, SMP) alone, stabilizes 15 of the 17 heavy metals fairly well. Relative effectiveness of SMP alone and in combination with SCAMP is shown in Table II. The use of hydrated calcium magnesium borate, that is, hydroboracite (HB), alone or in conjunction with SCAMP, SMP and mixtures thereof is also depicted in Table II.

The compositions of the present invention comprise an amount of each specified component which is effective to stabilize the heavy metals present in the materials being treated, as well as to control pH and acid gas. Specifically, compositions of the present invention contain from about 10% to about 100%, preferably from about 10% to about 50% SCAMP, from about 0% to about 90%, preferably from about 5% to about 50%, magnesium sulfite, and from about 0% to about 90%, preferably from about 10% to about 50% hydroboracite. A few examples of SCAMP-, SMP-, and HB-containing compositions found to be effective in achieving the goals of the present invention are as follows:

Ex. #	Phosphate-containing materials	Aluminum-containing materials	Alkaline earth-containing materials	Sulfonate	SMP wt %	HB wt %
1	10-15	0.1-10	30-40	0.1-10	40-60	0-10
2	15-25	0.1-30	50-60	0.1-10	0-30	0-30
3	30-50	0.1-25	10-30	0.1-10	30-50	0-25
4	5-15	0.1-10	30-50	0.1-10	30-50	0-35
5	5-15	0.1-10	50-70	0.1-10	0-40	0-25

When the compositions of the present invention are used for the stabilization of heavy metals, the end result is an inert, environmentally harmless product of the reaction between a heavy metal-containing matrix and the composition containing up to about 30% (by weight) glass network forming cations and up to about 35% network forming anions, up to about 65% glass network dwelling ions, and up to about 75% glass network modifying ions.

TABLE II

Heavy Metal	SCAMP	SMP	HB	SCAMP + SMP	SCAMP + HB	SMP + HB	SCAMP + SMP + HB
Sb	Poor	Fair	Fair	Fair	Good	Good	Good
As	Poor	Fair	Poor	Fair	Fair	Fair	Fair
Ba	Fair	Fair	Poor	Good	Fair	Fair	Good
Be	Poor	Fair	Fair	Fair	Good	Good	Good
Cd	Fair	Fair	Fair	Good	Good	Good	Good
Cr	Fair	Fair	Fair	Good	Good	Good	Good
Co	Fair	Poor	Fair	Fair	Fair	Fair	Good
Cu	Poor	Fair	Fair	Fair	Good	Good	Good
Pb	Fair	Fair	Fair	Good	Good	Good	Good
Hg	Fair	Fair	Fair	Good	Good	Good	Good
Mo	Poor	Fair	Fair	Fair	Good	Good	Good
Ni	Fair	Poor	Fair	Fair	Fair	Fair	Good
Se	Poor	Fair	Poor	Fair	Fair	Fair	Fair
Ag	Fair	Fair	Poor	Good	Fair	Fair	Good
U	Poor	Fair	Fair	Fair	Good	Good	Good

US 6,313,368 B1

7

8

TABLE II-continued

Heavy Metal	Relative Effectiveness in Stabilizing Heavy Metals						
	SCAMP	SMP	HB	SCAMP + SMP	SCAMP + HB	SMP + HB	SCAMP + SMP + HB
V	Poor	Fair	Fair	Fair	Good	Good	Good
Zn	Fair	Fair	Fair	Good	Good	Good	Good

The combination of SCAMP, SMP and HB outperforms the combination of SCAMP and SMP, as well as the combination of SMP and HB, and the combination of SCAMP and HB, although stabilization of all 17 hazardous heavy metals is accomplished by all four sets of product combinations. By way of example, a 3:2 ratio by weight of SCAMP to SMP has produced excellent results in controlling the leachability of heavy metals such as Pb, Cd, and Cr at 6 percent dosage of the product by weight of solids in ferrous foundry wastewater. By way of further example, a 1:1 ratio by weight of SMP to HB has produced good results in controlling acid gases in an industrial process. By way of another example, a 6:3:1 ratio by weight of SCAMP to SMP to HB has produced good results in controlling acid gases and pH as well as in controlling the leachability of all 17 heavy metals of Table I. Depending on the total concentration and the number of the heavy metals to be treated, dosages of no more than about 35 percent of the solids in a contaminated matrix have reduced the leaching of all 17 listed heavy metals to within permissible levels. In fact, dosages of less than about 10 percent by weight of the solids, even as low as about 3 percent, have been found to be effective in most cases. When SMP (or other magnesium sulfite-type composition) is used alone, it is used in an amount of from about 5% to about 50% by weight of the solids in the contaminated matrix. When hydroboracite is used alone, it is used in an amount of from about 5% to about 50% of the solids in the contaminated matrix.

Matrices contaminated with heavy metals and acid gases as well as those matrices requiring pH control are treated

with product compositions of this invention in a dry or a slurry form. A product of this invention is injected into the in-process dust stream or added and mixed thoroughly with in-process wastewater; or in the case of contaminated soil, it is admixed in a continuous or batch mixer. The resultant product is found to be environmentally harmless with the heavy metals stabilized, pH controlled and acid gases neutralized.

While the invention has been described in terms of various preferred embodiments, one skilled in the art will appreciate that various modifications, substitutions, omissions, and changes may be made without departing from the spirit thereof. Accordingly, it is intended that the scope of the present invention be limited solely by the scope of the following claims.

What is claimed is:

1. A method of stabilizing a heavy metal-containing matrix comprising mixing with said matrix an effective amount of sulfonated calcium aluminum magnesium phosphate to render said matrix inert.
2. A method of stabilizing a heavy metal-containing matrix comprising mixing with said matrix an effective amount of magnesium sulfite to render said matrix inert.
3. A method of stabilizing a heavy metal-containing matrix comprising mixing with said matrix an effective amount of hydroboracite to render said matrix inert.

* * * * *



US006191068B1

(12) **United States Patent**
Bhat

(10) **Patent No.: US 6,191,068 B1**
 (45) **Date of Patent: Feb. 20, 2001**

(54) **METHOD AND COMPOSITIONS FOR STABILIZATION OF HEAVY METALS, ACID GAS REMOVAL AND PH CONTROL IN CONTAMINATED MATRICES**

(75) **Inventor: Vasanth K. Bhat, Cincinnati, OH (US)**

(73) **Assignee: Bhat Industries, Inc., Cincinnati, OH (US)**

(*) **Notice: Under 35 U.S.C. 154(b), the term of this patent shall be extended for 0 days.**

(21) **Appl. No.: 09/244,996**

(22) **Filed: Feb. 4, 1999**

(Under 37 CFR 1.47)

(51) **Int. Cl.⁷ B01J 20/00; C01B 17/00; C01B 7/00; C01B 21/00; B09B 3/00**

(52) **U.S. Cl. 502/400; 423/242.1; 423/240 S; 423/239.1; 588/249; 588/901**

(58) **Field of Search 502/400, 526; 423/242.1, 240 S, 239.1; 252/183.14, 183.16, 182.11; 588/901, 249, 251, 256, 257; 501/45, 47, 49; 210/751, 912, 913, 914**

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,052,190	*	10/1977	Berliner	71/11
4,671,882		6/1987	Douglas et al.	210/720
4,889,640		12/1989	Stanforth	210/751
5,037,479		8/1991	Stanforth	106/691
5,719,029	*	2/1998	Bhat	423/242.1

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Grant & Hackh's Chemical Dictionary, 5th ed. p. 339, 1987.*

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(57) **ABSTRACT**

A composition comprising magnesium sulfite, triple super phosphate, and one of limestone and hydroboracite, useful for heavy metal stabilizing, controlling pH and/or removing acid gas from a solid, semi-solid, liquid or gaseous matrix.

12 Claims, No Drawings

US 6,191,068 B1

1

**METHOD AND COMPOSITIONS FOR
STABILIZATION OF HEAVY METALS, ACID
GAS REMOVAL AND PH CONTROL IN
CONTAMINATED MATRICES**

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to the treatment of contaminated materials. Specifically, it relates to methods and compositions for rendering inert a broad spectrum of heavy metals that may be present in hazardous and/or toxic matrices such as fly ash and slag from incinerators; process water from ink and paint manufacturing; process dust, water and sludge from ferrous and non-ferrous foundries; electric arc furnace dust, for example, from steel mills; hazardous waste, toxic waste, soils, sludges and sediments. Heavy metals including antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, mercury, molybdenum, nickel, selenium, silver, thallium, vanadium and zinc are reduced to a level of permanent stability meeting the glacial acetic acid leachate criteria set forth by the U.S. EPA in the Toxicity Characteristic Leaching Procedure (TCLP) and the water leach tests, for example, California or Indiana Water Leach Test, simulating leaching due to rain as it actually occurs in the environment, the most recent versions of such procedure and tests as of Feb. 1, 1998, incorporated herein by reference. The invention also relates to industrial processes that require acid gas removal from a contaminated matrix and pH control of a contaminated matrix.

2. Discussion of the Background

When biologically available, heavy metals leaching from soil, water or waste, as well as those released into the air are detrimental to all living beings. Permissible levels of heavy metal pollution are regulated by the local, state and federal authorities. Important sets of federal regulations include the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), which governs the Superfund program. One of the earliest remediation methods, the removal and hauling of heavy metal contaminated waste and soil to a landfill, while still in use, is being viewed by the public and the press as unacceptable. New regulations and continued desire to find better and/or inexpensive environmental pollution control, prevention and remediation techniques have driven potential hazardous and/or toxic waste generators toward new technologies. Encapsulation of heavy metal contaminated waste in Portland cement, for example, though meeting the letter of the environmental law, does not meet the spirit of the law when the encapsulated waste is exposed to rain. Heavy metals go into solution and become biologically available. Permanent stabilization by forming geochemically stable compounds of heavy metals is by far the best solution to this challenge. Certain industrial processes may also release acid gases which need to be removed. Often pH control of the contaminated matrix is also required.

Numerous methods, mostly multi-step and sequential-step, have been utilized to prevent the leaching of hazardous heavy metals in solid, semi-solid, liquid and/or gaseous complex matrices so that the waste is rendered suitable for disposal in a sanitary landfill. There has, however, been no suggestion to use sulfur-containing material such as magnesium sulfite (scrubber magnesium product) and/or boron-containing material such as hydroboracite for the purpose of providing heavy metal stabilization; to use hydroboracite, by itself for acid gas removal and pH control of the contami-

2

nated or treated matrix. Furthermore, there has been no suggestion of the use of phosphates such as triple super phosphate, phosphate rock, fines generated from screening and combining of phosphate fertilizers (TSP (triple super phosphate), MAP (monoammonium phosphate), DAP (diammonium phosphate), etc.) along with magnesium sulfite (scrubber magnesium product) and/or hydroboracite and/or limestone for the purpose of providing heavy metal stabilization, together with the additional benefits of acid gas removal and pH control, to contaminated or treated matrices in a single-step method or single-product composition.

U.S. Pat. No. 4,671,882 to Douglas discloses a multi-step process for heavy metal stabilization. Douglas does not prefer to use limestone because he believes that the use of limestone results in the production of carbon dioxide gas when added to acid solution and such gas would adversely affect the pH increasing step essential to his multi-step heavy metal stabilization process. Both U.S. Pat. Nos. 4,889,640 and 5,037,479 to Stanforth teach away from the use of limestone in his single-step and sequential-step heavy metal stabilization processes because he considers it as a non-reactive form of calcium and/or magnesium carbonate and a hinderance to heavy metal stabilization. The above-mentioned patents do not suggest any products or processes for acid gas removal.

OBJECTS OF THE INVENTION

It is the primary object of the present invention to provide a one-step method and single-product compositions that simultaneously stabilize heavy metals, remove acid gases and control pH in contaminated solid, semi-solid, liquid and/or gaseous complex matrices

It is a further object of the present invention to provide a new method for the simultaneous treatment of a wide variety of matrices including in-process and waste materials contaminated with a broad range of heavy metals classified by the U.S. EPA as hazardous, such that geochemically stable, substantially non-leaching compounds of heavy metals are formed and the contaminated matrices are rendered inert.

It is another object of the present invention to provide a new family of compositions that achieve permanent stability of leachable heavy metals in complex matrices exposed to actual environmental conditions.

It is still another object of the present invention to provide a method and a general range of compositions that stabilize more heavy metals than those in the prior art using a one-step treatment and using a single product which may contain one or more reactive agents.

It is yet another object of the present invention to provide a method and compositions that are more cost-effective than those of the prior art in stabilizing heavy metals in a wide variety of complex matrices.

SUMMARY OF THE INVENTION

In accordance with the present invention there is provided a method and compositions for the treatment of in-process hazardous materials and waste materials contaminated with hazardous heavy metals to or below levels of local, state and federal regulatory limits. Simultaneously, this invention provides a single-step method and single-product and multiple-product compositions for heavy metal stabilization, acid gas removal and pH control in contaminated complex matrices.

Specifically, the present invention relates to a multiple-product composition for the treatment of heavy metal-

US 6,191,068 B1

3

containing matrices comprising an effective amount of sulfur-containing material such as magnesium sulfite and at least one of limestone and/or boron-containing material such as hydroboracite and/or phosphate-containing materials (P) such as triple super phosphate, rock phosphate, phosphate fines or combinations thereof. Methods of using single-product compositions are also described.

DETAILED DESCRIPTION OF THE INVENTION

The objects set out above are preferably accomplished using one composition and a one-step application method, as opposed to using several different compositions and a multi-step or sequential application method to:

- (1) stabilize a broad spectrum of heavy metals including those listed by the U.S. EPA as hazardous (Table I);
- (2) control acid gases found in complex matrices, including industrial processes and waste; and
- (3) control pH of the contaminated and treated matrices.

This invention relates to compositions and methods for accomplishing these goals, as well as to method for preparing those compositions.

TABLE I

U.S. EPA List of Hazardous Heavy Metals

Antimony	Cadmium	Lead	Selenium	Zinc
Arsenic	Chromium	Mercury	Silver	---
Barium	Cobalt	Molybdenum	Thallium	---
Beryllium	Copper	Nickel	Vanadium	---

Ingredients that form salts of low solubility with the heavy metals in question here will also produce permanently stable, pH independent, complex, non-leaching compounds that immobilize the heavy metals when they contain glass network forming cations such as Si, B, P, Ge and mixtures thereof, and glass network forming anions such as O, S, Se, Te and mixtures thereof. In conjunction with ingredients containing the glass network forming ions, those containing network dwellers such as Al, Mg, Ga and mixtures thereof, and network modifiers such as Ca, Mg and mixtures thereof, are also found to help in stabilizing heavy metals contained in contaminated matrices. It is not necessary that glass actually be formed as a result of the reaction between heavy metals and the heavy metal stabilizer, but rather that the ingredients used to prepare the heavy metal stabilizers be capable of forming glass. It is preferred that salts of low water solubility (preferably less than 750 parts per billion) are formed as a result of the reaction between these ions and the heavy metals.

Thus, the invention provides permanently stable, pH independent, complex, non-leaching compounds that mobilize the heavy metals. In selecting the ingredients for heavy metal stabilizing compositions, it is preferred that they are capable of forming glass (that is, they contain glass network forming, network dwelling and/or network modifying ions), and that salts of low solubility are formed as a result of the reaction between these ions and the heavy metals in question. Sulfur-containing material such as magnesium sulfite or boron-containing material such as hydroboracite are compounds that fit both these criteria by themselves, as well as in conjunction with other ingredients.

Sulfonated Calcium Aluminum Magnesium Phosphate (SCAMP) referred to in U.S. Pat. No. 5,719,099 by itself outperforms phosphate fines referred to above in heavy metal stabilization. However, when either SCAMP or P is

4

combined in the presence of SMP (Scrubber Magnesium Product), with other ingredients such as hydroboracite (HB) or limestone (L) (the term "limestone" as used herein refers to limestone in the uncalcined or calcined state, of either high-calcium or dolomitic type and mixtures thereof), there appears to be no significant difference in performance between them as far as heavy metal stabilization. Stabilization of all 17 heavy metals listed as hazardous by the U.S. EPA can be accomplished in a single-step, along with acid gas and pH control using a product composition that comprises, consists of, or consists essentially inorganic sulfur-containing material(s) (such as magnesium sulfite, magnesium sulfate, calcium sulfite, sodium metabisulfite, calcium magnesium sulfite, epsom salt, gypsum, mixtures thereof) and P. An inexpensive source of magnesium sulfite that also contains minor amounts of magnesium sulfate is the Scrubber Magnesium Product (SMP). The use of inorganic sulfur-containing material (for example, SMP) alone, does stabilize 15 of the 17 heavy metals fairly well. Thus, this embodiment makes up part of the invention. Relative effectiveness of SMP alone or in combination with P is shown in Table II. The use of Hydrated Calcium Magnesium Borate, that is, Hydroboracite (HIB), alone or in conjunction with SMP, P and mixtures thereof is also depicted in Table II. Use of limestone (L) in lieu of hydroboracite in conjunction with SMP and P produces somewhat similar results in acid removal and pH control, but hydroboracite is superior to limestone in heavy metal stabilization applications. Nevertheless, when 1:1 substitution (by weight) of hydroboracite to limestone is made, formulae containing SMP, P and limestone have been only slightly inferior to those containing SMP, P and HB in heavy metal stabilization applications. Because limestone is cheaper than hydroboracite, it may be chosen over hydroboracite in formulae containing SMP and SCAMP or SMP and P for heavy metal stabilization applications. In fact, even in the absence of HB and SMP, P+L combinations such as triple super phosphate and limestone or phosphoric acid and limestone show that certain heavy metals (for example, Sb, Be, Cd, Cr, Cu, Pb, Mo, Ti, V, Zn) can be cost-effectively stabilized. If acid gas removal and/or pH control is the only objective, formulae containing materials selected from a group consisting of limestone, calcined magnesite, hydroboracite, or zeolites, and mixtures thereof, work very well.

The compositions of the present invention comprise an amount of each specified component which is effective to stabilize heavy metals present in the matrix being treated, as well as to control pH and acid gas. Specifically, compositions of the present invention contain from about 0% to 100%, preferably from about 10% to 50% inorganic sulfur-containing material such as SMP, from about 0% to 100%, preferably from about 0% to 50% HB, from about 0% to 90%, preferably from about 10% to 50% P, and from about 0% to 90%, preferably from about 0% to 80% L. Examples of SMP-, HB-, P- and L-containing compositions found to be effective in achieving the goals of the present invention are as follows:

Ex. #	SMP wt %	HB wt %	P wt %	L wt %
1	100	—	—	—
2	30-40	—	35-45	20-30
3	10-20	—	10-20	50-70
4	10-20	—	15-25	40-60
5	30-40	—	15-25	40-50

US 6,191,068 B1

5

6

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Ex. #	SMP wt %	HB wt %	P wt %	L wt %
6	—	100	—	—
7	—	30-40	35-45	20-30
8	—	10-20	10-20	50-70
9	—	10-20	15-25	40-60
10	—	30-40	15-25	40-50
11	—	—	40-90	10-60

When the compositions of the present invention are used for the stabilization of specific heavy metals as depicted in Table II, the end result is an inert, environmentally safe product of the reaction between a heavy metal-containing matrix and the composition containing up to about 30% (by weight) glass network forming cations and up to about 35% network forming anions, up to about 60% glass network modifying ions, and up to about 70% glass network modifying ions.

TABLE II

Heavy Metal	Relative Effectiveness in Stabilizing Heavy Metals						
	SMP	HB	P	SMP + P	HB + P	SMP + HB	SMP + HB + P
Sb	Fair	Fair	Poor	Fair	Good	Good	Good
As	Fair	Poor	Poor	Fair	Fair	Fair	Fair
Ba	Fair	Poor	Fair	Good	Fair	Fair	Good
Be	Fair	Fair	Poor	Fair	Good	Good	Good
Cd	Fair	Fair	Fair	Good	Good	Good	Good
Cr	Fair	Fair	Fair	Good	Good	Good	Good
Co	Poor	Fair	Fair	Fair	Fair	Fair	Good
Cu	Fair	Fair	Poor	Fair	Good	Good	Good
Pb	Fair	Fair	Fair	Good	Good	Good	Good
Hg	Fair	Fair	Fair	Good	Good	Good	Good
Mo	Fair	Fair	Poor	Fair	Good	Good	Good
Ni	Poor	Fair	Fair	Fair	Fair	Fair	Good
Se	Fair	Poor	Poor	Fair	Fair	Fair	Fair
Ag	Fair	Poor	Fair	Good	Fair	Fair	Good
Tl	Fair	Fair	Poor	Fair	Good	Good	Good
V	Fair	Fair	Poor	Fair	Good	Good	Good
Zn	Fair	Fair	Fair	Good	Good	Good	Good

In general, compositions for the treatment of heavy metal-containing matrices together with the additional benefits of acid gas removal and pH control, may be prepared by combining the following materials (a) and (b):

- (a) at least one inorganic sulfur-containing material selected from the group consisting of magnesium sulfite, calcium sulfite, magnesium sulfate, sodium metabisulfite, calcium magnesium sulfite, epsom salt, gypsum, and mixtures thereof (preferably magnesium sulfite, calcium sulfite, magnesium sulfate, or calcium magnesium sulfite, and most preferably magnesium sulfite in the form of scrubber magnesium product);
- (b) at least one phosphate-containing material (P) selected from the group consisting of phosphoric acid, rock phosphate, triple super phosphate, or fines or mixtures of fines of phosphate fertilizers such as triple super phosphate (TSP), monoammonium phosphate (MAP), diammonium phosphate (DAP) commonly referred to as phosphate fines and mixtures thereof (preferably rock phosphate, TSP or phosphate fines, and most preferably phosphate fines);

and optionally adding limestone, either uncalcined or calcined, either high-calcium or dolomitic type and mixtures thereof, and further optionally adding HB.

When inorganic sulfur-containing material from (a) such as magnesium sulfite (Scrubber magnesium Product, SMP)

alone is used for heavy metal stabilization, of the 17 heavy metals 15 are stabilized; Co and Ni are not. When the above composition of SMP+P is used, all 17 heavy metals including Co and Ni are stabilized with additional performance benefits of acid gas removal and pH control accrued with the addition of limestone.

In general, a boron- and phosphate-containing composition for the treatment of heavy metal-containing matrices together with the additional benefits of acid gas removal and pH control, may be prepared by combining the following materials:

- (a) at least one inorganic boron-containing material selected from the group consisting of hydroboracite, colemanite, ulexite, borax, and mixtures thereof (most preferably hydroboracite);
- (b) at least one phosphate-containing material selected from the group consisting of phosphoric acid, rock phosphate, triple super phosphate, or fines or mixtures of fines of phosphate fertilizers such as triple super phosphate (TSP), monoammonium phosphate (MAP), diammonium phosphate (DAP) commonly referred to as phosphate fines and mixtures thereof (preferably rock phosphate, TSP or phosphate fines, and most preferably phosphate fines);

and optionally adding limestone, of either uncalcined or calcined state, of either high-calcium or dolomitic type and mixtures thereof.

When boron-containing material from (a) such as hydroboracite (HB) alone is used, of the 17 heavy metals, only 13 are stabilized; As, Ba, Se, and Ag are not. When the above composition of HB+P is used, all 17 heavy metals including As, Ba, Se, and Ag are stabilized with the additional performance benefits of acid gas removal and pH control accrued without the addition of limestone. Limestone may be optionally included in the formula for cost benefits.

A sulfur- and boron-containing single product composition for the treatment of heavy metal-containing matrices together with the additional benefits of acid gas removal and pH control may be prepared by combining, mixing and reacting the following materials:

- (a) at least one inorganic sulfur-containing material selected from the group consisting of magnesium sulfite, calcium sulfite, magnesium sulfate, sodium metabisulfite, calcium magnesium sulfite, epsom salt, gypsum, and mixtures thereof (preferably magnesium sulfite, calcium sulfite, magnesium sulfate, or calcium magnesium sulfite, and most preferably magnesium sulfite in the form of scrubber magnesium product);
- (b) at least one boron-containing material selected from the group consisting of hydroboracite, colemanite, ulexite, borax, and mixtures thereof (most preferably hydroboracite);
- (c) at least one phosphate-containing material selected from the group consisting of phosphoric acid, rock phosphate, triple super phosphate, or fines or mixtures of fines of phosphate fertilizers such as triple super phosphate (TSP), monoammonium phosphate (MAP), diammonium phosphate (DAP) commonly referred to as phosphate fines and mixtures thereof (preferably rock phosphate, TSP or phosphate fines, and most preferably phosphate fines);

and optionally adding limestone, of either uncalcined or calcined state, of either high-calcium or dolomitic type and mixtures thereof. Although both SMP+HB and SMP+HB+P compositions will stabilize all 17 heavy metals, SMP+HB+P compositions outperform the former.

US 6,191,068 B1

7

Matrices contaminated with heavy metals and acid gases as well as those matrices requiring pH control are treated with product compositions of this invention in a dry or slurry form. A product of this invention may be injected into an in-process dust stream or added and mixed thoroughly with in-process wastewater; or in the case of contaminated soil, it is admixed, for example, in a continuous or batch mixer. The resultant product is found to be environmentally harmless with the heavy metals stabilized, pH controlled and acid gases neutralized.

Compositions of the present invention generally preferably comprise Scrubber Magnesium Product (SMP), Hydroboracite (HB), Phosphate fines of triple super phosphate, monoammonium phosphate, and/or diammonium phosphate, and Limestone (L), either calcined or uncalcined, whether of high-calcium or dolomitic or mixture thereof. Also included is the use of magnesium sulfite, all alone, in any form including as scrubber magnesium product, SMP, for heavy metal stabilization. Hydroboracite, HB, all by itself, as a heavy metal stabilizer or as an acid gas remover or as a pH controller is further included. Each of these materials in a heavy metal stabilizing application successfully stabilizes many heavy metals in contaminated matrices. SMP added to dust, water, sludge, soil or other contaminated matrices in quantities in the range of 3 to 35 percent by weight (based on total weight) has stabilized Sb, As, Ba, Be, Cd, Cr, Cu, Pb, Hg, Mo, Se, Ag, Tl, V, and Zn. Additions in the range of 3 to 35 percent by weight of HB have stabilized Sb, Be, Cd, Cr, Co, Cu, Pb, Hg, Mo, Ni, Tl, V, and Zn.

In heavy metal stabilizing applications, preferred compositions comprising L, SMP, HB, and P, the preferred weight percent of SMP is 30-40, HB+L is 20-30, and P is 35-45 based on total weight. For cost reasons, HB may be partially or completely replaced by L on a 1:1 weight basis. In compositions used for heavy metal stabilization, acid gas removal, and pH control, the preferred weight percent SMP is 10-20, P is 15-25, and L is 40-60 when more focus is placed on heavy metal stabilization; and the preferred weight percent SMP is 10-20, P is 10-20, and L is 50-70 when more focus is placed on acid gas removal (where L may be L, HB or HB+L). These compositions added at 3 to 35 weight percent of the contaminated matrix have successfully stabilized all 17 heavy metals and removed acid gases such as sulfur dioxide and/or hydrogen chloride.

When acid gas removal happens to be the only application, formulae containing materials selected from the group consisting of limestone, calcined magnesite, hydroboracite, or zeolites, and mixtures thereof, work very well. Combinations of limestone, calcined magnesite, and hydroboracite, or these materials alone have removed sulfur dioxide and hydrogen chloride. When nitrogen oxides are present, compositions containing zeolites are required. For acid gas removal and/or pH control applications, a preferred composition comprises limestone, hydroboracite or limestone+hydroboracite 30-40, calcined magnesite 30-40, and zeolite 30-40 weight percent based on total weight. Amount of composition used is preferably at least equal to the stoichiometric amount required to neutralize the acid gases in question and depends on the quantities and types of acid gases generated from the contaminated matrix. The use of the invention compositions and implementation of the methods described herein are within the skill of the ordinary artisan.

8

Compositions for use as heavy metal stabilizer (wt % based on total weight)

Triple Super Phosphate ¹	30-50 wt. %
Limestone ²	10-30 wt. %
Magnesium Sulfite ³	30-50 wt. %
Triple Super Phosphate ¹	15-25 wt. %
Limestone ²	50-70 wt. %
Magnesium Sulfite ³	0-30 wt. %
Triple Super Phosphate ¹	30-50 wt. %
Limestone ²	30-40 wt. %
Magnesium Sulfite ³	30-50 wt. %
Triple Super Phosphate ¹	15-25 wt. %
Limestone ²	50-80 wt. %
Magnesium Sulfite ³	0-30 wt. %
Triple Super Phosphate ¹	30-50 wt. %
Limestone ²	30-50 wt. %
Magnesium Sulfite ³	25-50 wt. %

¹May be substituted by or mixed with other invention phosphate-containing materials (P).

²Limestone can be either a high calcium limestone or dolomitic (containing calcium and magnesium) limestone. It can be uncalcined limestone or calcined limestone (that is, lime or dolime) or mixtures thereof. May be partially or completely substituted by hydroboracite on a 1:1 weight basis.

³Magnesium sulfite is an inorganic sulfur-containing material. Other inorganic sulfur-containing materials such as scrubber magnesium product, calcium sulfite, magnesium sulfate, sodium metabisulfite, calcium magnesium sulfite, Epsom salt and mixtures thereof can also be used in partial or complete place of magnesium sulfite.

Triple Super Phosphate¹ 15-25 wt. %

Limestone² 20-50% wt. %

Magnesium Sulfite³ 30-50 wt. %

Method or Process of Formulation

Product may be produced as follows:

1. Combine, mix, and react¹ triple super phosphate¹, and limestone² in a reactor.
2. Add magnesium sulfite³. Continue mixing and reacting.
3. Grind to make powdered product (e.g., hammer mill).

EXAMPLES OF PRODUCTION BATCHING

Example #1	
2000 lbs	Triple Super Phosphate
1200 lbs	Limestone (100 lbs Dolomitic Limestone and 200 lbs Dolime)
1800 lbs	Magnesium Sulfite
Example #2	
4000 lbs	Example #1
6000 lbs	Limestone (Calcined, that is, Dolime)
Example #3	
6000 lbs	Example #1
6000 lbs	Limestone (Dolime)
Example #4	
6000 lbs	Example #1
4000 lbs	Example #3
Example #5	
8000 lbs	Example #1
4000 lbs	Limestone (Dolime)
Alternatively,	
6000 lbs	Example #1
6000 lbs	Example #3

US 6,191,068 B1

9

10

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		Example #6
6000 lbs	Example #1	
4200 lbs	Limestone (Dolime)	
1800 lbs	Magnesium Sulfite	

⁴Heating unnecessary. Reaction, if any, is acid-base type reaction, which may provide heat in situ, as may grinding.

Method or Process of Application

Matrices contaminated with heavy metals and acid gases as well as those matrices requiring pH control are treated with invention composition (preferably 3-35 weight percent (total weight) dosage), in dry or slurry form. Powdered product is injected into in-process dust stream or added and mixed thoroughly with in-process wastewater; or in the case of contaminated soil, it is admixed in a continuous or batch mixer.

Phosphate fines is a term known in the art to be fines of phosphate fertilizers and can include one or more of triple super phosphate, monoammonium phosphate and diammonium phosphate.

Preferred embodiments of the invention include the following:

A. A method comprising single-step simultaneous combining, mixing and reacting with, and comprising single-product composition to render, complex (solid, semi-solid, liquid and/or gaseous) matrices contaminated with one or more of 17 heavy metals (Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Hg, Mo, Ni, Se, Ag, Ti, V, and Zn), often co-existing with acid gases such as sulfur dioxide, hydrogen chloride, and nitrogen oxides, completely inert, with the pH controlled to safe levels for alternate use or for disposal into sanitary landfills.

B. A method of making a sulfur- and phosphate-containing single-product composition of embodiment A for the treatment of a matrix contaminated with heavy metals often co-existing with acid gases comprising the steps of mixing the following materials:

(a) A sulfur-containing material selected from the group consisting of magnesium sulfite, calcium sulfite, magnesium sulfate, sodium metabisulfite, calcium magnesium sulfite, epsom salt, gypsum, and mixtures thereof (preferably magnesium sulfite, calcium sulfite, magnesium sulfate, or calcium magnesium sulfite, and most preferably magnesium sulfite in the form of scrubber magnesium product);

(b) A phosphate-containing material selected from the group consisting of phosphoric acid, rock phosphate, triple super phosphate, or fines or mixtures of fines of phosphate fertilizers such as triple super phosphate (TSP), monoammonium phosphate MAP), diammonium phosphate (DAP) commonly referred to as phosphate fines and mixtures thereof (preferably rock phosphate, TSP or phosphate fines, and most preferably phosphate fines);

and optionally adding limestone, of either uncalcined or calcined state, of either high-calcium or dolomitic type and mixtures thereof.

C. A method of making a boron- and phosphate-containing single-product composition of embodiment A for the treatment of a matrix contaminated with heavy metals often co-existing with acid gases comprising the steps of mixing the following materials:

(a) A boron-containing material selected from the group consisting of hydroboracite, colemanite, ulexite, borax, and mixtures thereof (most preferably hydroboracite);

(b) A phosphate-containing material selected from the group consisting of phosphoric acid, rock phosphate, triple super phosphate, or fines or mixtures of fines of phosphate fertilizers such as triple super phosphate (TSP), monoammonium phosphate MAP), diammonium phosphate (DAP) commonly referred to as phosphate fines and mixtures thereof (preferably rock phosphate, TSP or phosphate fines, and most preferably phosphate fines); and optionally adding limestone, of either uncalcined or calcined state, of either high-calcium or dolomitic type and mixtures thereof.

D. A method of making a sulfur-, boron- and phosphate-containing single-product composition of embodiment A for the treatment of a matrix contaminated with heavy metals often co-existing with acid gases comprising the steps of mixing the following materials:

(a) A sulfur-containing material selected from the group consisting of magnesium sulfite, calcium sulfite, magnesium sulfate, sodium metabisulfite, calcium magnesium sulfite, epsom salt, gypsum, and mixtures thereof (preferably magnesium sulfite, calcium sulfite, magnesium sulfate, or calcium magnesium sulfite, and most preferably magnesium sulfite in the form of scrubber magnesium product);

(b) A boron-containing material selected from the group consisting of hydroboracite, colemanite, ulexite, borax, and mixtures thereof (most preferably hydroboracite);

(c) A phosphate-containing material selected from the group consisting of phosphoric acid, rock phosphate, triple super phosphate, or fines or mixtures of fines of phosphate fertilizers such as triple super phosphate (TSP), monoammonium phosphate MAP), diammonium phosphate (DAP) commonly referred to as phosphate fines and mixtures thereof (preferably rock phosphate, TSP or phosphate fines, and most preferably phosphate fines);

and optionally adding limestone, of either uncalcined or calcined state, of either high-calcium or dolomitic type and mixtures thereof

E. A method according to embodiment B wherein sulfur-containing material is scrubber magnesium product which is the source for magnesium sulfite; and phosphate-containing material is the phosphate fines.

F. A method according to embodiment C wherein boron-containing material is hydroboracite; and phosphate-containing material is the phosphate fines.

G. A method according to embodiment D wherein sulfur-containing material is scrubber magnesium product which is the source for magnesium sulfite; boron-containing material is hydroboracite; and phosphate-containing material is the phosphate fines.

H. A method according to embodiment A wherein said single-product composition is sulfur-containing material, scrubber magnesium product which is the source for magnesium sulfite, used all by itself for heavy metal stabilization of 15 heavy metals exclusive of Co and Ni (that is, Sb, As, Ba, Be, Cd, Cr, Cu, Pb, Hg, Mo, Se, Ag, Ti, V, Zn).

I. A method according to embodiment A wherein said single-product composition is boron-containing material hydroboracite, used all by itself for heavy metal stabilization of 13 heavy metals exclusive of As, Ba, Se, and Ag (that is, Sb, Be, Cd, Cr, Co, Cu, Pb, Hg, Mo, Ni, Th, V, Zn) often co-existing with acid gases.

J. A single-product composition according embodiment B wherein sulfur-containing material is scrubber magnesium product which is the source for magnesium sulfite; phosphate-containing material is the phosphate fines.

US 6,191,068 B1

11

K. A single-product composition according to embodiment C wherein boron-containing material is hydroboracite; phosphate-containing material is the phosphate fines.

L. A single-product composition according to embodiment D wherein sulfur-containing material is scrubber magnesium product which is the source for magnesium sulfite; boron-containing material is hydroboracite; and phosphate-containing material is the phosphate fines.

M. A single product composition according to embodiment A wherein when the only objective is to remove acid gases such as sulfur dioxide, hydrogen chloride, and nitrogen oxides, comprises material selected from the group consisting of limestone (of either uncalcined or calcined state, of either high-calcium or dolomitic type, and mixture thereof), calcined magnesite, zeolites, and mixtures thereof.

N. A single-product composition according to embodiment A wherein when the objective is to remove acid gases in addition to heavy metal stabilization and pH control, comprises hydroboracite or limestone (of either uncalcined or calcined state, of either high-calcium or dolomitic type, and mixture thereof), or both.

O. A single-product composition according to embodiment A wherein the objective is to remove acid gases in addition to heavy metal stabilization and pH control, comprises phosphate-containing material such as triple super phosphate, rock phosphate, phosphate fines, phosphoric acid and mixtures thereof and limestone (of either uncalcined or calcined state, of either high-calcium or dolomitic type, and mixture thereof).

P. A method for acid gas removal and/or pH control of a non-heavy metal-contaminated solid, semi-solid, liquid or gaseous matrix, comprising contacting said matrix with a material selected from the group consisting of limestone, calcined magnesite, hydroboracite, zeolites and mixtures thereof, wherein if nitrogen oxides are present zeolite is present in said material.

Highly preferred invention compositions contain, by weight, 16-40% phosphate-containing material (P), 14-36% inorganic sulfur-containing material (e.g., SMP), and 24-70% of L, boron-containing material (e.g., HB), or L+boron-containing material. As noted above and throughout, limestone can be partially or wholly replaced by boron-containing material, and preferably by HB.

12

While the invention has been described in terms of various preferred embodiments, one skilled in the art will appreciate that various modifications, substitutions, omissions, and changes may be made without departing from the spirit thereof. U.S. Pat. No. 5,719,099 is incorporated herein by reference, as are U.S. provisional application Ser. No. 60/028,935 and U.S. regular application Ser. No. 08/961,823, now U.S. Pat. No. 5,985,778.

I claim:

1. A composition, comprising magnesium sulfite, triple super phosphate, and at least one of limestone and hydroboracite.

2. The composition as claimed in claim 1, wherein said limestone is uncalcined.

3. The composition of claim 1, comprising limestone and hydroboracite.

4. The composition of claim 1, wherein said composition comprises scrubber magnesium product which comprises magnesium sulfite.

5. The composition of claim 3, wherein said composition comprises scrubber magnesium product which comprises magnesium sulfite.

6. The composition of claim 1, comprising, by weight, 16-40% triple super phosphate, 14-36% magnesium sulfite, and 24-70% of at least one of limestone and hydroboracite.

7. A method for the treatment of a heavy metal-coning matrix comprising contacting said matrix with the composition of claim 1.

8. A method for the treatment of a heavy metal-containing matrix comprising contacting said matrix with the composition of claim 3.

9. A method for controlling the pH of a matrix, comprising contacting said matrix with the composition of claim 1.

10. A method for controlling the pH of a matrix, comprising contacting said matrix with the composition of claim 3.

11. A method for removing acid gas from a solid, semi-solid, liquid or gaseous matrix, comprising contacting said matrix with the composition of claim 1.

12. A method for removing acid gas from a solid, semi-solid, liquid or gaseous matrix, comprising contacting said matrix with the composition of claim 3.

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