**Title:** LAUNDRY WASH WATER TREATMENT

**Abstract:** A method for treating wastewater containing solid materials and one or more of fats, oils and grease which comprises simultaneously subjecting water to be treated to sparging air in the presence of singlet oxygen and/or hydrogen peroxide.

![Diagram of treatment process]

**Fig. 1**
LAUNDRY WASH WATER TREATMENT

This invention relates generally to the field of wastewater processing. The invention has particular utility in connection with treatment of laundry effluent. The waste water and will be described in connection with such utility, although other utilities are contemplated.

Waste waters from commercial laundry facilities and laundromats must be treated in order to remove toxic contaminants, bad odors and suspended solids. The waste water typically is treated by various means of filtration and chemical reaction designed to accomplish specific purification goals, as needed by particular users. The most common systems involve passing the water through layers of filtering media to remove solid particles and through chemically active media to reduce the water's hardness, improve its pH, and extract undesirable contaminants.

Water purification agents generally are categorized in terms of their function as filters, when designed to eliminate larger size suspended solids; clarifiers, when intended to remove smaller size particles and reduce opacity; softeners, to remove calcium and magnesium ions and reduce water hardness; and refiners, to extract chlorine, iron and organic compounds. Both anion and cation exchange resins are used to perforin a multiplicity of these functions.

The separation of solutes from water by means of selectively permeable membranes is also an effective and economical method of water purification. The processes of reverse osmosis, ultrafiltration, nanofiltration and electrodialysis all involve the use of membranes that have the ability to prevent the migration of most dissolved and suspended solids while allowing the passage of water through their pores.

During conventional laundry operations, the waste water from each cycle typically is disposed of to the sewer after use, and fresh water is fed to the washer machines through cold and hot feed systems to completely replace each load. The cold water feed is drawn directly from a utility supply, while the hot water feed is first heated and stored in a tank at about 150°F. to 180°F. As the washer machines process laundry, they call for both hot and cold water from these sources in order to provide the water utilized in the wash process. In most operations, the proportion of hot to cold water usage is about fifty/fifty. The resulting waste water is typically at about 120°F., and laden with detergent and softening chemicals, in addition to dirt and pollutants. Therefore, when waste water is drained to a sewage system or otherwise discarded, useful chemicals and valuable heat are also wasted with it. In addition, the contaminants left in the water often
require downstream water treatment before the effluent can be released to the
environment.

Thus, conventional laundry operations involve large water usage, high fuel
consumption for water heating, and wasteful disposal of active chemical ingredients in
the waste-water effluent, all of which affect the efficiency and operating costs of a
laundry.

The present invention provides improvements over prior system for reclamation
and reuse of waste-water affluent from laundry operations. In our co-pending
provisional application Serial No. 61/842,878, filed July 3, 2013, and its corresponding
PCT international Patent Application Serial No. PCT/US14/__________, filed July 1,
2014, (Attorney Docket No. AQUA1301PCT) we describe a system for removing fats,
oils and grease, and lint and other debris from washer effluent fluids in which the
effluent water is mechanically filtered by passing through dynamic screens which are
continuously or regularly replenished whereupon material capture is optimized with
minimal effect on water flow rate. With the filter system of our aforesaid co-pending
application, large amounts of grease and solid contaminants may be removed with
minimal water loss. The loaded or spent filter may then be dried and disposed of, or
incinerated, and the filtrate, after further processing is recycled or passed to waste.

The present invention provides a system of treating effluent water after the bulk
of the fats, oils, grease and solid debris has been removed, e.g., by mechanical filtering.
More particularly, in accordance with the present invention, the effluent water, after
removal of the bulk of fats, oils, grease, lint and other debris, is passed to one or more
treatment tanks where it is subjected to an air sparging and foam extraction wherein even
more oily materials, i.e. fats, oils and grease, are removed, while the air spargings and
foam extraction processes are taking place, a chemical reaction also takes place to
flocculate and oxidize both organic and inorganic materials in the laundry waste stream.
More particularly, the laundry waste stream is halogenated, typically chlorinated, and pH
stabilized, and the halogenated pH stabilized water is then sent to a second tank where
hydrogen peroxide is added while the water in the tank is being aerated. This allows for
formation of singlet oxygen which is a powerful oxidizer. The singlet oxygen reacts
with unwanted materials in the water, and oxidizes metal ions, forming metal oxide
which precipitate out. The singlet oxygen also breaks down various organic chemicals to
more filterable or trappable compounds that can be eliminated by later filtration or
reaction processes or may oxygenize organic compounds to form carbon dioxide.
As used herein the term contaminants include:

- "oils" are typically liquids; the term "fats" are usually solids at room temperature;
- the term "greases" are usually semi-solids, soft solids or high viscosity liquids, often with added solids, soaps and other ingredients. Other contaminants in waste water that can be removed include:

  - suspended solids - if fine enough need to be coagulated/flocculated, e.g., silica and tannins, etc.;
  - dissolved solids such as:
    - metallic ions that need to be oxidized and precipitated/flocculated; e.g. $Fe^{2+} \rightarrow Fe^{3+}(Fe(OH)_3)$;
    - cations that need to be insolubilized/flocculated; e.g. $Ca^{2+} \rightarrow Ca(OH)_2$;
    - metallic complexes with organic anions need to be destabilized/flocculated;
    - 'iron bacteria' need to be oxidized/destabilized/flocculated;
    - complex anions such as arsenate and chromate, etc.;
    - gases such as hydrogen sulfide ($H_2S$) or related anions such as $HS^-$ and $SO_3^{2-}$, or anions such as $NO_2^-$, etc.; and
    - unwanted micro-organisms such as bacteria, viruses, fungi, and other micro-biota.

Fig. 1 is a process flow diagram illustrating a preferred embodiment of the present invention;

Fig. 2 is a diagrammatic side view of a sparged airfoam extraction unit generating bubbles and foam in accordance with the present invention;

Fig. 3 illustrates three modes of capture of oil, suspended particles and flock in air bubbles in surfactant foam in accordance with the present invention;

Fig. 4 a representative sparged air process in accordance with the present invention, and show how a sparged air process and singlet oxygen chemical process combine to take full advantage of the surfactants in the laundry waste water, to make foam and float contaminants to the water surface;

Fig. 5 is a flow diagram illustrating the second phase of the system of the present invention;

Fig. 6 is a cross-sectional view of a First filter module in accordance with the present invention;
Figs. 7A and 7B show, respectively, filtering and backwashing modes of a second filter module, for example, a diatomaceous earth (DE) filter, in accordance with the present invention;

Fig. 8 illustrates a typical DE filter design; and

Fig. 9 a more generalized pressure leaf filter used for a DE filter with a DE pre-coat tank;

Fig. 10 graphically illustrates a DE filtration process including pre-coat filter and back wash;

Fig. 11A, 11B and 11C illustrate, respectively, large oil droppings plugging pores in activated carbon preventing further chemical "removal", organoclay adsorbs oil droplets on platelet surfaces efficiently in large quantities: and once large drops are removed by organoclay, activated carbon can trap smaller particles and molecules in pores efficiently;

Figs. 12 and 13 show molecules adsorbing onto solid surfaces, and illustrates how molecules may deposit more than one molecule thickness;

Fig. 14 shows an electrochemical cell in accordance with the present invention;

Fig. 15 illustrates microscopic action of ions with algae, virus, bacteria and scaling;

Fig. 16 illustrates how oxygen may be forced between high voltage plates to simulate corona discharge, and the oxygen is broken apart and combined into ozone;

Fig. 17 illustrates a system for ozone direct injection into a laundry washing machine;

Fig. 18 illustrates the ozone oxidation cycle;

Fig. 19 shows ozone solubility and temperature;

Fig. 20 charts concentration times the virus inactivation by ozone vs. temperature;

Fig. 21 charts the effective pH on the decay of ozone (T=15°C);

Fig. 22 graphically illustrates ozone's bacterial action on drug resistant genes.

Referring to Fig. 1 below, the process starts with elimination of the bulk of the fats, oils, grease, lint and other debris from the laundry effluent stream using the dynamic screen process as described in our aforesaid co-pending provisional application Serial No. 61/842.878, and corresponding PCT International Patent Application Serial No. PCT/US14_______, filed July 1, 2014. The dynamic screen process as described in
our aforesaid co-pending applications is able to efficiently simultaneously and
synergistically remove the bulk of the fats, oils, grease, lint and other debris from the
laundry washer effluent stream preventing fouling of the following chemical and
physical treatment tank processes that are essential for the purification of the waste water
for ultimate recycling back into the laundry process as clean process water. The overall
process is illustrated in Fig. 1.

This is done simply, with a minimum of maintenance required; and the spent
screen mesh media is automatically dewatered so that it can easily finish drying and be
discarded into landfill or incinerated without the need for hauling away sludge or
contaminated fluids that need permitting.

The extraction process fluid is now sent to a treatment tank (To) where it is
chlorinated by adding sodium hypochlorite (NaClO) (1) (if sufficient hypochlorite is not
present in the effluent fluid) as the first phase of the chemical treatment process. The
fluid is then prepared and the resulting fluid is now ready for air sparging and foam
extraction and chemical treatment. In this next tank (Ti) hydrogen peroxide (H₂O₂) (2)
is added while the tank is being aerated. The overall process is as follows:

a. Air is pumped at high volumes directly into a system of tubes placed near
   the bottom of a tank capable of holding the fluid effluent to be processed
   at the required temperature.

b. Air can be supplied by a pump or air compressor as needed to provide air
   at a sufficient volume and speed as to allow air to exit an array of tubes
   containing a number of holes.

c. The air may be pumped into a pressure vehicle with or without mixing
   with fresh or recycled water for the purposes of supersaturating the
   dissolved air.

d. The system of tubes includes an array of "branch arms" that have been
   drilled with a number of holes along the appropriate length of the tubes in
   a desired pattern and number.

e. The holes are of a size that will deliver "fairly large" bubbles, typically
to 1/64 in to ¼ in (0.39 mm to 6.35 mm), preferably 1/32 in to 3/16 in
(0.79 mm to 4.76 mm), more preferably 1/16 mm to 1/8 mm (1.58 mm to
3.175 mm) in size, at a speed and pressure, in concert with the air supply,
to overcome the head pressure in the tank at the depth defined as the "full
level" thus allowing the air to exit the sparging tube array and supply a
great degree of turbulence in the fluid as the bubbles rapidly reach the surface.

f. One aim of this bubble caused turbulence is to adequately mix the incoming streams of laundry effluent to reasonably homogenize the chemical variations from individual washers of different sizes being discharged at different laundry cycles (detergent, rinse, bleach i.e., chlorine or peroxide, rinse, final rinse with laundry sour), with different laundry loads and different laundry chemical recipes for different laundry types (shirts, towels, blankets, floor mats, napkins, etc.), different textiles (cotton, linen, polyester, etc.), and at different temperatures (hot wash, cold wash, etc.).

g. Another aim of the bubble caused turbulence is to adequately mix the chemicals to be added to the various chemical treatment tanks (To, T1, T2, T3 etc.); these chemicals might be alkalis e.g. NaOH and the like, acids e.g. Citric acid and the like, bleaches (oxidizers) e.g. NaCIO or H2O2 and the like, surfactants of various types and chemical formulations (e.g. anionic surfactants e.g. sodium dodecyl sulfate and the like): nonionic surfactants, e.g. polyethylene oxide/polypropylene oxide derivatives such as triblock copolymers of ethylene oxide and propylene oxide and the like and others as known by practitioners of the art; or soaps of various types, e.g. Sodium oleate, potassium laurate and the like, sequestrants/chelators for "softening the water" e.g. sodium citrate, and the like, or foam stabilizers (e.g. Sodium Carboxymethylcellulose and the like).

h. Another aim of the bubble caused turbulence is to form a large volume of stabilized foam to be formed and also rise to the surface. This foam will be stabilized by soaps and surfactants found in the laundry effluent, having been added by the laundry facility as part of the operation, or formed by "saponification" of fatty acids and fatty esters, e.g. diglycerides and triglycerides, as examples, having been removed from the laundry being washed, or by being added during the chemical treatment phase of the process. Additional alkali may also be added to facilitate saponification for further fat removal and surface tension lowering.

i. The purpose of the stabilized foam so formed is to "capture" suspended materials as it swirls and rises to the surface. See Figs. 3 and 4.
j. This suspended material is expected to contain the following items: coagulates and flocculates formed by the oxidation and/or destabilization and precipitation of metallic ions in solution e.g. iron, manganese, nickel, copper and the like, F.O.G. particulates or emulsions that have been pH or surface charge destabilized, micro-fibers that passed through the lint traps used to capture macro-fibers, silt, and other insoluble materials suspended in the fluid.

k. Once captured in the stabilized foam by surface tension, hydrogen bonding, electrostatic forces, van der Waals forces, physical entanglement, adhesion, absorption or other mechanisms, the contaminant laden foam will rise to the surface The surface foam is expected to be influenced by the rapid flow of water into and out of the holding tanks and proceed to the exit end where it can be extracted in a variety of manners. It can be physically pushed or skimmed to an overflow outlet; it can be blown with air or a water spray to a similar outlet; it can be allowed to overflow a baffle or weir construction; or, most preferably it can be vacuum extracted, as will be described below.

**Sparged Air Foam Extraction** takes place in one or more chemical treatment tanks and continues to remove even more oily materials - F.O.G. 'fats, oils and grease' - that were removed by the laundering process and suspended in the waste water. Large volumes of air create foam that is extracted by vacuum and de-aerated for disposal. The combination of sparging and vacuum extraction of the foam also removes large quantities of surfactants and soaps as part of the process of efficiently post treating the effluent for recycling.

While the air sparging and foam extraction processes are taking place, a chemical reaction also takes place that will flocculate and oxidize both organic and inorganic materials in the laundry waste stream.

Singlet Oxygen (¹O₂) is generated as will be described below according to the following reaction:

\[
H_2O_2 + NaClO \rightarrow O_2 + NaCl + H_2O
\]

Singlet oxygen is an activated and highly energetic form of oxidizing agent formed by the reaction of hydrogen peroxide (H₂O₂) and sodium hypochlorite (NaClO).
The hydrogen peroxide (oxygen bleach) is added in concentrated form, e.g. 50% to the diluted solution of sodium hypochlorite (chlorine bleach) already in the washer discharge fluid. The resulting reactions yield floculates and smaller organic molecule fragments with lower COD/BOD requirements. These floculated particles and any unused singlet oxygen micro-bubbles get swept up to the surface along with the macro-bubbles formed from the laundry detergent surface wetting agents and sparged air, along with other suspended solids and oil droplets. See again Figs. 3 and 4.

Unlike standard Dissolved Air Flotation (DAF) methods, the large bubbles cause turbulence to make lots of foam. The air doesn't have to be dissolved in the fluid. The surfactant wetting of the particles and the bubbles formed are the driving force to get contaminants to the surface.

Thus, flocculation, oxidation, sanitation plus flotation and removal are simultaneous and synergistic.

Summarizing to this point, the present invention, in part, employs:

**Aeration:**
- i.e., air sparging & oxidation to lower BOD (Biological Oxygen Demand) in waste water;

**Agitation:**
- i.e., Air injection for turbulent mixing of chemicals in liquids in the treatment tank;

**Oxidation:**
- i.e., activated oxidation to cause flocculation and destroy microorganisms; and

**Flotation:**
- i.e. foam generation to float floc and fats, oil and grease to surface for vacuum removal.

A feature and advantage of the present invention is that conventional chemical flocculants (inorganic and organic) do not need to be added to the water to form the flocs. This also eliminates the need to remove these contaminants.

**BOD and COD removal** from wastewater

Hydrogen peroxide has been used to reduce the BOD and COD of industrial wastewaters for many years. There are specific situations which justify its use. These include:
- Pre-digestion of wastewaters - which contain moderate to high levels of compounds that are toxic, inhibitory, or recalcitrant to biological treatment (e.g., pesticides, plasticizers, resins, coolants, and dyestuffs)

- Pretreatment of high strength / low flow wastewaters - where bio-treatment may not be practical - prior to discharge to a Publicly Owned Treatment Works (POTW)

- Enhanced separation of entrained organics by flotation and settling processes

- Supply of supplemental Dissolved Oxygen (DO) when biological treatment systems experience overloads or equipment failure.

Hydrogen peroxide can be used as a stand-alone treatment or as an enhancement to existing physical processes, depending on the situation encountered and the regulations in force.

Hydrogen peroxide is one of the most versatile, dependable and environmentally compatible oxidizing agents. The relative safety and simplicity of its use as an oxidizing agent has led to the development of a number of applications in wastewater systems. The strong oxidizing power of hydrogen peroxide makes it suitable for the destruction of a variety of pollutants. Optimization of conditions using hydrogen peroxide to destroy these pollutants can involve control of pH, temperature and reaction time.

Hydrogen peroxide also oxidizes the hydrogen sulfide and promotes bio-oxidation of organic odors. Hydrogen peroxide decomposes to oxygen and water (2 H₂O₂ → 2 H₂O + O₂) adding dissolved oxygen to the system, thereby offsetting some of the Biochemical Oxygen Demand.

Pollutants that are more difficult to oxidize require hydrogen peroxide to be activated with catalysts, or take other more effective approaches.

Generating Singlet Oxygen - \(^{1}\text{O}_2\) - is one such approach; and is unique.

The singlet oxygen approach provides higher oxidation potential, thereby allowing more powerful and more rapid oxidation of both standard and stubborn pollutants.

The singlet oxygen generated is more powerful than hydrogen peroxide by itself, and is much more powerful than regular triplet oxygen, sodium hypochlorite and even
stronger than ozone. See Oxidizing Agent vs. Oxidizing Potential Table 1 below (ORP is in Volts).

Combining hydrogen peroxide and singlet oxygen also allows for a broader capability for oxidation, molecular digestion and bio-hazard destruction. With adjustments, a full range of Reactive Oxygen Species, including Free Radicals are available:

This process also presents further opportunities to enhance Advanced Oxidation Processes (AOP) using ozone (O₃), UV light, and titanium dioxide (TiO₂) photo-catalyst approaches as will be described below.

TABLE 1

<table>
<thead>
<tr>
<th>Oxidizing Agent</th>
<th>Oxidizing Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Hydroxyl radical</td>
<td>·OH = 2.80</td>
</tr>
<tr>
<td>2. Singlet Oxygen</td>
<td>^O₂ = 2.42</td>
</tr>
<tr>
<td>3. Ozone</td>
<td>O₃ = 2.07</td>
</tr>
<tr>
<td>4. Hydrogen Peroxide</td>
<td>H₂O₂ = 1.77</td>
</tr>
<tr>
<td>5. Perhydroxyl radical</td>
<td>HO₂⁻ = 1.70</td>
</tr>
<tr>
<td>6. Potassium Permanganate</td>
<td>KMnO₄ = 1.67</td>
</tr>
<tr>
<td>7. Hypochlorous Acid</td>
<td>HClO = 1.59</td>
</tr>
<tr>
<td>8. Chlorine dioxide</td>
<td>ClO₂ = 1.50</td>
</tr>
<tr>
<td>9. Chlorine</td>
<td>Cl₂ = 1.36</td>
</tr>
<tr>
<td>10. Triplet Oxygen</td>
<td>O₂ = 1.23</td>
</tr>
<tr>
<td>11. Bromine</td>
<td>Br₂ = 1.09</td>
</tr>
<tr>
<td>12. Sodium Hypochlorite</td>
<td>NaClO = 0.94</td>
</tr>
</tbody>
</table>
Table of relative oxidation power (in Volts) of common Oxidizing Agents for water treatment

Hydrogen Peroxide can generate a complex set of Reactive Oxygen Species that oxidizes many chemicals and breaks them down to smaller molecules that are safer and easier to remove. Additionally, some reactions can cause new and larger molecules to form that are insoluble and can add to the floe that can be removed, while other reactions cause the formation of radicals that can cause additional degradation and insolubilization to occur that further assists in removing contaminants in the process fluid.

The Hydroxyl radical is a highly reactive, short lasting, non-specific oxidant. Hydroxyl radicals have a half-life in the order of nanoseconds ($10^{-9}$ seconds) or 1,000 times shorter than Singlet Oxygen with a half-life in the order of microseconds ($10^{-6}$ seconds) or 1,000 times longer than hydroxyl radicals. Oxidation reactions with Singlet Oxygen are more specific in nature: both include the ability to generate additional radical species that can oxidize, decompose or crosslink organic contaminants.

<table>
<thead>
<tr>
<th>Oxidizing Reagent</th>
<th>Oxidizing Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyl Radical</td>
<td>2.80</td>
</tr>
<tr>
<td>Singlet Oxygen</td>
<td>2.42</td>
</tr>
<tr>
<td>Ozone</td>
<td>2.07</td>
</tr>
<tr>
<td>Hydrogen Peroxide</td>
<td>1.77</td>
</tr>
</tbody>
</table>

On the other hand, Hydrogen peroxide can last for many minutes in the water. This allows other peroxidation reactions to take place that could not occur in the shorter reaction windows allowed by singlet oxygen and/or the hydroxy! radical.

In addition to acting as an oxidant itself, hydrogen peroxide ($H_2O_2 = HO-OH$) in solution is also a source of the highly reactive hydroxy! radical (-OH). For example:
Hydrogen peroxide can also react with ozone \((O_3)\) to produce hydroxy radicals.

\[
\text{H}_2\text{O}_2 + 2 \text{O}_3 \rightarrow 2 \cdot \text{OH} + 3 \text{O}_2
\]

### Destruction of Sodium Hypochlorite

**Reaction Equation:**

\[
\text{OCT} + \text{H}_2\text{O}_2 \rightarrow ^1\text{O}_2 + \text{Cl}^- + \text{H}_2\text{O} \quad (\text{O}_2^* = \text{singlet oxygen})
\]

(hypochlorite + hydrogen peroxide → oxygen + chloride + water)

**Theoretical Weight Ratio:** 0.67 lbs \(\text{H}_2\text{O}_2\) (100%) per lb OCT

**Optimum reaction rates** occur at a pH of 8 - 9, while acceptable rates occur from 7.5 - 10.5.

Hydrogen peroxide reacts with free available chlorine in solutions (hypochlorite) at pH > 7. While there is no upper limit to the pH (e.g., \(\text{H}_2\text{O}_2\) can be used to dechlorinate effluent from caustic/chlorine odor scrubbers at \(pH > 12.5\)), as a practical matter, pH 8.5 is preferred in order to provide an instantaneous reaction.

In most cases the oxygen produced by the reaction will remain dissolved in the solution (saturation is about 10 ppm Dissolved Oxygen (D.O.) at 20°C). Where higher concentrations of chlorine are involved, the solutions will effervesce from the \(^1\text{O}_2\) evolved. Reaction with inorganic or organic contaminants in the water will reduce the amount of bubbles that will be released. The original destruction reaction is mildly exothermic (liberating 37 kcal/mole).

Providing an amount of Hydrogen Peroxide in excess of the amount needed to destroy the theoretical hypochlorite concentration will ensure that:

- all of the hypochlorite (OCl) will be converted to NaCl
- the maximum amount of \(^1\text{O}_2\) is available for oxidation and sanitation reactions
- additional \(\text{H}_2\text{O}_2\) is available for additional reactions as peroxide or as hydroxyl radicals.

For maximum efficiency of delivery of the hydrogen peroxide into the effluent to be treated, high concentrations, that are readily available, are recommended. (See chart below).

<table>
<thead>
<tr>
<th>Specifications</th>
<th>27%</th>
<th>35%</th>
<th>50%</th>
<th>70%</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{O}_2) content, % by weight</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Product diluted at terminals</td>
<td>26.6 - 27.4</td>
<td>35.0 - 35.8</td>
<td>50.0 - 50.8</td>
<td>70.0 - 70.8</td>
</tr>
<tr>
<td>Stability, 24 hours @ 00° C</td>
<td>&gt;96.0%</td>
<td>&gt;96.0%</td>
<td>&gt;96.0%</td>
<td>&gt;96.0%</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>Typical Properties</td>
<td>27%</td>
<td>35%</td>
<td>50%</td>
<td>70%</td>
</tr>
<tr>
<td>Loss in % assay, 1 yr, 25° C</td>
<td>&lt;0.5</td>
<td>&lt;0.7</td>
<td>&lt;1.0</td>
<td>&lt;1.4</td>
</tr>
<tr>
<td>Apparent pH</td>
<td>&lt;3.7</td>
<td>&lt;3.7</td>
<td>&lt;3.0</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Active oxygen content, %</td>
<td>12.7</td>
<td>16.5</td>
<td>23.5</td>
<td>32.9</td>
</tr>
<tr>
<td>Specific gravity (20° C/4° C)</td>
<td>1.10</td>
<td>1.13</td>
<td>1.20</td>
<td>1.29</td>
</tr>
<tr>
<td>Lbs/gal (kg/M or g/L) (°20° C)</td>
<td>9.2(1102)</td>
<td>9.4(1126)</td>
<td>10.0(1198)</td>
<td>10.8(1294)</td>
</tr>
<tr>
<td>Boiling point, ° C (° F)</td>
<td>105(222)</td>
<td>108(226)</td>
<td>114(237)</td>
<td>126(259)</td>
</tr>
<tr>
<td>Freezing point, ° C (° F)</td>
<td>-23(-9)</td>
<td>-33(-27)</td>
<td>-52(-62)</td>
<td>-80(-118)</td>
</tr>
</tbody>
</table>

These acid stabilized dilutions are most effective and economical in de-chlorination and singlet oxygen production, as well as in peroxide oxidation processes. Typically 35 and 50% concentrations are to be recommended for use. Using these concentrations also maximizes flocculation kinetics.

The "super-oxidation" process of the present invention uses the available chemical energy to oxidize, insolubilize and flocculate unwanted molecules. Some of these reactions will break down molecular size and make them innocuous, or capable of being adsorbed by activated carbon. Some organic molecules will be totally oxidized (mineralized) to carbon dioxide (CO₂) and others will be cross-linked to make them larger and insoluble, allowing them to be filtered out. Some will be turned into other reactive species to assist in other types of reactions.

Reactions with Microbes

Additionally, chemicals such as Sodium Hypochlorite (NaOCl), Hydrogen Peroxide (H₂O₂), Ozone (O₃), Hydroxyl Radical (OH) and Singlet Oxygen (O₁) can be used to sanitize and disinfect water by destroying bacteria and viruses.

Both NaOCl and H₂O₂ are potent antiseptics individually, but the combination has been shown to be synergistic due to the generation of singlet oxygen (O₁); this reactive oxygen species is a powerful oxidant that rapidly kills bacterial cells by penetrating through and beyond the cell wall.

That is to say, by reacting with the sodium hypochlorite added to the hydrogen peroxide forms Singlet Oxygen which is a much more powerful oxidizer than the hypochlorite bleach added (NaClO) or the hydrogen peroxide added (H₂O₂), or even ozone (O₃). The reaction byproducts formed by the rapid reaction are singlet oxygen (O₁), more water (H₂O₁), and salt (NaCl). The activated oxygen then reacts with unwanted chemicals in the waste water. This oxidizes metal ions, such as iron (Fe₂⁺), and
causes them to precipitate which will allow them to be filtered out. Singlet oxygen also
reacts with organic chemicals, such as surfactants, solvents, dyes, fats, proteins, etc., and
breaks them down to more filterable or trappable compounds that can be eliminated by
later filtration processes; or may even oxidize them completely to form carbon dioxide
\((\text{CO}_2)\), which in an alkaline fluid \((\text{pH}>7)\) like laundry water will form bicarbonate ions
\((\text{HCO}_3^-)\). The combined process causes this mix of chemicals to flocculate, forming
small suspended clumps of materials that can also be filtered out. Any activated singlet
oxygen \((\text{O}_2)\) not used at this point converts into normal atmospheric oxygen, otherwise
known as ground state triplet oxygen \((^3\text{O}_2)\) that we all breathe.

Simultaneously and synergistically, air is "sparged" into the tank - a process by
which large volumes of air bubbles are being forced into the water containing the
oxidation products. This results in a lot of agitation and mixing of the process water, and
since the process water contains surfactants (surface active agents added as detergents in
the washing process) large volumes of foam are produced. This surfactant foam
stabilizes the bubbles so that they do not burst when they rise to the surface.
Additionally, all of the floe particles that are formed, plus any suspended fats, oils and
grease (F.O.G.) that survive at this point, plus any microfibers that may still exist, all rise
to the surface with the foam and flow downstream to the end of \(T_1\), where this mix of
materials may be vacuum extracted.

Vacuum extraction can take place in an "open" tank allowing free flow of air. A
pipe connected to a vacuum source can be placed into the body of the collected foam as a
simple nozzle or a broader shaped orifice, or a multiplicity of nozzle openings to
efficiently capture the foam. Once captured the foam will be drawn into a tank under low
pressure. This, with or without mechanical assistance by a moving structure in the
enclosed tank, will cause the foam to expand as the gas within the bubble walls try to fill
the vacuum, and the bubble walls will break, leaving a small portion of liquid (the
remnants of the bubble wall formed of water and surfactant/soap) and the entrapped
F.O.G., flocculates, micro-fibers and other suspended debris. This can be discarded when
the tank is emptied. This process will remove very little water.

Vacuum extraction can also take place in a closed tank not allowing free flow of
air. A pipe connected to a fitting near the surface of the water will drop the pressure
within the tank as compared to the atmosphere outside the tank if the air flow is rapid
enough. This reduced pressure will allow the head of foam in the tank to expand and find
the pipe opening; additionally, with enough air flow, it has been demonstrated that
expanding foam can be forced to overflow even a partially closed tank into a waiting receptacle. However, having the foam enter into the vacuum canister is still a preferred method for ultimate disposal, since the foam can be collapsed more easily and completely in the larger pressure differential of the canister, especially with added mechanical striking and or vibration.

Vacuum extraction can take place in one or more tanks, and the tanks may be constructed with baffles, vanes, weirs and the like to optimize fluid and or foam flow. The vacuum source may be centralized or individualized for each treatment tank to optimize extraction rates and/or prevent chemical cross-talk complications.

In the vacuum, the foam collapses into a small amount of liquid containing all of the unwanted F.O.G., floe and fibers carried by the foam. This extraction can then be discarded. See Appendix A which provides further details of the sparging system and the below described chemical processing in accordance with the present invention.

The chemical processing continues in the next tank (T₂) with the addition of more H₂O₂ to continue oxidation of the more slowly oxidized organic molecules, along with additional sparging and foam extraction. More unwanted chemicals are removed or destroyed.

The oxidation processes in T₁ and T₂ with singlet oxygen and hydrogen peroxide (along with the addition of NaClO in To) also kill a variety of micro-organisms, e.g., bacteria, viruses, cysts, etc, thus sanitizing the process water as well. Additionally, the dissolved oxygen level (DO) of the water is kept high and hydrogen sulfide (¾S) present is changed to harmless sulfate ions (SO₄²⁻), and color in the process water is bleached.

Furthermore, the Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) of the effluent water is greatly reduced, thereby lowering the impact on local water treatment plants and local waterways.

The next process step begins in tank (T₃) with the addition of citric acid which reduces the pH of the processed water in the following manner:

\[
\text{HO-COOH}_3 + 3 \text{NaOH} \rightarrow \text{Na}^+ \text{O-COOH}_3 \text{O}\text{Na}^+ + 3 \text{H}_2\text{O}
\]

The resulting sodium citrate molecule acts as a sequestering agent and complexes multivalent ions present in solution (Ca²⁺; Mg²⁺; etc.), thus "softening the water", preventing formation of "soap scum", and allowing more efficient detergency during the
upcoming laundry cycle using this recycled water. Citric acid is already used as a
"laundry sour" in the final rinse water cycle in the washers. Finally, citric acid reduces any remaining hydrogen peroxide to water and oxygen. The final exit stream from the citric acid reduction process is passed to a multi-stage water polishing filtration process, as will be described below.

Because of the proprietary processes used the filter media used in the water polishing process will last longer, it needs to be back flushed less often (saving more water) and needs replacing less often, thus saving money.

The next Phase of the system from for laundry water recycling uses both physical and chemical filtration to deliver high quality recycled water for laundry applications. A typical Customized Modular Filter Array sequence comprises the following:

1. **Glass Bead (GB) filter**: particles down to 20-30μ

2. **Diatomaceous Earth (DE) filter**: particles down to 5μ / removal of cysts

3. **Organo-CSay (OC) filter**: large oil and organic molecule filter

4. **Activated Carbon (AC) filter**: small organic molecule filter / removal of gases, odors, colors

5. **Activated Zeolite (AZ) filter**: particles down to 2μ / removal of multivalent ions, e.g., Ca, Mg, Fe, etc.

Referring to Fig. 5, the first module (Fig. 6) in the array begins the physical filtration sequence and contains a relatively coarse media capable of filtering particles down to a range between 20μ to 50μ in diameter depending upon requirements. Typical filter media is sand, glass beads, crushed-recycled glass, or it could be a mixed bed media filter, for an example: anthracite/gravel/garnet.

<table>
<thead>
<tr>
<th>Material</th>
<th>Size Range (mm)</th>
<th>Uniformity Coefficient</th>
<th>Specific Gravity</th>
<th>Hardness (MOH scale)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracite Coal</td>
<td>0.8 - 1.2</td>
<td>&gt; 1.85</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>Silica Sand</td>
<td>0.3 - 0.6</td>
<td>&gt; 1.5</td>
<td>3.0</td>
<td>7.0</td>
</tr>
<tr>
<td>Garnet Sand</td>
<td>0.2 - 0.4</td>
<td>&gt; 1.5</td>
<td>7.5 - 8.0</td>
<td></td>
</tr>
<tr>
<td>Silica Gravel</td>
<td>1.0 - 50</td>
<td>N/A</td>
<td>3.0</td>
<td>7.0</td>
</tr>
<tr>
<td>GAC</td>
<td>0.8 - 1.2</td>
<td>&lt; 2.0</td>
<td>1.5 - 3.0</td>
<td>N/A</td>
</tr>
</tbody>
</table>

If "iron bacteria" was a severe issue, a gravel pre-filter optionally could be used to prevent fouling the sand or glass bead filter of choice.

These filter types (as all of the recommended filters in this phase of the process, should be back-washed periodically to maintain filter efficiency and keep back pressure from climbing too high. See Fig. 7.
Next in line is a physical filter Fig. 8 capable of filtering particles down to 2µ - 10µ in diameter, such as a standard diatomaceous earth (DE) filter. Although this type filter requires back-loading with filter media after back-flush ing. Figs. 9 and 10, the advantage with this media is that contaminants are discarded with each cycle, so materials that might extrude through a media at higher pressures, e.g., greases, partially dissolved starches, etc, and reach the next filter and fouling them, are more likely to be eliminated. Zeolite filters are capable of filtering to this particle level, but are subject to fouling with oil and grease and generally should not be used in this position. This stage begins the chemical/physical section of the filter array.

This type of filter media can still capture particles, but the main advantage of this media is its ability to remove oil and other organic chemicals from water. Organoclay is an organically modified phyllosilicate, derived from a naturally occurring clay mineral. By exchanging the original interlayer cations for organocations (typically quaternary alkylammonium ions) an organophilic surface is generated. The result is a neutral surfactant with a solid base, which is the organoclay:

\[
\begin{align*}
\text{CH}_3 \\
\text{C}^{\text{4+}}(\text{C}^{\text{4-}})_9 - \text{N}^+ - \text{CH}_2 - \text{CH}_2 - \text{NH}_2 \\
\text{CH}_3
\end{align*}
\]

\[
\text{Montmorillonite}
\]

Positively charged quaternary ammonium ion for treating clay surface.

This chemically altered volcanic ash consists primarily of the clay mineral, such as Montmorillonite. This clay in its natural state can absorb up to seven times its weight in water, after treatment it can absorb only 5 to 10 per cent of its weight in water, but 40 to 70 per cent in oil, grease, and other sparingly-soluble, hydrophobic and chlorinated hydrocarbons.

The amine attracts and binds the oil droplet thus removing that droplet from water. Because the partition reaction takes place "outside" of the clay particle (in contrast to adsorption of oil by carbon which takes place inside its pores) the organoclay does not foul quickly and can continue to capture additional oily organic materials.

Thus, organophilic clay (OC) functions as a pre-polisher to activated carbon, ion exchange resins, and filter membranes (to prevent fouling), and as a post polisher to oil/water separators, dissolved air flotation (DAF) units, and skimmers. They are
excellent adsorbers for the removal of oil, surfactants, and solvents, including methyl
ethyl ketone (MEK), t-butyl alcohol (TBA), etc. See Figs. 9, 10 and 11A-1 1C.

Accordingly, by removing oil and grease at an extremely high volume/weight ratio, organophilic clays can save an end user 50% or more of operating costs. Once it is saturated, the organo-clay media may be disposed in a landfill. Pre-polishing with OC can greatly extend the filtration efficiency and lifetime of granular activated carbon (GAC) before discarding & replacing or regeneration & replacing that media.

OC can completely remove free hydrocarbons from wastewater and also remove dissolved hydrocarbons including benzene, toluene, ethylbenzene, and xylene (BTEX). When used in conjunction with a polishing stage of granular activated carbon, organoclay removes dissolved and free hydrocarbons to levels well below current water quality standards.

As well known, granular activated carbon has an enormous surface area due to the large number of pores of various dimensions throughout the particle. Typical surface area = 689 meters$^2$/gm.

Different size pores trap different size chemicals

* Macropores have a radius greater than 25nm
♦ Mesopores have a radius 1 - 25nm
4 Micropores have a radius less than 1nm

*Sub-Micropores have a radius less than 0.4mn

Physically, activated carbon binds materials by adsorption.

Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface.

Activated carbon also can be used as a substrate for the application of various chemicals to improve the adsorptive capacity for some inorganic (and problematic organic) compounds such as hydrogen sulfide (H$_2$S), ammonia (NH$_3$), formaldehyde (HCOH), radioisotopes iodine-131$^{(131)}$ and mercury (Hg). This property is known as chemisorption, which is a kind of adsorption that involves a chemical reaction between the surface and the adsorbate. New chemical bonds are generated at the adsorbant surface. In contrast to chemisorptions, physisorption leaves the chemical species of the adsorbate and surface intact. See Figs. 12 which shows molecules adsorbing onto solid surfaces, and illustrating how molecules may deposit more than one molecule thick.
Tannins are a mixture of large and medium size colored molecules. Carbons with a combination of macropores and mesopores adsorb tannins. The ability of a carbon to adsorb tannins is reported in parts per million concentration (range 200 ppm-362 ppm).

Some carbons have a mesopore (20 Å to 50 Å, or 2 to 5 nm) structure which adsorbs medium size molecules, such as the dye methylene blue. Methylene blue adsorption is reported in g/lOOg (range 11-28 g/lOOg).

Activated carbon does not bind well to certain chemicals, including alcohols, glycols, strong acids and bases, metals and most inorganics, such as lithium, sodium, iron, lead, arsenic, fluorine, and boric acid. Activated carbon does adsorb iodine very well however.

Activated carbon properties are determined by its porosity, the specific surface area, texture characteristics, and surface functional groups. Acid-base, oxidation-reduction and specific adsorption are strongly dependent on the composition of these surface functional groups.

The surface of conventional activated carbon is reactive, capable of oxidation by atmospheric oxygen and ozone. Oxidation in the liquid phase is carried by wide range of reagents (HN0₃, H₂O₂, KMnO₄) and thus is capable of removing these compounds from water.

Through the formation of a large number of basic and acidic groups on the surface of oxidized carbon, sorption and other properties can differ significantly from the un-oxidized surface.

GAC is used in water treatment to adsorb the following soluble substances:

- Organic, non-polar substances such as:
  - Mineral oil
  - BTEX
  - Poly aromatic hydrocarbons (PAHCs)
  - Chlorinated hydrocarbons
  - Phenol

- Halogenated substances: I, Br, Cl
- Odor
- Taste
- Yeasts
- Various fermentation products
Surfactants i.e., Substances which are dispersible in water but have a long hydrocarbon tail

\[ \text{X} \text{X} \text{X} \text{X} \text{X} \text{OSO}_3^\text{N}^\text{+} \]

SDS - Sodium dodecyl sulfonate - anionic Surfactant

Factors that influence the performance of active carbon in water:

- The type of compound to be removed. Compounds with relatively high molecular weight and low solubility are better adsorbed. Compounds are much smaller than particles.
- The concentration of the compound to be removed. The higher the concentration, the higher the carbon consumption.
- Presence of other organic compounds which will compete for the available adsorption sites.
- The pH of the waste stream. For example, acidic compounds are better removed at lower pH.
- A higher number of functional groups such as double bonds or halogen compounds.
- Increasing polarisability of the molecule. This is related to the electron clouds within the molecule.

All compounds can be adsorbed to some extent. In practice, activated carbon is used for the adsorption of mainly organic compounds along with some larger molecular weight inorganic compounds such as iodine and mercury. See Chart Below for relative organic adsorbability.

Liquid Phase Adsorption - The molecules go from the bulk phase to being adsorbed in the pores in a semi-liquid state. The driving force for adsorption is the ratio of the concentration to the solubility of the compound.
Adsorption is caused by London Dispersion Forces, a type of Van der Waals Force which exists between molecules. These forces are extremely short ranged and therefore sensitive to the distance between the carbon surface and the adsorbate molecule. The forces are additive; the adsorption force is the sum of all interactions between all the atoms. This results in activated carbon having the strongest physical adsorption forces of any material known to mankind. See Fig. 13, which depicts the adsorption of an organic molecule to a carbon surface due to molecular attraction forces.

Reactivation

Once granular carbon is saturated or the treatment objective is reached, it can be recycled, by thermal reactivation, for reuse. Reactivation involves treating the spent carbon in a high temperature reactivation furnace to over 800°C. During this treatment process, the undesirable organics on the carbon are thermally destroyed.

Recycled carbon may be slightly less activated than the original media.

Reactivating activated carbon by thermal reactivation meets the environmental need to minimize waste, reducing C02 emissions and limiting the use of the world’s resources.

Activated carbon (activated charcoal) can have a surface of greater than 1000m²/g. This means 3g of activated carbon can have the surface area of a football field.

Backwashing GAC periodically during filtration is needed to prevent plugging of surface pores.

**FIFTH Filter (activated natural zeolite)**

Synthetic and natural zeolites are hydrated aluminosilicates with symmetrically stacked alumina and silica tetrahedra which result in an open and stable three-dimensional honeycomb structure with a negative charge. The negative charge within the pores is neutralized by positively charged ions (cations) such as sodium.

The simplest synthetic zeolite is the zeolite A with a molecular ration of one silica to one alumina to one sodium cation. The zeolite-A synthesis produces precisely duplicated sodalite units which have 47% open space, ion exchangeable sodium, water of hydration and electronically charged pores. These properties lead to the various uses of natural and synthetic zeolites.

High purity zeolite media is now available that achieves a ≤5µ nominal rating for particle radius filtering.

Zeolites are widely used in industry for water purification, and have a basic chemical unit structure as follows:
Zeolites are microporous aluminosilicate minerals with complicated chemical formulae: (Clinoptilolite: (Na,K,Ca)$_2$Al$_3$(Al,Si)$_2$Si$_3$O$_12$H$_2$O) and orderly geometric structure:

**CLINOPTILOLITE FRAMEWORK MODEL**

Generally speaking, natural zeolites are hydrated aluminosilicates. They consist of an open, three-dimensional cage-like structure and a vast network of open channels extending throughout. Loosely bound, positively charged atoms called cations, are attached at the junctures of the negatively charged aluminosilicate lattice structure. The aluminosilicate framework provides exceptional strength and stability to the lattice structure.

The channels, typically 0.3 to 0.7 nanometers in diameter (3 to 7 angstroms, slightly larger than a water molecule), selectively screen molecules according to size and exchangeable cations. Molecules too large to pass through the entry channel are excluded, thus giving rise to the term "molecular sieve".

The molecular structure, surface area, surface charge density, and cation exchange capacity (CEC) of each particular zeolite will determine its loading, shrinking, swelling and stability under various conditions.

Zeolites have a rigid, three-dimensional crystalline structure (similar to honeycomb) consisting of a network of interconnected tunnels and cages. Zeolites in
general have high specific surface areas and their rigid framework limits shrinking and swelling.

Water moves freely in and out of these pores but the zeolite framework remains rigid. The pore and channel sizes are nearly uniform, allowing the crystal to act as a molecular sieve. The porous zeolite is host to water molecules and ions of potassium and calcium, as well as a variety of other positively charged ions, but only those of appropriate molecular size to fit into the pores are admitted creating the "sieving" property. See Table 2.

<table>
<thead>
<tr>
<th>Table 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pore size of Zeolite channel (4.2) vs. water (2.6) and small organic molecules in Angstroms</strong> (1Å = 0.1nm)</td>
</tr>
<tr>
<td><strong>Cation Exchange</strong></td>
</tr>
</tbody>
</table>
| Perhaps the most commercially valuable and dynamic property of zeolite is its cation exchange capacity (CEC). Cation exchange occurs when two or more positively charged compounds or elements exchange places on a negatively charged host. Exchange sites on natural zeolites are primarily occupied by 3 major cations: potassium (K), calcium (Ca), and sodium (Na) (other elements such as magnesium (Mg) may also be present).

The ability to release beneficial elements while capturing and binding other, often less desirable, materials makes zeolite an idea! media for the selective adsorption of certain elements and compounds from soil, water and air.
A classic example of cation exchange is the removal of ammonia from water and air. When a molecule of ammonia (NH$_3$) is hydrated, the reaction produces ammonium (NH$_4^+$), which is readily exchanged for all or part of the calcium, potassium and magnesium cations contained in Zeolite and adsorbed on to its stable aluminosilicate lattice:

\[
\begin{align*}
\text{Ca}^{2+} & \text{ } \text{Na}^{+} \\
\text{Na}^{+} & \text{ } \text{Ca}^{2+}
\end{align*}
\]

Illustration depicting typical water softening behavior - adsorbing Ca$^{2+}$ and releasing Na$^+$ ions

This reaction is reversible with NaCl, allowing the zeolite to be replenished with Na$^+$ ions

The illustration above depicts a negatively-charged zeolite to which (positive) sodium ions (Na$^+$) are attached. Calcium or magnesium ions in the water displace sodium ions, which are released into the water. In a similar way, positively-charged zeolites bind negatively-charged chloride ions (CP), which get displaced by bicarbonate ions in the water. As the zeolites become converted to their Ca$^{2+}$ and HCO$_3^-$ forms they gradually lose their effectiveness and must be regenerated. This is accomplished by passing a concentrated brine solution though them, causing the above reaction to be reversed.

Various cations are exchanged at media surfaces to different degrees. The order of preference or selectivity for a specific cation to be exchanged is a complex function of charge and strength of solvation. In dilute solutions, the general rule is that ions with the highest charge and the lowest strength of solvation are preferentially exchanged. A partial list of relative affinities for ions exchanged at cation exchange sites is contained in the Table 3 below.
Cation Exchange Relative Affinity Table

Although sodium zeolite treated water is nearly free of all hardness, some hardness leakage normally does occur. The amount of leakage depends primarily on the raw water hardness, sodium concentration and softener regeneration level.

The bed is regenerated by reversing the softening reactions. Exhausted sodium zeolite resin is regenerated by exposure to a concentrated brine solution - sodium chloride. Concentrated brine used for sodium zeolite regeneration is 26% by weight sodium chloride.

Particulate contaminants such as iron or aluminum in raw water supply can foul the zeolite media surfaces and be detrimental to the exchange process. Aluminum may be present in the raw water supply, but problems associated with it generally arise from the use of aluminum compounds for flocculation. Whenever iron or other metallic contaminants are present, the softener must be backwashed thoroughly and a suitable bed cleaner applied during regeneration.

Sources of Water Hardness
Thus the final zeolite filter module should deliver clear (non-turbid) softened water.

The resulting water from the aforesaid process streams will be:

- Very low in suspended solids (TSS)/turbidity
- Very low in dissolved organic solids
- Low in COD/BOD
- Low in F.O.G.
- Low in water hardness
- Low in Fe/Mn/CoANi
- Low in surfactant
- Moderate pH (7.5-8.5)
- Free from Cl₂/OCl⁻
- Free from H₂S/NH₃
- Free from NO₂⁻/SO₃²⁻
- Free from color/odor
- Free from E. Coli
- High in Dissolved Oxygen (DO)

However, as time goes on, the water may build up in:

- Na⁺/K⁺
- Cl⁻/SO₄²⁻/HCO₃⁻
- Salinity
- Conductivity
- Total Dissolved Solids (TDS)

Complexes with citric acid may help stabilize bio-active silver ions

A benefit of copper-silver ionization is that ions remain in the water for a long period of time. This causes long-teen disinfection and protection from re-contamination. Copper and silver ions remain in the water until they precipitate or absorb to bacteria or algae, and are removed from water by filtration after that. See Fig. 15.
IONS That Must Be Monitored in the Incoming Water Supply & the Recycled Water

Optionally, the resulting water from the aforesaid process streams may be subjected to an electro metallization process which provides silver and copper ions (and zinc ions as needed) to provide a residual sanitizing element to keep the water bacteria, virus and algae free in storage.

Referring to Fig. 14, the next step involves copper-silver ionization brought about by electrolysis. An electric current is created through a copper-silver aqueous solution, causing positively charged copper and silver ions to form. Copper-silver ionization is essentially not dependent on temperatures. It is active in the entire water system; and it is used by water bottling companies and companies that recycle water throughout the United States. Copper-silver ionization also is applied in hospitals and nursing homes. Copper-silver ionization can sufficiently kill Legionella bacteria to prevent the distribution of the Legionella bacteria.

Electrically charged copper ions (Cu\(^{2+}\)) in the water "search" for particles of opposite polarity, such as bacteria, viruses and fungi. Positively charged copper ions form electrostatic compounds with negatively charged cell walls of microorganisms. These compounds disturb cell wall permeability and cause nutrient uptake to fail. Copper ions penetrate the cell wall and as a result they will create an entrance for silver ions (Ag\(^{+}\)). These silver ions penetrate the core of the microorganism. Silver ions then bond to various parts of the cell, such as the DNA and RNA, cellular proteins and respiratory enzymes, causing all life support systems in the cell to be immobilized. That is to say, silver ions break through the cell wall attaching and the DNA of the microbe to stop cell replication, and disruption of the microbe.
As a result, there is no more cellular growth or cell division, causing bacteria to no longer multiply and eventually die out. The ions remain active until they are absorbed by a microorganism.

Copper-silver affectivity depends on the pH value of the water. Copper ions mainly exist when the pH value = 9 as Cu(CO₃)²⁻. Chlorine ions (Cl⁻) cause silver-chlorine complex formation. When this occurs, silver ions are no longer available for disinfection.

At a pH value of 9, only one tenth of all Legionella bacteria are removed, so storage water should be held at 7.5-8.5. When dissolved solid concentrations are high, silver will precipitate. This means silver ions are no longer available for disinfection. Therefore, TDS must be held down (primarily Chloride, Sulfate, Phosphate and Carbonate).

OZONE Treatment

The next step in the process involves an optional ozone treatment of the process water after the filtration and electrometallization process. Ozone is an unstable molecule which readily gives up one atom of oxygen providing a powerful oxidizing agent which is toxic to most waterborne organisms. It is a very strong, broad spectrum disinfectant that is widely used, it is an effective method to inactivate harmful protozoa that form cysts. It also works well against almost all other pathogens. Ozone is made by passing oxygen through ultraviolet light or a "cold" electrical discharge. To use ozone as a disinfectant, it must be created on-site and added to the water by bubble contact. Some of the advantages of ozone include the production of fewer dangerous by-products and the absence of taste and odor problems (in comparison to chlorination).

\[ \text{O}_3 + \text{H}_2 \text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^- \]

Ozone forms Hydrogen Bonds with Water Increasing Solubility

Ozone is made by passing oxygen through ultraviolet light or a "cold" electrical discharge. To use ozone as a disinfectant, it must be created on-site and added to the water by bubble contact. Some of the advantages of ozone include the production of fewer dangerous by-products and the absence of taste and odor problems (in comparison to chlorination).
Ozone may be created from Oxygen from UV light or Electric Corona Discharge. See Fig. 16, and is injected into the wash water (see Fig. 17).

Ozone water treatment systems used in laundry applications can increase the life of linens and reduce water use, natural gas consumption, and chemical and detergent costs. Ozone is active in cold water (limiting hot water use since ozone is very limited in water solubility >40°C), is used in place of detergents, and is consumed in the washing process, leaving no residuals in the wastewater.

**Schematic of Ozone Direct Injection into Laundry Washing Machine**

Ozone Oxidizes and Destroys Contaminants

The decomposition of ozone gas produces mono-atomic & diatomic oxygen: \[ 2O_3 \rightarrow 2O_2 + 2O \] . See Fig. 18.

**Ozone Oxidation Cycle**

However ozone gas has limited solubility in hot water (>40°C) so is normally injected into cold water washing operations, thus saving heating costs as well. However, the efficacy of ozone can depend upon whether ozone is injected directly into the each washer or injected into the incoming water supply for a bank of washers. See also Fig. 19 and Table 4, which shows the half-life of ozone in water at different temperatures.

**Ozone (O₃) Dissolved in water (pH 7)**

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Half life</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>30 min</td>
</tr>
<tr>
<td>20</td>
<td>20 min</td>
</tr>
<tr>
<td>25</td>
<td>15 min</td>
</tr>
<tr>
<td>30</td>
<td>12 min</td>
</tr>
<tr>
<td>35</td>
<td>8 min</td>
</tr>
</tbody>
</table>

**Table 4: half-life of ozone in water at different temperatures**

Referring to Fig. 20, which chart shows that as the temperature increases, less ozone is needed to achieve the same kill effect vs. lower temperatures. The reason is that elevated temperatures reduce pathogen’s ability to resist oxidants. Elevated temperatures with ozone use have a compounding killing effect.

Ozone decomposes partly into -OH radicals. When the pH value increases, formation of -OH radicals also increases, in solutions with a high pH value, there are more hydroxide ions (OH⁻) present, see formulas below. These hydroxide ions act as an initiator for the decay of ozone:

\[ O_3 + OH^- \rightarrow HO_2^- + O_3 \]
\[ 2 \text{O}_3 + \text{HOr} \rightarrow \cdot \text{OH} + \text{O}_2 + \text{O}_3 \]

The radicals that are produced during reaction 2 can introduce other reactions with ozone, causing more \( \cdot \text{OH} \) radicals to be formed.

See also Fig. 21 which charts the effect of pH on the decay of ozone (T-15°C).

**Ozone Solubility**

- The solubility of ozone in water depends on the water temperature and the ozone concentration in the gas phase. Values in Table 5, below, are dissolved \( \text{O}_3 \) -

Units in g/m³.

<table>
<thead>
<tr>
<th>O₃ GAS</th>
<th>0°C</th>
<th>5°C</th>
<th>10°C</th>
<th>15°C</th>
<th>20°C</th>
<th>25°C</th>
<th>30°C</th>
<th>35°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 g/m³</td>
<td>16</td>
<td>12.5</td>
<td>9.75</td>
<td>7.75</td>
<td>6.0</td>
<td>4.75</td>
<td>3.75</td>
<td>3.0</td>
</tr>
<tr>
<td>50 g/m³</td>
<td>32</td>
<td>25</td>
<td>19.5</td>
<td>15.5</td>
<td>12.0</td>
<td>9.5</td>
<td>7.5</td>
<td>6.0</td>
</tr>
<tr>
<td>75 g/m³</td>
<td>48</td>
<td>37.5</td>
<td>29.25</td>
<td>23.25</td>
<td>18.0</td>
<td>14.25</td>
<td>11.25</td>
<td>9.0</td>
</tr>
<tr>
<td>100 g/m³</td>
<td>64.0</td>
<td>50.0</td>
<td>39.0</td>
<td>31.0</td>
<td>24.0</td>
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**TABLE 5**

- Note: \( *14.25\) g/m³ = 1% ozone; \( 50\) g/m³ = 3.5% ozone; \( 100\) g/m³ = 7.0% ozone
- Ozone gas (\( \text{O}_3 \)) is 13 times more soluble in water than \( \text{O}_2 \) gas.
- Even at higher temperatures and lower concentrations, Ozone is very efficient at killing bacteria, since their resistance to oxidation becomes much lower.
Ozone (O₃), as an oxidizer, which can be dissolved in water, is a broad spectrum disinfectant that is 3,000 times faster in eliminating bacteria, viruses and other pests than chlorine.

Ozone's bactericidal action destroys drug resistant genes. See Fig. 22.

However ozone does not have the residual effectiveness of chlorine in water so long term water stability requires other means; but Ozone will break down to form breathable Oxygen (O₂).

Chemicals like Sodium Hypochlorite (NaOCl), Hydrogen Peroxide (H₂O₂); Ozone (O₃), Hydroxyl Radicals (·OH) and Singlet Oxygen (O₂) can all be used to sanitize and disinfect water by destroying bacteria and viruses.

Both NaOCl and H₂O₂ are potent antiseptics individually, but the combination has been shown to be synergistic due to the generation of singlet oxygen (¹O₂); this reactive oxygen species is a powerful oxidant that rapidly kills bacterial cells by penetrating through and beyond the cell wall.

Ozone (O₃) reacts directly with these micro-organisms by attacking cell walls and indirectly through hydroxyl radicals. Ozone can also react with UV light and/or hydrogen peroxide in what is called an Advanced Oxidation Process (AOP) to produce hydroxyl radicals. Hydrogen peroxide (H₂O₂) and/or UV light can also generate hydroxyl radicals (·OH).

Although Advanced Oxidation Processes using ozone do introduce hydroxyl radicals, these O·H radicals would likely be scavenged in the cell wall, and their journey to the DNA would be hampered by other cell constituents. The traveling distance of ·OH radicals in a cell can be to be only 6-9 nm. The diffusion distance in a cell for singlet oxygen ¹O₂ is about 200-270 nm — or about 30 times more; and it has a much longer half-life (microseconds vs. nanoseconds), allowing ¹O₂ to be a more efficient disinfectant in many instances, by allowing attack on the cell wall and on critical internal portions of the cell. So, singlet oxygen is a potent disinfectant, known to disable a wide range of bacteria and viruses, and most non-enveloped viruses are shown to be inactivated by singlet oxygen.

While a preferred embodiment of the invention has been described, various changes may be made without departing from the spirit and scope thereof. Also, one or more of the process stages may be eliminated and/or used as a stand-alone process including the grease and lint extraction station, the sparged air foam extraction station, the singlet oxygen activation process station, the citric acid reduction process station, and
the electrochemical process station, depending on the particular waste water being treated, and the end use of the treated water. Also, while the invention has been described in particular for use in connection with treatment of laundry effluent water, the invention advantageously may be used for treating other waste waters including industrial waste waters including factory waste waters, manufacturing process waste waters, transportation waste waters including waste waters from filling stations, vehicle wash installations, air fields, trains and the like. By way of example, the sparged air foam extraction system may operate efficiently with only the chemicals present in the laundry effluent. However, varying loads and types of soil, grease, proteins, and other contamination may vary during the day or during other time intervals, and it may be necessary to add additional chemicals to the tanks. Moreover, it is also necessary to monitor the chemical constituency of the incoming water supply, which may also vary, so it is expected that a monitoring system to test certain key factors in the process. So necessary probes will be inserted at key junctures to measure parameters such as pH, Temperature, Oxidation Reduction Potential (ORP), Conductivity, Turbidity, and other pertinent process parameters to facilitate process control. These may be automated and tied into a control structure with the appropriate software, user interface and remote diagnostic and control features.

Additionally, on site and off site periodic testing of other more difficult to measure parameters (e.g. BOD, COD, TDS, O&G, etc.) may be made a part of the process.

Optionally, in a preferred embodiment, the sparged air foam extraction process may use the singlet oxygen activation process system to improve the flocculation and digestion of F.O.G. and other organic contaminants. This will be done by ensuring an adequate amount of NaClO arrives from the washer effluent and/or is added into the T0 tank to generate sufficient singlet oxygen (O2), a much higher oxidation potential chemical than triplet oxygen (3O2 - normal atmospheric oxygen), or Sodium Hypochlorite (NaClO) or even Hydrogen Peroxide (H2O2 - the preferred oxidizer in the standard sparged air foam extraction process). This process will take place "simultaneously and synergistically" when the NaClO encounters the H2O2 and forms the O2 and H2O in the chemical treatment tanks. The peroxide, which is also acidic (pH<3 as supplied) will be added in slight excess to totally decompose the hypochlorite into salt (NaCl) and to make the singlet oxygen reactions take place, behind a baffle at the front of each tank to insure maximum concentration and effect of the peroxide/singlet
oxygen reactions which are extremely rapid, and to allow the unreacted peroxide to carry out the slower oxidation reactions that can take place in the turbulent flow areas of the tank. Any peroxide that survives direct chemical reaction will decompose to \( \frac{3}{4} \) and H2O.

The final process step is the citric acid reduction process reaction in the final tank. This process reduces the pH to 7.5-8.5 in preparation for entry into the customized modular filter array where a variety of physical and chemical filtration processes are carried out to provide the final purification steps that will allow the final process water to be fit for use as incoming laundry water. Additionally, should any peroxide happen to survive into the final tank the citric acid will reduce the peroxide to water. The citric acid and any by-products of that reaction also will act as pH buffers and stabilize the water pH. The citric acid also acts as a chelating agent capturing and "caging" hard water multivalent cations such as Ca\(^{++}\) and Mg\(^{++}\) and prevents them from forming soap scum, and calcium scale that can contaminate the filter array, the washing machines and cause soil deposits on the clothes and/or diminish the detergency activity in the wash cycles.

Other similar chemicals such as sodium citrate, an alkali metal salt (Li, Na, K) of citric acid, or a combination thereof, can also be used instead of or in addition to citric acid. Also useful are acids such as gluconic acid, malic acid and tartaric acid which are given as exemplary

Further details of the invention are set forth in the attached Appendix A which forms a part of this application.
Claims:

1. A method for treating wastewater containing contaminant materials including one or more of solids, fats, oils and grease which comprises simultaneously subjecting water to be treated to sparging air in the presence of singlet oxygen and/or hydrogen peroxide.

2. The method of claim 1, wherein the singlet oxygen is formed by reaction of hydrogen peroxide and sodium hypochlorite in alkaline conditions.

3. The method of claim 1 or claim 2, including the step of passing the water, after the water is subjected to air sparging and singlet oxygen, to a multi-stage filtration system.

4. The method of claim 3, wherein the multi-stage filtration system comprises one or more filter media selected from the group consisting of sand, glass, beads, diatomaceous earth, organo-clay, activated carbon and activated zeolite.

5. The method of any of claims 1-4, further including the step of adjusting the pH of the filtered water.

6. The method of claim 5, wherein the pH of the filtered water is adjusted by addition of sodium citrate, citric acid, an alkali metal salt (Li, Na, K) of citric acid, gluconic acid malic acid or tartaric acid, or a combination thereof.

7. The method of any of claims 1-6, further including the step of subjecting the filtered water to electrically charged silver and/or copper ions.

8. The method of any of claims 1-7, further including the step of subjecting the filtered water to ozone.

9. The method of any of claims 1-8, further including the step of subjecting the filtered water to citric acid reduction.

10. The method of any of claims 1-9, wherein the contaminant materials are selected from the group consisting of suspended solids such as silica and tannins, dissolved solids such as metallic ions that need to be oxidized and precipitated/flocculated: such as Fe+2 → Fe+3 (Fe(OH)₃), cations that need to be insolubilized/flocculated: such as Ca+2 → Ca(OH)₂, metallic complexes with organic anions need to be destabilized/flocculated, iron bacteria' need to be oxidized/destabilized/flocculated oxidized/destabilized/flocculated, complex anions such as arsenate and chromate, gases such as hydrogen sulfide or related anions such as HS⁻ and SO₃²⁻, or anions such as NO₂⁻, bacteria, viruses, fungi, and other micro-biota.
A method for treating wastewater containing debris and contaminants, and grease which comprises subjecting water to be treated to sparging air whereby to form a foam entrapping the debris and contaminants, and removing the foam, at least in part.

The method of claim 11, wherein the foam is removed at least in part using a vacuum.

The method of claim 11 or claim 12, wherein the debris and contaminants contaminant materials including one or more of solids, fats, oils and grease.

The method of any of claims 11-13, wherein the contaminant materials are selected from the group consisting of suspended solids such as silica and tannins, dissolved solids such as metallic ions that need to be oxidized and precipitated/flocculated: such as Fe+2 → Fe+3 (Fe(OH))₃, cations that need to be insolubilized/flocculated: such as Ca+2 → Ca(QH)₂, metallic complexes with organic anions need to be destabilized/flocculated, iron bacteria’ need to be oxidized/destabilized/flocculated oxidized/destabilized flocculated, complex anions such as arsenate and chromate, gases such as hydrogen sulfide or related anions such as HS⁻ and SO₃⁻, or anions such as NO₂⁻, bacteria, viruses, fungi, and other micro-biota.

The method of any of claims 11-14, including the step of passing the water, after the water is subjected to air sparging and vacuum removal, to a multi-stage filtration system.

The method of claim 15, wherein the multi-stage filtration system comprises one or more filter media selected from the group consisting of sand, glass, beads, diatomaceous earth, organo-clay, activated carbon and activated zeolite.

The method of any of claims 11-16, further including the step of adjusting the pH of the filtered water.

The method of claim 17, wherein the pH of the filtered water is adjusted by addition of sodium citrate, citric acid, an alkali metal salt (Li, Na, K) of citric acid, gluconic acid, malic acid or tartaric acid, or a combination thereof.

The method of any of claims 11-18, further including the step of subjecting the filtered water to electrically charged silver and/or copper ions.

The method of any of claims 11-19, further including the step of subjecting the filtered water to ozone.

The method of any of claims 11-20, further including the step of subjecting the filtered water to citric acid reduction.

35
Fig. 3

Fig. 4

Fig. 5
Fig. 8

Fig. 9

Fig. 10
Oil Droplet Removal

Activated carbon granule. Pore species of activated carbon, binded by emulsified oil

Clay platelets, modified with quaternary amine, remove emulsified oil on the clay surface

Activated carbon downstream of organoclay, ready to remove the more soluble compounds

Fig. 11A  Fig. 11B  Fig. 11C

Fig. 12
At the negative electrode (-) \[ \text{Ag}^{+}_{\text{aq}} + e^- \rightarrow \text{Ag}_{\text{cl}} \]

At the positive electrode (+) \[ \text{Ag}_{\text{cl}} \rightarrow \text{Ag}^{+}_{\text{aq}} + 2e^- \]

The microscopic action of the ions with the algae, virus, bacteria and scaling
Fig. 16

Fig. 17
Ozone (O₃) causing oxidation & decomposition.

Activated Oxygen (O₃)

Electrical discharge causes an oxygen molecule (O₂) to split.

Diatomic Oxygen (O₂)

Ozone formation

Ozone (O₃) is formed

Oxygen atom (O)

Oxygen molecule (O₂)

Highly reactive oxygen atom (O)

Fig. 18

Ozone Solubility & Temperature

Ozone gas in water at different conditions:
- Low dissolved ozone at high temp (25°C)
- High dissolved ozone at low temp (5-20°C)

Fig. 19
Figure 20

CT Values for Virus Inactivation by Ozone vs. Temperature

1 mg/l = 1 ppm
CT = concentration x time

Figure 21: effect of the pH on the decay of ozone (T=15°C)
Fig. 22
**INTERNATIONAL SEARCH REPORT**

**International application No.**
PCT/US2014/045152

**A. CLASSIFICATION OF SUBJECT MATTER**

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

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC(8) - C02F 1/24 (2014.01)  
USPC - 210/704, 705, 706

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

CPC - C02F 1/24 (2014.09)

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

PatFT, AppFT, Orbit, Google Scholar

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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<td>US 4,008,136 A (WILLIAMS) 15 February 1977 (15.02.1977) entire document</td>
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Further documents are listed in the continuation of Box C.

* Special categories of cited documents:
  "A" document defining the general state of the art which is not considered to be of particular relevance
  "E" earlier application or patent but published on or after the international filing date
  "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  "O" document referring to an oral disclosure, use, exhibition or other means
  "P" document published prior to the international filing date but later than the priority date claimed

**Date of the actual completion of the international search**
22 September 2014

**Date of mailing of the international search report**
7 OCT 2014

**Authorized officer:**
Blaine R. Copenheaver

PCT Helpdesk: 571-272-4300
PCT OBP: 571-272-7774

**Form PCT/ISA/210** (second sheet) (July 2009)
This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. □ Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. □ Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ✗ Claims Nos.: 5-10, 14-21 because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

1. □ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. □ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. □ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

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

Remark on Protest

□ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

□ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

□ No protest accompanied the payment of additional search fees.