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(54) **PROCESS AND SYSTEM FOR TREATING WASTE FROM THE PRODUCTION OF ENERGETICS**

(52) **U.S. Cl.** ..... **210/743; 210/757; 210/758; 210/804; 210/259; 210/202; 210/206; 210/96.1**

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(57) **ABSTRACT**

A waste stream from energetics processing is treated using a pre-filter having media, preferably sand, and a metal that has a reducing potential, preferably elemental iron ( $Fe^0$ ). The pre-filter is connected to a zero-valent metal column reactor. The waste stream is pumped through the pre-filter to trap solids and deoxygenate it, then enters the reactor and is subjected to a reducing process. Most of the  $Fe^0$  is transformed to the ferrous ion ( $Fe^{+2}$ ), added to the resultant product, and fed to a continuous stirred tank reactor (CSTR) in which Fenton oxidation occurs. This product is then sent to a sedimentation tank and pH-neutralized using a strong base such as sodium hydroxide (NaOH). The aqueous portion is drawn off and the sludge pumped from the sedimentation tank. Both tanks are monitored and controlled to optimize required additives, while monitoring of pressure drop across the pre-filter and column reactor establishes replacement requirements.

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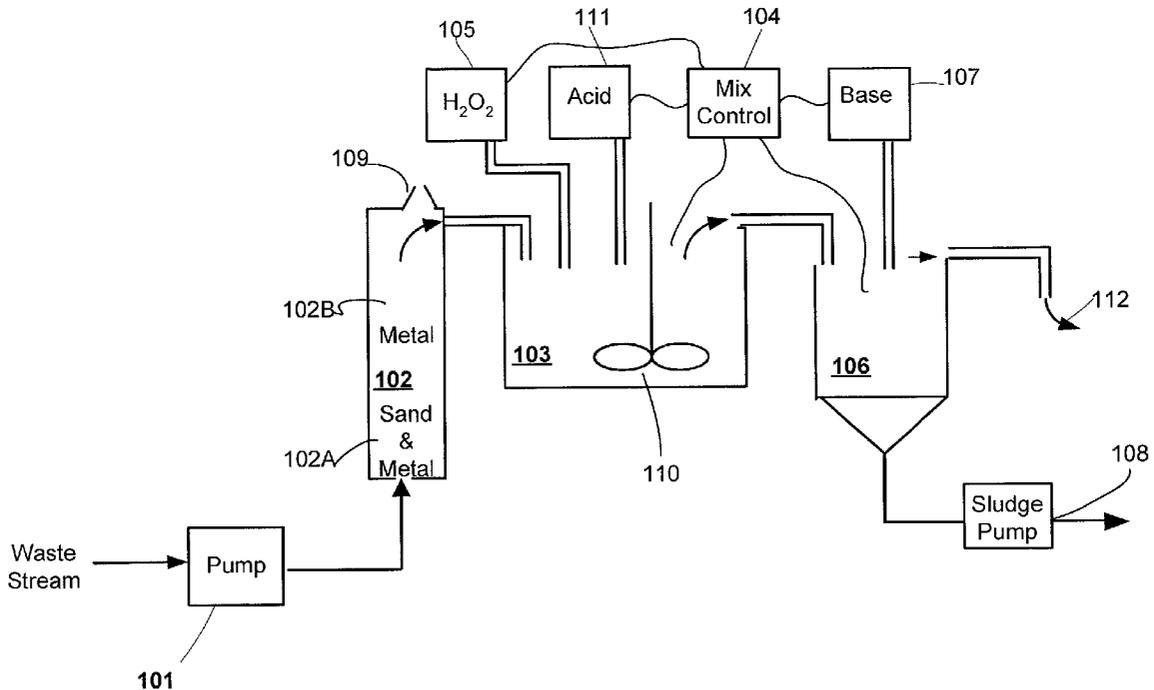
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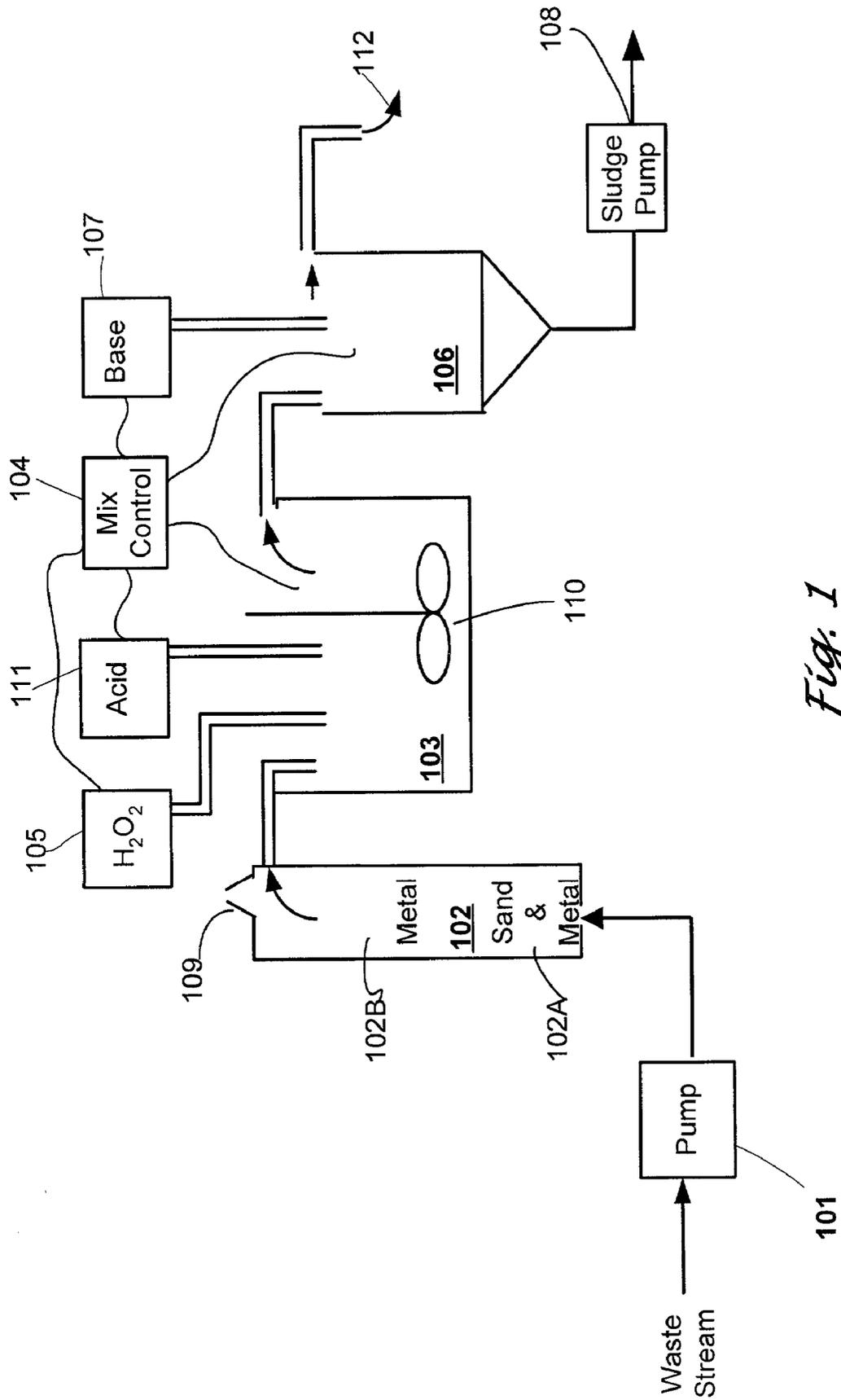
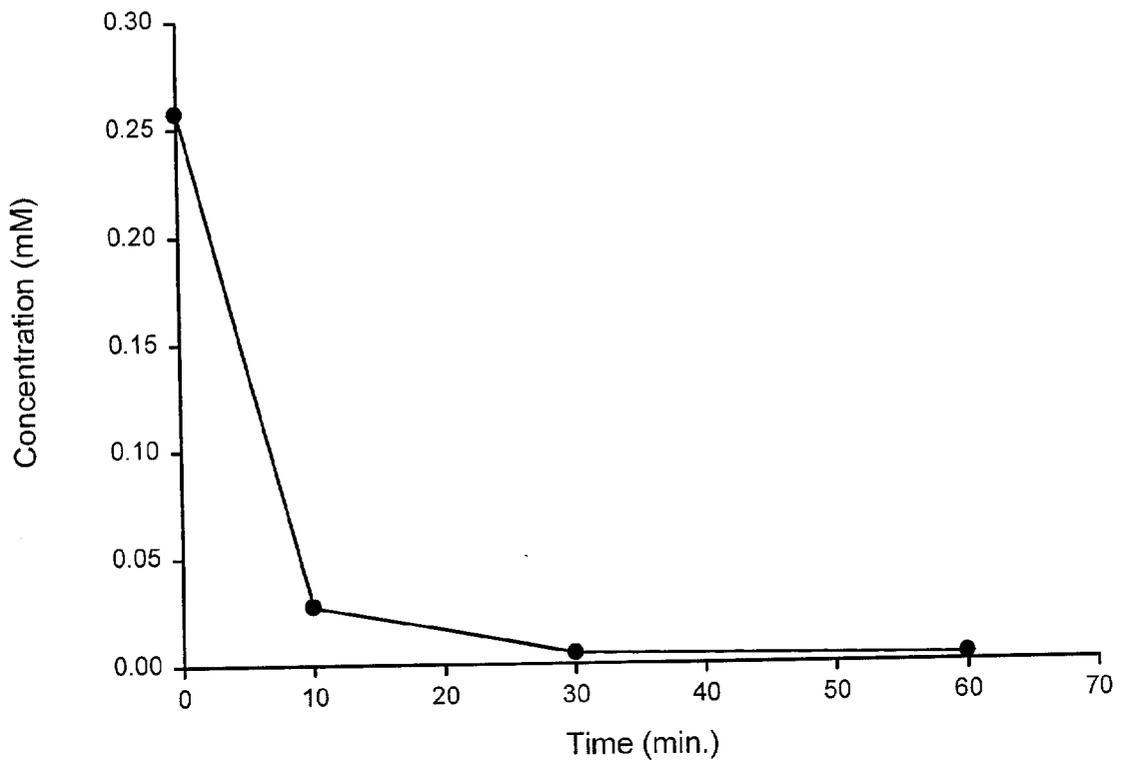


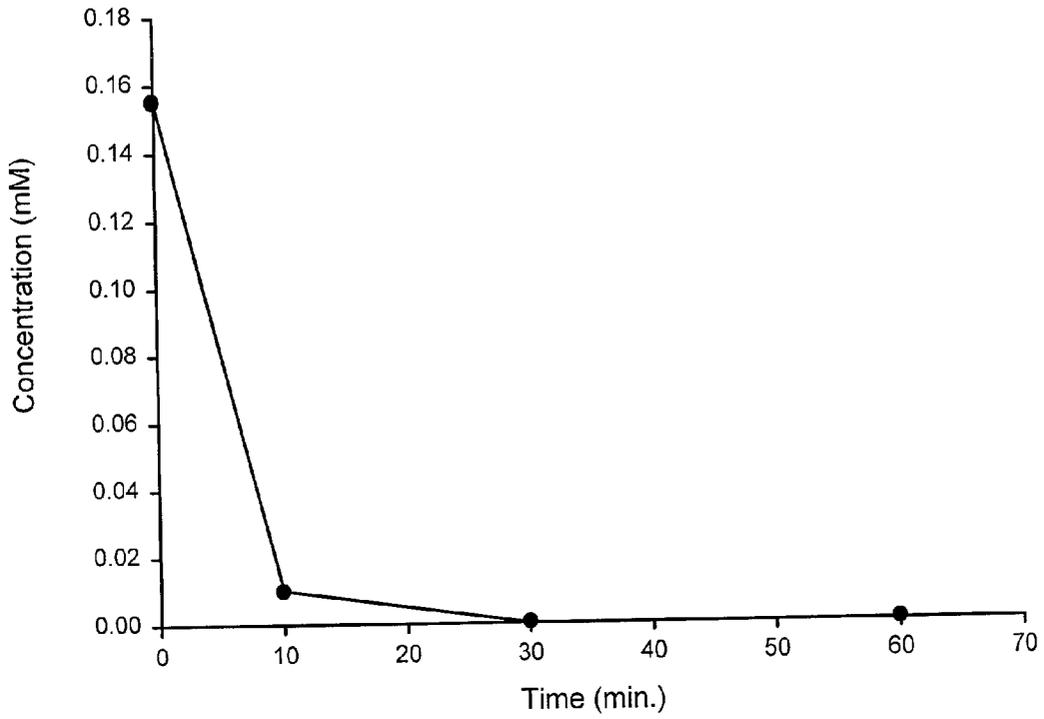
Fig. 1

### Break Down of TNT



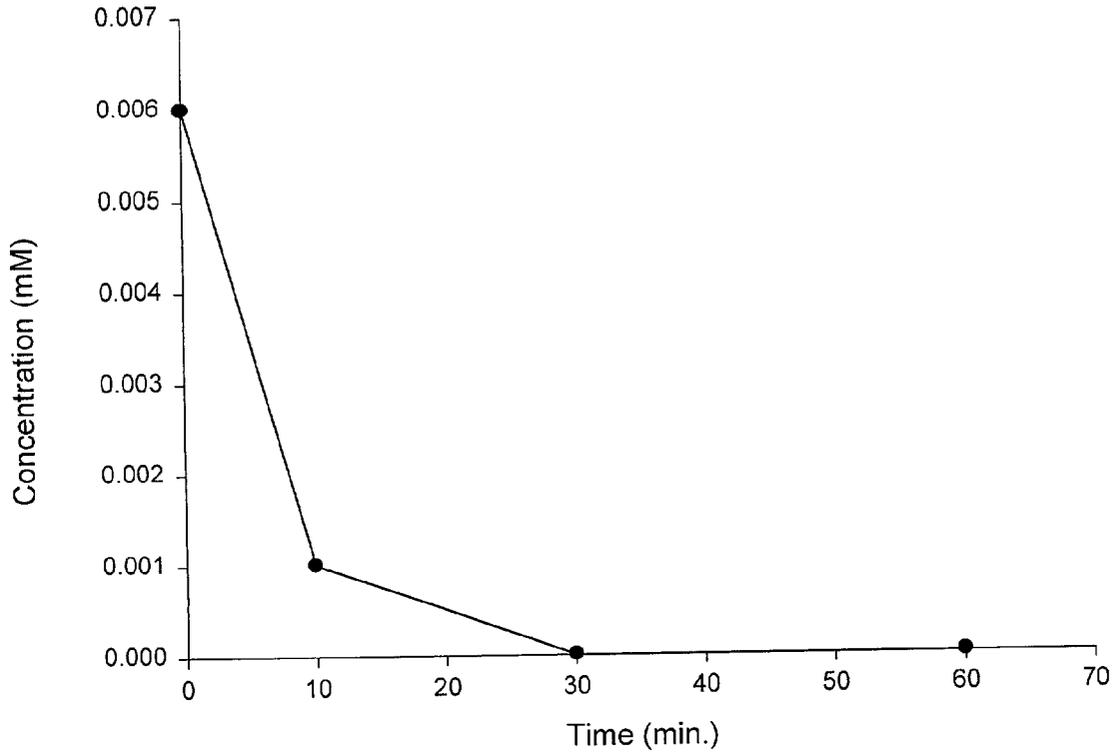
*Fig. 2*

### Break Down of RDX

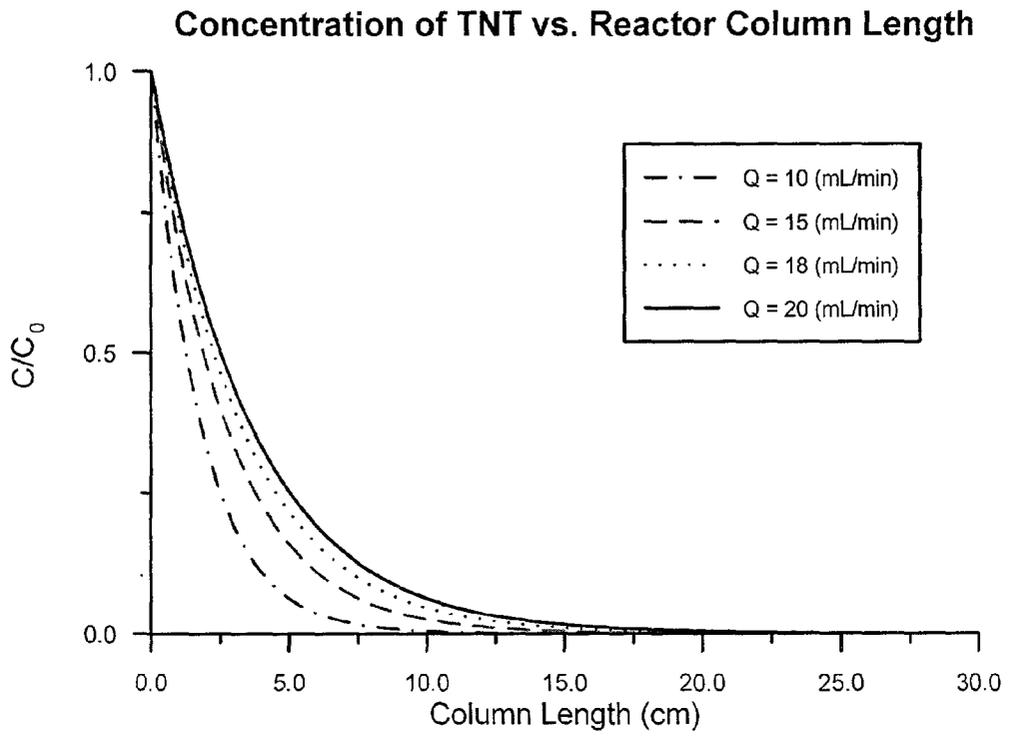


*Fig. 3*

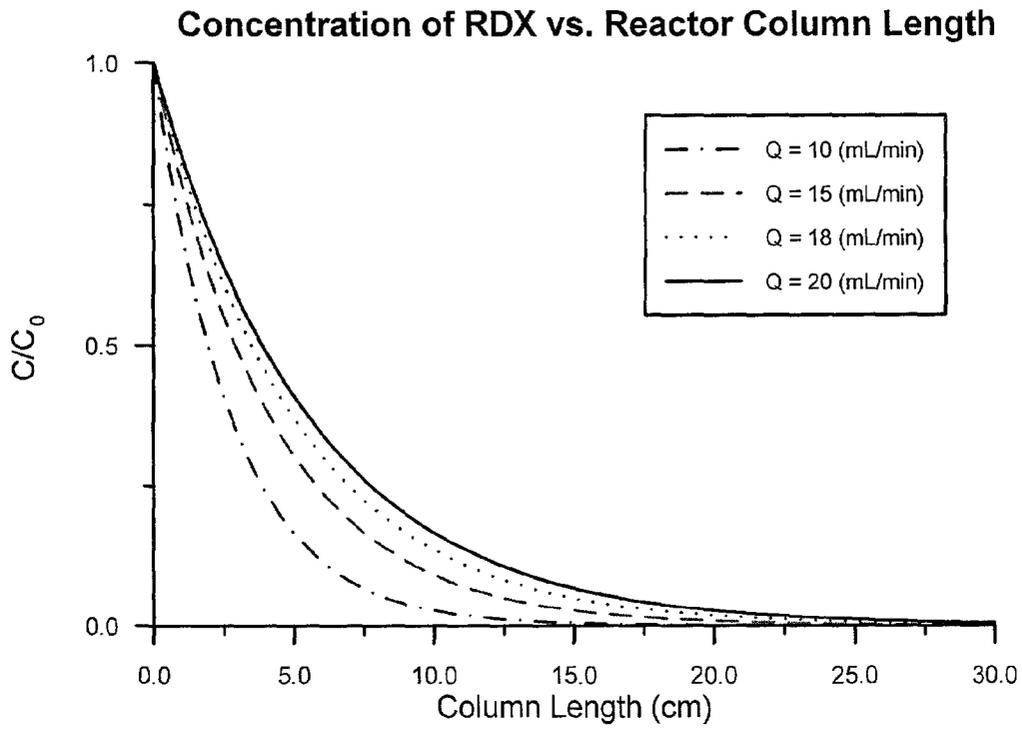
### Break Down of HMX



*Fig. 4*



*Fig. 5*



*Fig. 6*

## PROCESS AND SYSTEM FOR TREATING WASTE FROM THE PRODUCTION OF ENERGETICS

### STATEMENT OF GOVERNMENT INTEREST

[0001] The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

### BACKGROUND

[0002] Carbon sorption is the conventional method for treating munitions manufacturing waste containing explosive compounds such as 2,4,6 trinitrotoluene (TNT), trimethylenetrinitronitramine (RDX), and tetramethylenetetranitramine (HMX). The liquid form of this waste is termed "pinkwater." Typically using granulated activated carbon (GAC) filters, the waste is passed through the GAC with the explosive constituents removed by sorbing onto the carbon. This method is non-destructive, i.e., the sorbed molecules of contaminant remain intact chemically. Thus, the process generates spent contaminant-laden GAC filters that require further treatment, to include regeneration of the carbon filter for re-use or safe disposal at the end of the filter's useful life. The U.S. military and its contractors generate substantial amount of spent GAC from pinkwater treatment and would save considerable resources by replacing the GAC filtration process with a process that actually destroys or neutralizes energetic contaminants.

[0003] Thus, it is a given that conventional sorbing processes have several disadvantages that are immutable. Further, direct oxidation by chemical or biological processes is not as efficient as sequential reduction/oxidation processes due to the relatively oxidized nature of energetics.

[0004] It is known to use the Fenton reaction for oxidizing hydrocarbons to their constituents. Typically, the oxidizing agent used in the reaction is hydrogen peroxide,  $H_2O_2$ . Mixed with a metallic salt,  $H_2O_2$  produces a free radical that breaks the bonds of a hydrocarbon molecule in an exothermic reaction. This results in a low-free-energy-state generally associated with the production of carbon dioxide ( $CO_2$ ) and water.

[0005] Elemental iron ( $Fe^0$ ) oxidizes to  $Fe^{+2}$  in the presence of oxygen. This removes most of the oxygen from the solution and contributes to the solution attaining an anaerobic state.

[0006] Zero-valent iron has been used in permeable reactive barriers (PRBs), an emerging technology that has been applied in recent years to remediate groundwater contaminated with a wide range of pollutants. Permeable Reactive Barrier Technologies for Contaminant Remediation, EPA/600/R-98/125, U.S. EPA, Sep. 1998; Field Applications of In Situ Remediation Technologies: Permeable Reactive Barriers, EPA/542/R-99/002, U.S. EPA, June 1999. Iron is a strong reducing agent ( $E^0 = -0.44V$ ) and can reduce relatively oxidized pollutants, including chlorinated solvents, metals, nitrate, and radionuclides. U.S. EPA (Sep. 1998).

[0007] Researchers have shown that iron can reduce TNT, RDX, and HMX at high rates. Hundal, L. S., et al., Removal of TNT and RDX from Water and Soil Using Iron Metal, *Environmental Pollution*, 97: 55-64, 1997. Further, the Fenton reaction is an established process applied to treat a wide

variety of pollutants in hazardous wastes, wastewater, and groundwater. Eckenfelder, W. W., The Role of Chemical Oxidation in Waste Treatment Processes, *Proceedings of the First International Symposium on Chemical Oxidation*, Technomic Publishing Co., Inc., Lancaster, Pa., pp. 1-10, 1992; Huang, C. P. et al., Advanced Chemical Oxidation: Its Present Role and Potential Future in Hazardous Waste Treatment, *Waste Management*, 16: 361-377, 1993.

[0008] The well-known Fenton reaction has been used in a number of recent patents dealing with environmental remediation. For example, for in-situ subterranean treatment of contaminated ground water or soil, the following employ the Fenton reaction as at least a part of their process: U.S. Pat. No. 6,206,098, In situ Water and Soil Remediation Method and System, to Cooper et al., Mar. 27, 2001 using a catalyst prior to injection of an oxidizer to initiate the Fenton reaction; U.S. Pat. No. 5,967,230, In situ Water and Soil Remediation Method and System, to Cooper et al., Oct. 19, 1999; and U.S. Pat. No. 5,611,642, Remediation Apparatus and Method for Organic Contamination in Soil and Groundwater, to Wilson, Mar. 18, 1997, describing a subterranean system for implementing the Fenton reaction.

[0009] U.S. Pat. No. 5,789,649, Method for Remediating Contaminated Soils, to Batchelor, et al., Aug. 4, 1998, describes the use of zero-valent iron and a catalytic metal to degrade chlorinated compound contaminated soil. U.S. Pat. Nos. 5,611,936, 5,616,253, Apr. 1, 1997; and 5,759,389, Jun. 2, 1998, all entitled Dechlorination of TCE with Palladized Iron, all to Fernando, et al., describe a method to dechlorinate TCE with elemental iron having a palladium coating.

[0010] Zero-valent iron is used for at least part of the remediation process in establishing subterranean permeable reactive barriers as described in U.S. Pat. No. 5,733,067, Method and System for Bioremediation of Contaminated Soil Using Inoculated Support Spheres, to Hunt, et al., Mar. 31, 1998; U.S. Pat. Nos., 5,833,388, Nov. 10, 1998, and 5,975,800, Nov. 2, 1999, both entitled Method for Directing Groundwater Flow and Treating Groundwater In Situ, both to Edwards and Dick; U.S. Pat. No. 5,857,810, In Situ Chemical Barrier and Method of Making, to Cantrell and Kaplan Jan. 12, 1999; and U.S. Pat. No. 6,207,114, Reactive Material Placement Technique for Groundwater Treatment, to Quinn, et al., Mar. 27, 2001.

[0011] Zero-valent iron powder has been used for in-situ decontamination of halocarbons and metals more noble than iron as described in U.S. Pat. No. 5,975,798, In Situ Decontamination of Subsurface Waste Using Distributed Iron Powder, to Liskowitz et al., Nov. 2, 1999. U.S. Pat. No. 6,132,623, Immobilization of Inorganic Arsenic Species Using Iron, to Nikolaidis, et al., Oct. 17, 2000, describes the use of zero-valent iron to immobilize inorganic arsenic species. U.S. Pat. No. 5,783,088, Method of Removing Oxidized Contaminants from Water, to Amonette, et al., Jul. 21, 1998, describes treatment of oxidized contaminants using a layered aluminosilicate incorporating Fe (II).

[0012] U.S. Pat. No. 5,538,636, Process for Chemically Oxidizing Highly Concentrated Waste Waters, to Gnann et al., Jul. 23, 1996, uses the Fenton reaction together with electrolysis and multiple steps of neutralization to purify wastewater and address problems associated with the sludge resulting therefrom.

## SUMMARY

[0013] The process provided by a preferred embodiment of the present invention transforms the energetic compounds in waste associated with munitions production and decommissioning. It eliminates the need for subsequent treatment or re-generation with attendant concerns of possible secondary contamination. The process involves at least one pre-filtration and two sequential reduction and oxidation reactions and a post-reaction neutralization process to break down energetics to innocuous end products such as carbon dioxide, water, and environmentally benign products precipitated in a sludge.

[0014] The two-step treatment process combines two known treatment technologies: zero-valent metal reduction and Fenton oxidation. It also provides a final "polishing" step in which the acid pH of the mixture resulting from the Fenton reaction is neutralized and sediment settled out of the aqueous mixture.

[0015] It capitalizes on the advantages of each of the individual reduction and oxidation reactions and the resulting synergism of their serial combination. The neutralization post-treatment step enables re-use of the water by-product and stabilizes any resulting precipitated sludge.

[0016] The system uses a pre-filter containing filter media and a zero-valent metal, a first vessel for conducting the Fenton oxidation, and a second vessel for pH-neutralizing the treated waste and allowing it to settle prior to drawing off water for re-use and pumping any resultant sludge for further disposition. The system is designed to handle those highly oxidized waste streams that would not ordinarily lend themselves to Fenton oxidation, such as those containing energetics, in particular TNT, RDX, HMX, and combinations thereof.

[0017] The pre-filter system may use natural material as filter media such as sand or diatomaceous earth or manmade material such as polystyrene particles. Although elemental iron ( $\text{Fe}^0$ ) is the most cost-effective and efficient to use, metals such as tin, aluminum, zinc, magnesium, nickel, palladium, platinum, and combinations thereof may be used with the filter media. Upon reaction of the elemental iron with the waste stream, at least part of it is converted to the ferrous ion ( $\text{Fe}^{+2}$ ) and combined with the filtered and now initially treated waste stream. The iron and sand may be incorporated in a replaceable vented cartridge, the venting providing for safely dumping accumulating gases, such as hydrogen.

[0018] The system may also use a mix control module to facilitate automated control of the mix within the Fenton oxidation reactor and the settling tank. The mix control module monitors and controls the pH of each of the reactor and the settling tank as well as the amount of the oxidizer, typically hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), and metal ion, typically the ferrous ion  $\text{Fe}^{+2}$ , in the Fenton reactor. A preferred reactor would be of the continuous stirred tank reactor (CSTR) type. Alternatively, the Fenton reactor could be a tank provided with an impeller mixer.

[0019] For the settlement tank, pH is neutralized to within the range of 6.0-8.0 by adding a base, such as NaOH, and suspended solids are permitted to settle, forming sludge. A sludge pump is provided for emptying the settling tank periodically as needed.

[0020] In a preferred embodiment, the Fenton reactor is positioned lower than the zero-valent reactor thus enabling gravity feed of the filtered and reduced waste stream from the zero-valent reactor to the Fenton reactor. Likewise the settling tank is positioned lower than the Fenton reactor thus enabling gravity feeding of the contents of the Fenton reactor to the settling tank. The integrated use of a preferred embodiment of the present invention in the processing line of a manufacturing plant is envisioned.

[0021] Also provided is a method for filtering and deoxygenating a waste stream containing suspended and colloidal highly oxidized solids. The method comprises:

[0022] physically filtering the waste stream while establishing a reducing environment via use of zero-valent metal as part of the filtering;

[0023] subjecting the filtered waste stream to zero-valent metal reduction in a zero-valent metal column reactor;

[0024] subjecting the product resultant from the zero-valent column to a Fenton oxidation reaction in a Fenton reactor; and

[0025] pH-neutralizing the output of the Fenton reactor in a sedimentation tank.

[0026] The process permits reclaiming most of the aqueous portion of a waste stream's constituents and renders any sludge benign and suitable for possible re-use or safe disposal. The process further provides for automated monitoring and control of both the Fenton reactor and the settling tank.

[0027] Advantages of a preferred embodiment of the present invention include:

[0028] uses low-cost scrap metal as the zero-valent metal, typically scrap iron;

[0029] filters and treats both liquids, such as pink-water and solids, such as the constituents of TNT, RDX and HMX;

[0030] provides for venting Hydrogen gas at the top of the zero-valent reactor;

[0031] provides a pH monitoring and control system to optimize the Fenton reaction;

[0032] treats energetic compounds in a controlled reactor;

[0033] eliminates the need for GAC and concomitant regeneration and solid waste disposal;

[0034] presents a small footprint when compared to conventional waste processors;

[0035] suitable for use as a mobile system, to include trailer-mounting;

[0036] eliminates a complex environmental monitoring system needed for both the process and resultant products (sludge,  $\text{CO}_2$ , and clean water); and

[0037] achieves lower overall system capital and maintenance costs; and

[0038] achieves lower cost of final by-product disposal.

[0039] monitors the process easier and at less cost; and

[0040] requires a low skill level for system operation.

[0041] Compared to presently used methods, a preferred embodiment of the present invention replaces traditional GAC filtration while reducing the need for subsequent processing and regeneration of the GAC.

#### BRIEF DESCRIPTION OF DRAWINGS

[0042] FIG. 1 is a schematic of a system embodying a preferred embodiment of the invention, presenting the sequential zero-valent metal reduction and Fenton oxidation process.

[0043] FIG. 2 is a graph presenting the results of TNT reduction with zero-valent iron.

[0044] FIG. 3 is a graph presenting the results of RDX reduction with zero-valent iron.

[0045] FIG. 4 is a graph presenting the results of HMX reduction with zero-valent iron.

[0046] FIG. 5 presents the relationship for estimated concentrations of TNT vs. zero-valent metal column reactor length at various flow rates using the design equation in which the rate constant,  $k$ , is  $0.0285 \text{ s}^{-1}$ , the column inside diameter (ID) is 2.5 cm, and the porosity is 0.66.

[0047] FIG. 6 presents the relationship for estimated concentrations of RDX vs. zero-valent metal column reactor length at various flow rates using the design equation in which the rate constant,  $k$ , is  $0.0185 \text{ s}^{-1}$ , the column ID is 2.5 cm, and the porosity is 0.66.

#### DETAILED DESCRIPTION

[0048] A preferred embodiment of the present invention incorporates pre-filtration and two reduction/oxidation reaction processes seriatim. Pre-filtration employs a filter media, such as a fine sand and a zero-valent metal, to filter solids and de-oxygenate the waste stream. The first process involves the use of a metal having an inherent reducing potential, typically elemental iron ( $\text{Fe}^0$ ) available as scrap iron, while the second process facilitates the well-known Fenton reaction.

[0049] A schematic diagram of a preferred embodiment of the present invention is illustrated in FIG. 1. A waste stream is provided via a pump 101. The first treatment uses a pre-filter 102A and a zero-valent metal column reactor 102B. A pre-filter 102A containing sand and zero-valent metal filters solids, such as particles of TNT, RDX, HMX, nitroglycerin (NG), and “de-oxygenates” the aqueous portion of the waste stream through a chemical reducing reaction facilitated by the zero-valent metal in the pre-filter 102A and the zero-valent column reactor 102B. The ratio of sand to metal is maintained at a level sufficient to treat the expected waste stream, with a typical value of 85% sand to 15% elemental iron. Next, the product from the pre-filter 102A, i.e., filtered water containing energetic compounds, is reduced in the zero-valent column reactor 102B. Both the pre-filter 102A and the zero-valent metal column reactor 102B are vented to prevent accumulation of hydrogen gas by providing a breather 109 at the top of the zero-valent column reactor 102B.

[0050] The Fenton reaction reactor 103 uses iron released from a zero-valent column reactor 102B as  $\text{Fe}^{+2}$ , together with injected hydrogen peroxide 105,  $\text{H}_2\text{O}_2$ , to complete the remediation of the pinkwater and associated solid wastes. To optimize the reaction, provision is made for injection of an acid 111, typically sulfuric acid, to maintain a sufficiently low pH of 2.0-3.0. Normally, the amount of  $\text{Fe}^{+2}$  generated in the zero-valent column reactor 102B will be sufficient to carry the Fenton reaction. Should this not be the case, the same injection system used to provide the acid 111 may be used to supplement the Fenton reaction with additional metal. An impeller mixer 110 is provided in the Fenton reaction tank 103 to insure complete mixing and subsequent transformation of the energetic intermediates.

[0051] A settling tank 106 into which a strong base 107, such as sodium hydroxide (NaOH), is mixed is provided to both neutralize the resultant product and to separate the aqueous part from the solids. This tank 106 is also monitored via a controller 104 to maintain optimum pH. The solids are removed as a benign sludge by a sludge pump 108 while the aqueous portion 112 is re-cycled as needed.

[0052] Scrap iron is an industrial waste material that is readily available and relatively inexpensive. A sand and iron pre-filter 102A, with an inherently long service life, facilitates a passive process that requires little maintenance or regeneration, requiring only a pump 101 to draw the waste stream into it. Degradation of zero-valent iron does not generate toxic by-products. The reduction products of the energetics may be of concern, however. The subsequent Fenton oxidation process, fully oxidizing the reduction products to benign constituents such as  $\text{CO}_2$ , water, and benign inorganic compounds, breaks down these products.

[0053] It may be difficult for Fenton’s reagent alone to oxidize energetics due to their highly oxidized nature. This is addressed uniquely in a preferred embodiment of the present invention by using a combination of a pre-filter 102A and a zero-valent metal column reactor 102B to reduce the explosives to products that are much more amenable to processing using the Fenton reaction. Yet another advantage of a preferred embodiment of the present invention is the use of the  $\text{Fe}^{+2}$  (a degradation by-product of the pre-treatment process) in the subsequent Fenton reactor 103, thereby reducing the need for supplying commercial ferrous additives.

[0054] This innovative treatment system specifically removes and “mineralizes” TNT and heterocyclic nitramines (RDX and HMX) from pinkwater.

[0055] The U.S. Army Engineer Research and Development Center (ERDC) in cooperation with the University of Delaware conducted bench scale tests on the processes of the instant invention. Refer to FIGS. 2-4 for results of TNT, RDX and HMX reduction experiments conducted on bench scale reactors using these commonly available materials: sand and scrap iron in a pre-filter 102A, scrap iron in a zero-valent column reactor 102B, hydrogen peroxide and sulfuric acid added to a first vessel comprising the Fenton reactor 103, and sodium hydroxide to base-neutralize the resultant acidic waste stream in a second vessel. The majority of TNT (FIG. 2) in solution was removed within 30 minutes. Similarly, RDX (FIG. 3) and HMX (FIG. 4) in solution were completely removed within 30 minutes.

[0056] Refer to FIGS. 5 and 6. Preliminary experiments using a glass column of 2.5 cm diameter filled with scrap

iron rapidly reduced TNT (FIG. 5) and RDX (FIG. 6). Results from the column study show that the concentrations of TNT and RDX in column effluent can be predicted using the advection-dispersion-reaction equation:

$$\frac{\partial C_A}{\partial t} = D_L \frac{\partial^2 C_A}{\partial x^2} - u \frac{\partial C_A}{\partial x} - k C_A \quad (1)$$

[0057] where  $C_A$  is the concentration of the contaminant in the aqueous phase;  $t$  is time;  $D_L$  is the longitudinal dispersion coefficient,  $x$  is the coordinate in the flow direction;  $\mu$  is mean interstitial water velocity and  $k$  is a constant selected for a class of contaminants.

[0058] To evaluate whether the metal pre-treatment in the pre-filter and zero-valent metal column reactor 102B will enhance the subsequent Fenton oxidation process, experiments were carried out to study mineralization of the reduction products of the explosive compounds by Fenton's reagent ( $H_2O_2$  and  $Fe^{+2}$ ). A five-fold increase was observed in mineralization of TNT due to  $Fe(0)$  pre-treatment. In another study,  $H_2O_2$  (40 mM) was added to effluent from a zero-valent metal column reactor 102B, which received a wastewater containing TNT and RDX. No TNT or RDX was detected in the effluent, indicating that TNT and RDX were completely reduced to TAT and the ring cleavage products of RDX, respectively. Subsequent  $H_2O_2$  addition mineralized 50% of TAT and greater than 95% of RDX reduction products within 100 minutes.

[0059] Refer to FIG. 1. A pump 101 provides the waste to a preferred embodiment 100 of the present invention. A preferred embodiment uses a unit 102 that incorporates a pre-filter 102A containing filter media and zero-valent metal for filtration of solids and de-oxygenation of the wastewater stream and a zero-valent metal column reactor 102B to reduce the highly oxidized state of the energetics in the waste stream; a Fenton reaction vessel 103 to which a strong oxidizer, typically hydrogen peroxide, is added to mineralize the metal-treated energetics in the waste stream; a mix control system 104; a supply 105 of oxidizer; a neutralization and sedimentation tank 106; and a source 107 of a strong base. The waste stream may be fed to the Fenton reaction vessel 103 via gravity feed. Likewise, the clean water from the neutralization and sedimentation tank 106 may be gravity fed to a holding tank, or the like. A sludge pump 108 is an option for removing sediment from the neutralization and sedimentation tank 106 for further disposal.

#### EXAMPLE

[0060] A pump 101 supplies a waste stream, e.g., pinkwater, to the bottom of a pre-filter 102A containing a mixture of sand and zero-valent iron in a ratio of 15:85. The iron de-oxygenates the pinkwater as the iron transforms from  $Fe^0$  to  $Fe^{+2}$ , and the sand filters colloidal and suspended particles from the pinkwater. The pre-filter 102A may be provided in the form of a disposable cartridge, or be an adapted sand filter available from swimming pool supply companies.

[0061] As the pinkwater flows upwards through the zero-valent metal column reactor 102B, the energetics contained therein are reduced quickly by the zero-valent iron. For

example, TNT is reduced to triaminotoluene (TAT) and RDX and HMX are reduced to ring-cleavage products. The effluent, which carries the reduction products and corrosion by-products, such as the ferrous ion ( $Fe^{+2}$ ), then exits from the top of the column 102B and flows to the Fenton reaction vessel 103 by gravity. A gas vent 109 is located at the top of the column 102B to release any hydrogen gas generated from the anaerobic reduction process.

[0062] The Fenton oxidation process takes place in a Fenton reaction vessel 103 that in one configuration is a completely stirred tank reactor (CSTR) 103 that uses an externally powered mixing paddle 110. To the CSTR 103, a hydrogen peroxide solution is added continually to produce "Fenton's reagent" (i.e., hydrogen peroxide ( $H_2O_2$ ) plus  $Fe^{+2}$ ). In the presence of  $Fe^{+2}$ , hydrogen peroxide decomposes to form the hydroxyl radical ( $OH^\cdot$ ), a very strong oxidizing agent, with  $E^0 = +2.33V$ , that quickly oxidizes the reduction products of the energetics to stable end products such as carbon dioxide, water, and a nitrate. For the Fenton reaction to occur optimally, the pH in the CSTR 103 is maintained within a range of 2.0-3.0 using a mix control system 104 (e.g., pH meter, recorder, and automated controller) to add the necessary pH reducer, such as a sulfuric acid solution ( $H_2SO_4$ ), from an acid source 111. The contents of the CSTR 103 are continuously stirred with one or more mixing paddles 110, such as those used with impeller mixers. Under normal operation, addition of iron to the CSTR 103 is not required. However, should the need arise, iron, as a ferrous ion ( $Fe^{+2}$ ), may be injected in the same manner as the acid.

[0063] The treated effluent from the CSTR 103 flows into a neutralization and sedimentation tank 106 by gravity, where it is pH-neutralized by adding a base, such as sodium hydroxide (NaOH), from a supply tank 107 or other source. By bringing the pH to a neutral value in the range of 6.0-8.0, a sludge containing a ferric hydroxide is formed from precipitation of the ferric ion. The sludge is collected and removed at the bottom of the neutralization and sedimentation tank 106 via a sludge pump 108. The treated water 112 exits the top of the neutralization and sedimentation tank 106 and may be re-used.

[0064] Although a preferred embodiment of the present invention focuses on pinkwater treatment, any waste containing energetic compounds (explosives, propellants, and other pyrotechnic compounds) may be treated efficiently by this system and method. For example, waste generated from demilitarization activities; air scrubber fluids or solution containing energetic compounds; clean-up site lagoon water containing energetic compounds; and ground water contaminated with energetics that is pumped to the surface for treatment.

[0065] Although specific functions for this system and method have been described, other functions using the described apparatus and method are not excluded from falling within the ambit of the claims herein.

We claim:

1. A system for treating a waste stream that may contain suspended and colloidal solids, comprising:

a pre-filter containing a zero-valent metal and media suitable for filtering

at least some of said solids from said waste stream;

a zero-valent metal column reactor operably connected to said pre-filter,

wherein after said waste stream is treated therein and a first treated waste stream is output;

a first vessel in which initial contents include an oxidizer to be combined

with said first treated waste stream,

wherein said contents of said first vessel are adjusted to optimize the amount of said oxidizer and a metal ion resultant from processing said waste stream with said zero-valent metal in said zero-valent metal column reactor,

wherein said contents of said first vessel are further adjusted to optimize the pH of said contents of said first vessel, and

wherein said contents of said first vessel are stirred as part of treating said contents prior to output as a second treated waste stream; and

a second vessel for accepting said second treated waste stream as at least part of its contents,

wherein said second treated waste stream is pH-neutralized,

wherein said contents of said second vessel are further adjusted to optimize pH of said contents of said second vessel, and

wherein said second treated waste stream is permitted to settle prior to drawing off at least one final product suitable for reuse.

2. The system of claim 1 in which said waste stream results from operations involved with the handling of energetic materials.

3. The system of claim 2 in which said energetic materials are composed of constituents selected from the group consisting essentially of TNT, RDX, HMX, nitroglycerin (NG), and constituents and combinations thereof.

4. The system of claim 1 in which said filter media is a naturally occurring material

5. The system of claim 4 in which said naturally occurring material is sand.

6. The system of claim 1 in which said filter media is manmade.

7. The system of claim 1 in which said metal is selected from the group consisting of: iron, tin, aluminum, zinc, magnesium, nickel, palladium, platinum, and combinations thereof.

8. The system of claim 7 in which said metal is predominantly elemental iron ( $\text{Fe}^0$ ), wherein, upon reaction of said elemental iron with said waste stream, at least part of said elemental iron is converted to the ferrous ion ( $\text{Fe}^{+2}$ ) and combined with said first treated waste stream.

9. The system of claim 1 in which said pre-filter is a replaceable cartridge.

10. The system of claim 1 in which said zero-valent metal column reactor is vented to reduce accumulation of gasses that may result from reactions therein.

11. The system of claim 1 further comprising a mix control module, wherein automated control of the characteristics of said contents of said first and second vessels is accomplished via said mix control module, wherein said mix

control module at least monitors and controls the pH of each of said first and second vessels, and wherein said mix control module controls the amount of said metal ion and said oxidizer in said first vessel.

12. The system of claim 1 further comprising an impeller mixer for use in said first vessel.

13. The system of claim 1 in which said first vessel is a continuously stirred tank reactor (CSTR).

14. The system of claim 1 in which said oxidizer is hydrogen peroxide ( $\text{H}_2\text{O}_2$ ).

15. The system of claim 1 in which said second vessel is a pH-neutralizing and sedimentation tank, wherein the pH of said second treated waste stream is neutralized within the range of 6.0-8.0 by adding a base, and wherein any said suspended solids within said second treated waste stream are permitted to settle, forming sludge.

16. The system of claim 15 in which said base comprises at least some sodium hydroxide (NaOH).

17. The system of claim 15 further comprising at least one sludge pump for emptying said sedimentation tank of sludge.

18. The system of claim 1 in which said first vessel is positioned lower than said zero-valent metal column reactor thus enabling gravity feed of said first treated waste stream from said zero-valent metal column reactor, and further positioning said second vessel at a position lower than said first vessel thus enabling gravity feeding of said second treated waste stream to said second vessel.

19. A method for treating a waste stream containing at least some highly oxidized suspended and colloidal solids, comprising:

physically filtering at least some of said solids in a pre-filter;

establishing a reducing environment for removing oxygen via use of at

least one zero-valent metal as a reducing agent,

wherein the output of said physical filtering and reducing environment is a first treated waste stream;

subjecting said first treated waste stream to a Fenton oxidation reaction in

a first vessel,

wherein said Fenton oxidation reaction is monitored and controlled, and wherein the output of said Fenton oxidation reaction is a second treated waste stream; and

pH-neutralizing said second treated waste stream in a second vessel prior

to reclaiming at least a portion of said second output waste stream's

constituents;

wherein said second waste stream is permitted to settle in a tank to precipitate any remaining said solids in sludge.

20. The method of claim 19 in which said solids comprise at least one energetic material.

21. The method of claim 20 in which said energetic material is selected from the group consisting of: TNT, RDX, HMX, nitroglycerin (NG), and constituents and combinations thereof.

22. The method of claim 19 in which said metal is selected from the group consisting of: iron, tin, aluminum, zinc, magnesium, palladium, nickel, platinum, and combinations thereof.

23. The method of claim 22 in which said metal is predominantly elemental iron (Fe<sup>0</sup>), wherein, upon reaction of said elemental iron with said waste stream, at least part of said elemental iron is converted to the ferrous ion (Fe<sup>+2</sup>) and combined with said first treated waste stream.

24. The method of claim 19 in which said pH neutralizing is accomplished by adding a base.

25. The method of claim 24 in which said base is at least some sodium hydroxide (NaOH).

26. The method of claim 19 in which said sludge is pumped from said tank.

27. The method of claim 19 in which at least one of said reclaimed constituents is water suitable for reuse.

28. The method of claim 19 in which said first vessel is positioned lower than said zero-valent metal column reactor thus enabling gravity feed of said first treated waste stream from said first vessel, and further providing said second vessel at a position lower than said first vessel thus enabling gravity feeding of said second treated waste stream to said second vessel.

29. The method of claim 19 further comprising optimizing performance of said system by monitoring and controlling:

- pH of each of said first and second vessels;
- amount of said oxidizer in said first vessel; and
- amount of said metal ion in said first vessel.

30. A processing plant that incorporates a system for remediating a waste stream containing at least some suspended and colloidal solids, the system comprising:

- a pre-filter containing a zero-valent metal and media suitable for filtering
- at least some of said solids from said waste stream;
- a zero-valent metal column reactor operably connected to said pre-filter,
- wherein after said waste stream is treated therein and a first treated waste stream is output;
- a first vessel in which initial contents include an oxidizer to be combined with said first treated waste stream,
- wherein said contents of said first vessel are adjusted to optimize the amount of said oxidizer and a metal ion resultant from processing said waste stream with said zero-valent metal in said zero-valent metal column reactor,
- wherein said contents of said first vessel are further adjusted to optimize the pH of said contents of said first vessel, and
- wherein said contents of said first vessel are stirred as part of treating said contents prior to output as a second treated waste stream; and
- a second vessel for accepting said second treated waste stream as at least part of its contents,
- wherein said second treated waste stream is pH-neutralized,
- wherein said contents of said second vessel are further adjusted to optimize pH of said contents of said second vessel, and
- wherein said second treated waste stream is permitted to settle prior to drawing off at least one final product suitable for reuse.

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