Usage of Nitrous acid and Chlorine Dioxide in Residuals Disinfection and Stabilization

Robert S. Reimers1, Lisa S. Pratt-Ward1, Dwight D. Bowman2 and Jan A. Oleszkiewicz3

1 Tulane’s School of Public Health and Tropical Medicine, New Orleans, Louisiana, USA
2 Cornell’s College of Veterinary Medicine, Ithaca, New York, USA
3 University of Manitoba’s School of Engineering, Winnipeg, Manitoba, Canada

Abstract: Tulane researchers developed the Neutralizer process, which utilized chlorine dioxide, sulfuric acid and nitrous acid to disinfect biosolids. From this work, it was noted that nitrous acid was the primary disinfecting agent to inactivate helminth eggs under an acid environment pH less than 3.3. The process was observed to be effective and would produce a Class A biosolid within 4 to 24 h depending upon the dosage of nitrous acid in the range of 1500 to 400 mg/L, respectively. The Neutralizer® Process is able to control the ORP with chlorine dioxide, which is much less expensive and more reliable than ozone in a municipal residuals environment. Thereby, the usage of acid treatment of municipal sludge viable. By utilizing chlorine dioxide and nitrous acid under acidic conditions, the Neutralizer® Process has demonstrated disinfection of biosolids by reducing the fecal coliform and viral densities to less than detectable limits, and helminth eggs to 0% viability. This process also is able to assist in the stabilization of both digested and raw wastewater residuals, as demonstrated by volatile solids reduction and respirometer testing. The acid treated biosolids may have beneficial uses, such as a fertilizer, soil amendment and sod grass production.

Keywords: Residuals Disinfection, Nitrous Acid, Chlorine Dioxide, Oxidant Stabilization

INTRODUCTION

In 2003, the Neutralizer process was developed to disinfect and stabilize municipal sludge. The process was observed to be effective and produce a Class A disinfected biosolids within 2 to 24 hours depending upon the dosage of the nitrous acid in the range of 1800 to 400 mg/L as nitrous acid respectively at a pH of 2.3 and in the presences of chlorine dioxide (Reimers et. al., 2006). In the early 1990s, the Synox process was developed, which was approved as a process to further reduce pathogens (PFRP) by USEPA’s Pathogen Equivalency Committee (PEC) (Reimers et. al., 1991 and USEPA, 2003). The problem with this process was related to the utilization of ozone to hold the oxidation-reduction potential (ORP) at greater than 50 MV. The process was very expensive and therefore, commercially not viable. The modified Neutralizer process is able to control the ORP with chlorine dioxide, which is much less expensive and requires one-tenth the dosage that ozone requires.

This paper discusses the process of disinfection by utilize the Neutralizer Process, which uses sulfuric acid, chlorine dioxide and nitrous acid. In both the lab and in pilot runs, the Neutralizer inactivates the pathogenic bacteria, enteric virus and helminth eggs in raw municipal sludge, aerobically digested sludge and anaerobically digested sludge. The system, uses nitrous acid at 1800 to 400 mg/L depending upon the retention time, holds the pH at 2.3 and adds 50 to 150 mg/L of chlorine dioxide. By reducing the oxidation agent dose by one order of magnitude or more the process become viable commercially.

The use of chlorine dioxide for odor control in the petroleum industry was developed in the 1970s. The concepts can be transferred and utilized in municipal sludge stabilization. This process uses the chlorine dioxide and nitrous acid to assist in the stabilization process. This acid process utilizes chlorine dioxide, which is a strong oxidant especially under acidic conditions. The compound can effectively oxidize many EDCs and other refractory organics. It has been effective in reacting with odorous organics such as mercaptans, sulfide compounds and tertiary amines, which are class 4 odor compounds. The odor impacting compounds are categorized from
category 1, having a low odor threshold to the category 4, having high odorous impacts. It should be noted that as long as the oxidation-reduction potential (ORP) is kept above (~) 200 mV, then there will not be the production of odor producing compounds during their degradation. This process has moved to field application with a number of plants in Florida with the initial plant in Clay County.

Disinfection Process Description 3

The Neutralizer® Process provides a method of treating liquid municipal sludge or slurries. The process uses chlorine dioxide and nitrous acid synergistically to disinfect municipal sludge at doses shown in Table 1. This system has been tested on raw sludge and on digested sludges (aerobically and anaerobically digested municipal sludge) for pathogen reduction and vector attraction reduction and stabilization (Reimers, et. al., 2006).

Table 1: Chemical Additive and their Concentrations

<table>
<thead>
<tr>
<th>Additive Composition</th>
<th>Concentration Applied</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine dioxide (ClO₂)</td>
<td>50 – 150 mg/L</td>
</tr>
<tr>
<td>Sodium nitrite (NaNO₂)</td>
<td>3000 mg/L to 800 mg/L depending upon the retention time of 2 to 12 hours, pH, and ORP</td>
</tr>
<tr>
<td>Sulfuric acid (H₂SO₄)</td>
<td>volume added varies with sludge</td>
</tr>
<tr>
<td>• Lowers pH to 2.2-3.0</td>
<td></td>
</tr>
<tr>
<td>Hydrated lime [Ca(OH)₂], caustic [NaOH] or soda ash</td>
<td>volume added varies with sludge</td>
</tr>
<tr>
<td>• Raises pH to desired level</td>
<td></td>
</tr>
</tbody>
</table>

Process steps are elucidated below:

1. Chlorine dioxide addition (50-150 mg/L). Flow meter signal to a Process Logic Controller (PLC) for chemical addition. ORP monitor signals PLC to maintain adequate ORP through chlorine dioxide addition.

2. Chlorine dioxide contact time with continuous mixing (2 hours to 12 hours). PLC monitors recirculation/mixing.

3. Acidification of sludge (to pH 2.2-3.0). pH meters signal PLC to drive chemical pumps in order to maintain specified pH. PLC monitors recirculation/mixing.

4. Nitrite addition (≥1800 mg/L to 600 mg/L as HNO₂). PLC drives chemical pump to add specified volume of nitrite. Nitrite converts to nitrous acid at specified pH and ORP. Nitrous acid contact time (2 to 12 depending hours on the respective nitrous acid concentration in a closed system).

5. Hydrated lime, caustic or other suitable alkaline agent on discharge to raise pH to ~6.0 or desired level for beneficial use.

The first operational plant is in Clay County, Florida where the municipal sludge is coming from a 3 MGD activated sludge wastewater plant. The Neutralizer process is treating thickened municipal secondary sludge. This field pilot plant is designed to produce Class A disinfected domestic wastewater residuals that has a multitude of value-added end uses options. The following sludge characteristics are being monitored:

- Total and volatile sludge solids
- Temperature
- pH
- ORP
- Alkalinity
- Total phosphorus
- Total nitrogen along with TKN
- Metal analysis as required for land application
- Viable helminth ova
- Enteric viruses
- Fecal coliforms
- Clostridium perfringens
It should be noted that this process has effectively disinfected municipal sludge in raw, aerobically digested or anaerobically digested on a bench-scale and pilot scale basis. This disinfection has inactivated helminth eggs, enteric viruses, spore-forming bacteria, *Salmonella* and fecal coliform bacteria (Reimers et. al., 2006).

**Stabilization**

The problem with the above short- and long-term stabilization processes is the concerns with the odors produced from alkaline stabilization. The odor problem created by stabilization processes is related to mercaptans or tertiary alkyl amines, which are 4 odor producing compounds, respectively (Jacobs et.al., 1991 and Striebig, 1999). The higher the class, the more offensive the odor would be. For comparison purposes, hydrogen sulfide is rated a Class 4 odor-producing compound. Odor control in alkaline biosolids processing can be accomplished by the following techniques:

1. Chemical alteration, adsorption or absorption of odor causing compounds,
2. Masking with another odor,
3. Dispersion below threshold detection limits, or
4. Raise the ORP to inhibit the growth of sulfate reducing bacteria.

This is achieved by utilizing chlorine dioxide and metallic oxides, which react with sulfide compounds and alkyl amines within minutes. Work at Tulane has noted potential reduction of odor with the usage of iron oxide additives, aluminum oxide additives and chlorine dioxide. By utilizing these inexpensive reagents, the cost of disinfection/stabilization may drop below 350 dollars per dry ton.

Over the past ten years, the development of long-term stabilization has been achieved by one of three methods:

1. Oxidation-reduction agent dosage,
2. Chemical alteration of degradable along with tertiary alkyl amines plus the inhibition of tertiary alkyl amines, which the ferrate process falls under, or
3. Trapping the odorous compounds in close alkaline treatment systems.

Chlorine dioxide controls odors in raw and digested municipal sludges at pHs around 6 to 7. This short-term stabilization has been observed in Tulane labs with chlorine dioxide at dosages of 50 to 200 mg/L as chlorine dioxide. At these dosages, the odor and bacterial activity appeared to be controlled for 4 to 6 days for thickened municipal sludge at 2 to 4% suspended solids. With chlorine dioxide, the oxidative reduction potential (ORP) increases as the pH of the solution drops. Therefore, at pH of 2, the ORP should increase at least one volt or increase the oxidative capability of chlorine dioxide (Reimers et. al., 2006). Since the chlorine dioxide is a Pearson Soft Acid, then it would react specifically with the amine and sulfide containing compounds.

Tests have been conducted to evaluate vector attraction reduction and stabilization, including assessments of volatile solids reduction, respirometer testing and specific oxygen uptake rate testing. Bench scale experiments noted stability through decreased oxygen uptake as well as volatile solids reduction. When the pH is less than 7.0, there is a small quantity (10 to 30 mg/L as nitrous acid) residual, which inhibits the bacterial growth and holds the ORP above 50 mV thereby inhibiting mercaptan production. Further field testing has observed a reduction of volatile solids over 50 percent.

Recent pilots’ studies are shown in Tables 2. The degradable organics were reduced approximately 68 percent and remaining degradable organics appears to be attributed to the soluble organics as noted in Table 2.
Table 2: Degradable Organics in Municipal Sludge (mg of O₂/g DWS)

<table>
<thead>
<tr>
<th>Sample</th>
<th>COD</th>
<th>BOD</th>
<th>TOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Sludge</td>
<td>938</td>
<td>310</td>
<td>150</td>
</tr>
<tr>
<td>Treated Sludge</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>768</td>
<td>107</td>
<td>85</td>
</tr>
<tr>
<td>B</td>
<td>224</td>
<td>89</td>
<td>77</td>
</tr>
<tr>
<td>Average</td>
<td>496</td>
<td>98</td>
<td>81</td>
</tr>
<tr>
<td>Cake</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw</td>
<td>984</td>
<td></td>
<td>2,060</td>
</tr>
<tr>
<td>Treated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>919</td>
<td></td>
<td>1,720</td>
</tr>
<tr>
<td>B</td>
<td>754</td>
<td></td>
<td>788</td>
</tr>
</tbody>
</table>

Percent removal of total organic carbon (TOC) = 46%; Percent removal of biochemical oxygen demand (BOC) = 68%; TOC is about 83% of the BOD

This reduction of degradable organics of around 68 percent appears to support the volatile suspended solids reductions shown in Table 3. They range from 74 to 56 percent, which is in the range of reduction of the degradable organics in the process schemes, yet the solids reduction itself was not appreciable with a possible increase due to some precipitation of calcium sulfate. Currently, further testing is being conducted looking at the nature of the degradability from respirometer testing. In addition, testing of degradation will be assessed with respect to ORP control so that inhibition of odor producing compounds can be assessed. If the ORP is greater than -200 mV, this production can be greatly reduced. Preliminary testing has observed a possible further ten percent reduction of volatile solids, which was noted with non-seed aerobic digestion testing.

Table 3: VSSR Results on 10 Florida Municipal Wastewater Sludges
(Calculated from the Van Kleck Equation)

<table>
<thead>
<tr>
<th>Plant</th>
<th>VSSR</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ormand Beach</td>
<td>72.9</td>
<td>Oxidation Ditch</td>
</tr>
<tr>
<td>Flagler Beach</td>
<td>56.4</td>
<td>Extended Aeration</td>
</tr>
<tr>
<td>Fleming Island</td>
<td>67.1</td>
<td>Oxidation Ditch</td>
</tr>
<tr>
<td>Spencer</td>
<td>74.5</td>
<td>Oxidation Ditch</td>
</tr>
<tr>
<td>South Plant</td>
<td>63.9</td>
<td>Oxidation Ditch</td>
</tr>
<tr>
<td>Ridault</td>
<td>70.1</td>
<td>Oxidation Ditch</td>
</tr>
<tr>
<td>Miller Street</td>
<td>62.3</td>
<td>Extended Aeration</td>
</tr>
<tr>
<td>Orange Park</td>
<td>69.4</td>
<td>Oxidation Ditch</td>
</tr>
<tr>
<td>St. Augustine</td>
<td>65.1</td>
<td>Oxidation Ditch</td>
</tr>
<tr>
<td>Harbour Road</td>
<td>69.4</td>
<td>Oxidation Ditch</td>
</tr>
</tbody>
</table>

End-use Products

The Neutralizer process produces viable value-added products for applications such as soil amenders, fertilizer agents, remediation soils and sod grass production. These treated soils can be engineered and have potential to assist remediation of contaminated soils at both low and high pHs. Tulane studies have been undertaken to determine the ability of engineered soils to immobilize lead ion (Pb⁺) from urban soil samples known to contain lead (Liu, 1998). A high binding capacity of lead to the iron oxide was noted but binding of lead ion to the biosolids was also observed. The lead ion was immobilized by the soil at pH values as low as 1 to 2. This work indicated the potential for developing an engineered soil blend using animal rather than human biosolids for remediation of lead and possibly other heavy metal contaminated soils. For example, an engineered soil for lead remediation is proposed with a blend of biosolids, silt and iron oxide. Two studies (Chaney et al., 1998 and Heneghan, 1998) have shown that lead is bound in soil with this type of amender at a typical stomach pH of 1 to 2 and thus not available as free lead to children in contact with the soil.
Fertilizers are commonly described on the basis of their nitrogen, phosphorus and potassium content. For example, a common class of retail fertilizer contains 8% total organic/inorganic nitrogen as “N”, 8% phosphorus as “P₂O₅” and 8% potassium as “K₂O”. Unfortunately, biosolids seldom have high contents of these nutrients. (Reimers et al., 2005).

The development of turf grass farms is another value-added product option. The land will use this Neutralizer stabilized biosolids to add nutrients and adjust the soil pH to a favorable soil composition for turf grass growth. The process could use 10 tons of biosolids per acre of turf grass. The cost was determined by dividing the cost per acre by 10 tons dried biosolids applied per acre. The costs of this process are outlined below in Table 4.

Table 4: Cost of Turf Grass Production (Reimers et al., 2005)

<table>
<thead>
<tr>
<th>Grass</th>
<th>Cost per acre ($)</th>
<th>Cost/dry ton biosolids ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zoysin</td>
<td>3,700</td>
<td>370</td>
</tr>
<tr>
<td>Bermuda</td>
<td>3,000</td>
<td>300</td>
</tr>
<tr>
<td>St. Augustine</td>
<td>2,800</td>
<td>280</td>
</tr>
</tbody>
</table>

The usage of biosolids has noted the enhanced growth in many soil situations since this Neutralizer process appears to hydrolyze many of the organics such as proteins. These hydrolyzed protein material are more amenable for increased plant productivity. This is especially important where the soils have been depleted of organic, which is common in the Southern part of the United States.

In the late 1990’s, there have been preliminary field studies conducted by Louisiana and Arkansas Agricultural Extension Agencies which denoted increased crop yields and quality with the land application of Class B biosolids. In St. James and St. Charles Parishes, Class B semi-anerobically digested biosolids were applied in sugarcane fields, which had 0.5% organic content. The sugarcane yields increased 100% (Hendrich, 1998).

In Arkansas studies, the crops were compared in quality with and without biosolids. The crops that did not receive biosolids had 8 to 10 percent crude protein content, and the crops receiving land applied biosolids had crude protein content between 18 to 21 percent. This increase of 100% in crude protein content is a very important factor that could have major future implications in food’s enhanced nutrient value of the crops (Arkansas Agriculture Extension Service, 1998). In these studies, the wheat crops had an increase in yield greater than 25 percent and a similar increase of crude protein content greater than 33 percent. In the winter, 60 acres of farmland had 2.2 dry tons of biosolids per acre distributed and this wheat had an increase of protein content greater than 15.5 percent. Again this could enhance both crop production and quality (Arkansas Agriculture Extension Service, 1998).

As a result of recent studies, there is increased concern about liability from the land application of Class B disinfected biosolids due to pathogens, EDCs and metals especially outside the United States. By using the Neutralizer process, these concerns due to liability can be resolved. In addition, the use of the oxidant and acid environment will enhance the potential availability of nutrients and organics for agriculture reuse.

CONCLUSION AND RECOMMENDATIONS

The overall bench-scale and pilot studies on the utilization of chlorine dioxide-nitrous acid disinfection process yielded the optimization of the treatment process parameters including the following; percent total solids, chlorine dioxide concentration and contact time, ORP, pH, nitrous acid concentration and contact time and pressure. The finalized recommendations are as follows:

- Percent total solids: less than or equal to 4
- Chlorine dioxide concentration: 50 to 150 mg/L (greater for 4% anaerobically digested sludges)
- Chlorine dioxide contact time: 2 to 12 hours
- Oxidation-reduction potential: greater than 50 mV
• pH; 2.3
• Nitrous acid concentration: 1800 to 600 mg/L
• Nitrous acid contact time: 2 to 12 hours respectively
• Pressure: 15 to 60 psig or greater depending upon the sludge characteristics

The understanding of the biosolids stabilization is being developed and understood so that oxidants such as chlorine dioxide can assist in many other applications. Finally, the use of Neutralizer process has merit in use as a soil amender, fertilizer agent, remediation soil and sod grass production.

In course of this study, the following should be recommended:

• The mechanism of disinfection of nitrous should be delineated.
• A pilot-scale/demonstration test under the worst-case-scenario should be conducted at a specific wastewater plant. The first full scale installation is operational as of March 2007.
• This disinfection process has the potential to be used to disinfect other waste such as animal manures and medical waste.
• The process should destroy residual wastes containing endocrine-disruptor compounds and personal-care pharmaceutical products.

REFERENCES


Liu, S. 1997, Doctoral of Science Dissertation, Tulane University, “Removal of Toxic Metals from Landfill Leachate and Wastewater by Spent Bauxite.” School of Public Health and Tropical Medicine, Department of Environmental Health Sciences, New Orleans, Louisiana.


