

SOIL AQUIFER TREATMENT WITH SULFUROUS ACID

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Abstract

In areas where open stream discharge is not feasible, or land application of recovered wastewater for irrigation is not economically or technically feasible, soil aquifer treatment (SAT) is often employed. This article addresses the cost effectiveness of using acid to increase percolation rates of SAT systems, and the amount and cost of sulfurous acid as compared to sulfuric acid required for adjusting water and soil pH for soil aquifer treatment and land applications. Sulfurous acid is safer to handle, less costly, and may be land applied at a higher pH 6.5 than the approximate pH 2 of sulfuric acid to deliver the same amount of acidity to reduce soil and water bicarbonate/carbonates and increase groundwater penetration. From field tests conducted at Montalvo Municipal Improvement District's wastewater treatment facility, it was found that using sulfurous acid at a pH of between 3 to 7.5 to acidify treated wastewater for reinjection into the aquifer improved water penetration and the quality of the treated wastewater, which was clearer than that of non acidified treated wastewater. Preliminary tests indicate sulfurous acid treatment reduced the number of percolation ponds required to handle the treated wastewater flows, and the frequency of the ripping cycle to open the percolation ponds, thus minimizing the pond area footprint required for soil aquifer treatment.

Introduction

Where soil and groundwater conditions are favorable for artificial recharge of groundwater through infiltration basins, a high degree of upgrading can be achieved by allowing partially-treated sewage effluent to infiltrate into the soil and move down to the groundwater. The unsaturated or "vadose" zone then acts as a natural filter to remove essentially all suspended solids, biodegradable materials, bacteria, viruses, and other microorganisms. Significant reductions in nitrogen, phosphorus, and heavy metals concentrations can also be achieved.¹

After the sewage is removed, the infiltrate passes through the vadose zone, and before reaching the groundwater is usually allowed to flow some distance through the aquifer before it is collected or discharged into the ocean in coastal regions. This additional movement through the aquifer can produce further purification (removal of microorganisms, precipitation of phosphates, adsorption of synthetic organics, etc.) of the sewage. Since the soil and aquifer are used as natural treatment, these systems are called soil-aquifer treatment systems or SAT systems. Soil-aquifer treatment is, essentially, a low-technology, advanced wastewater treatment system. It also has an aesthetic advantage over conventionally treated sewage in that water recovered from an SAT system is not only clear and odor-free but it comes from a well, drain, or via natural drainage to a stream or low area, rather than directly from a sewer or sewage treatment plant. Thus, the water has lost its connotation of sewage and the public see it water more as coming out of the ground (groundwater) than as sewage effluent, which is an important factor in the public acceptance of sewage reuse schemes.

While SAT systems give considerable water quality improvement to the sewage effluent, the quality of the resulting renovated water is not often as good as that of the native groundwater. Thus, SAT systems must be designed and managed to prevent encroachment of sewage water into the aquifer outside the portion of the aquifer used for soil-aquifer treatment.

Infiltration basins for SAT systems are located in soils that are permeable enough to give high infiltration rates. This requirement is important where sewage flows are relatively large, where excessive basin areas should be avoided (due to land cost) and where evaporation losses from the basins should be minimized. The soils, however, should also be fine enough to provide good filtration and quality improvement of the effluent as it passes through. Thus, the best surface soils for SAT systems are in the fine sand, loamy sand, and sandy loam range. Materials deeper in the vadose zone should be granular and preferably coarser than the surface soils. Soil profiles consisting of coarse-textured material on top and finer-textured material deeper down should be avoided because of the danger that fine suspended material in the sewage will move through the coarse upper material and accumulate on the deeper, finer material. This could cause clogging of the soil profile at some depth, where removal of the clogging material would be very difficult.

¹ The following discussion of Soil Aquifer Treatment systems is taken from F. Brissaud, Chapter 2 entitled "Groundwater recharge with recycled municipal wastewater: "criteria for health related guidelines," at pages 10-14, www.who.int/entity/water_sanitation_health/wastewater/wsh0308chap2.pdf

Vadose zones should not contain clay layers or other soils that could restrict the downward movement of water and form perched groundwater mounds. Aquifers should be sufficiently deep and transmissive to prevent excessive rises of the groundwater table (mounding) due to infiltration. Groundwater tables should be at least 1 meter below the bottom of the infiltration basins during flooding. Above all, soil and aquifer materials should be granular. Fractured-rock aquifers should be protected by a soil mantle of adequate texture and thickness (at least a few meters). Shallow soils underlain by fractured rock are not suitable for SAT systems.

These SAT systems also require periodic maintenance and monitoring. Bare soil is often the best condition for the bottom of infiltration basins in SAT systems. Occasional weeds are no problem but too many weeds can hamper the soil drying process, which delays recovery of infiltration rates. Dense weeds can also aggravate mosquito and other insect problems. Low water depths (about 20 cm) may be preferable to large water depths (about 1 m) because the turnover rate of sewage applied to shallow basins is faster than for deep basins of the same infiltration rate, thus giving suspended algae less time to develop in shallow basins. Suspended algae can produce low infiltration rates because they are filtered out on the basin bottom, where they clog the soil. Also, algae, being photosynthetic, remove dissolved carbon dioxide from the water, which increases the pH of the water. At high algal concentrations, this can cause the pH to rise to 9 or 10 which, in turn, causes precipitation of calcium carbonate. This cements the soil surface and results in further soil clogging and reduction of infiltration rates. Because suspended algae and soil clogging problems are reduced, shallow basins generally yield higher hydraulic loading rates than deep basins.

During flooding, organic and other suspended solids in the sewage effluent accumulate on the bottom of the basins, producing a clogging layer which causes infiltration rates to decline, if not acidified. Drying of the basins causes the clogging layer to dry, crack, and form curled-up flakes; the organic material also decomposes. These processes restore the hydraulic capacity so that when the basins are flooded again, infiltration rates are close to the original, high levels. However, as flooding continues, infiltration rates decrease again until they become so low that another drying period is necessary.

Depending on how much material accumulates on the bottom of infiltration basins, periodic removal of this material is necessary. Removing the material by raking or scraping is much better than mixing it with the soil with, for example, a disk harrow. The latter practice will lead to gradual accumulation of clogging materials in the top 10 or 20 cm of the soil, eventually necessitating complete removal of this layer, which could be expensive.

For clean secondary sewage effluent with suspended solids concentration of 10 to 20 mg/l, flooding and drying periods can be as long as 2 weeks each, and cleaning of basin bottoms may be necessary only once a year or once every 2 years. Primary effluent, with much higher suspended solids concentration, will require a schedule which might be 2 days flooding-8 days drying, and basin bottoms might be expected to require cleaning at the end of almost every drying period. The best schedule of flooding, drying, and cleaning of basins in a given system must be evaluated by on-site experimentation.

To minimize SAT maintenance costs and promote better filtration, pretreatment of the wastewater is required by removing many of the constituents of the wastewater

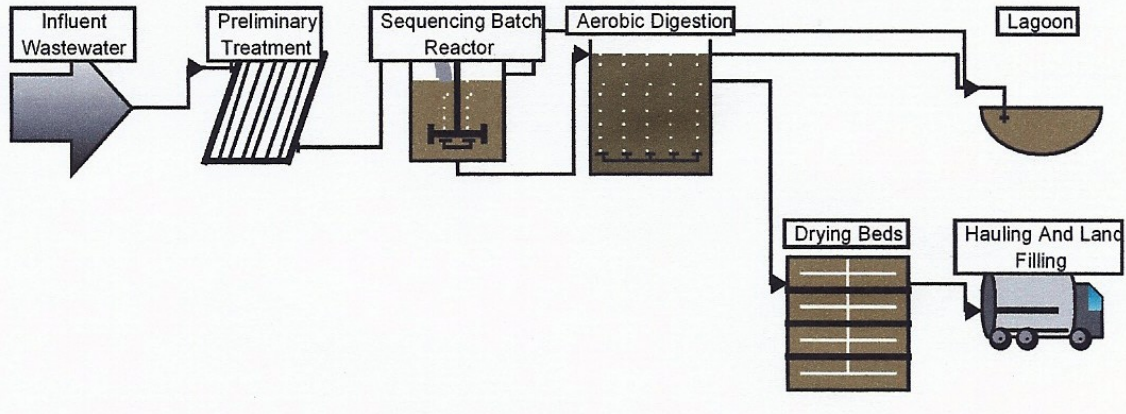
before ground water injection. The SAT system then uses soil as an effective filter to remove microorganisms from sewage effluent (except, of course, coarse soils such as sands and gravels, or fractured rock). According to F. Brissaud, many studies indicate essentially complete fecal coliform removal after percolation of 1 to a few meters through the soil. However, much longer distances of underground travel of microorganisms have also been reported. Usually, these long distances are associated with macro pores, as may be found in gravelly or other coarse materials, structured or cracked clay soils, fractured rock, cavernous limestones, etc. Bacteria are physically strained from the water, whereas the much smaller viruses are usually adsorbed. This adsorption is favored by a low pH, a high salt concentration in the sewage, and high relative concentrations of calcium and magnesium over monovalent cations such as sodium and potassium. Human bacteria and viruses immobilized in the soil do not reproduce, and eventually die. Most bacteria and viruses die in a few weeks to a few months, but much longer survival times have also been reported.

The main constituent that must be removed from raw sewage before it is applied to an SAT system is suspended solids. Reductions in BOD and bacteria are also desirable, but less essential. In larger municipalities, sewage typically receives conventional primary and secondary treatment, where the secondary treatment removes mostly biodegradable material (BOD's).

Primary effluent would have a higher BOD and suspended solids content than secondary effluent and this would result in somewhat lower hydraulic loading rates for the SAT system and would require more frequent basin cleaning. However, elimination of the secondary step in conventional pretreatment of the effluent would result in very significant cost savings for the overall system. Most of the solids were removed via the sequential batch reactors where solids floated to the top or dropped to the bottom out of the treated wastewater. This prefiltering of the solids not only extends the maintenance cycle of the SAT system

SAT is employed at the Montalvo Municipal Improvement District's wastewater treatment facility in Ventura, California after solids separation. Montalvo Municipal Improvement District owns the Montalvo Water Pollution Control Plant (Plant), located at 3555 Ventura Road, Montalvo, California. Treated domestic and commercial wastewaters are discharged under Waste Discharge Requirements contained in Order No. 87-092, adopted by the Regional Board on June 22, 1987.

An overview of a typical wastewater treatment processing sequence provides bar screening, comminuting, influent holding tank, two independent sequencing aerobic and denitrification batch reactors, with discharge into a percolation pond. The waste activated wastewater liquids between the floating and settling solids in the sequencing batch reactors is extracted and discharged to the subsurface through four evaporation/percolation ponds with a combined capacity of two million gallons. The aerobic and denitrification treated solids and liquids have polymers added to aid in separation and are sent to woven polypropylene bags on drying beds to collect the solids. The liquids from the woven polypropylene bags in the drying beds are collected and recirculated back through the sequencing batch reactors for nitrification/denitrification. No off-site transfer or usage of treated wastewater is presently employed. As there is no off-site disposal of the treated liquids, effluent limitations are not exceeded. The drawing below outlines a general overview of the processing sequence.



The actual equipment layout of the Montalvo wastewater treatment system comprises an influent wet well, muffin monster grinder, flow screen bar rake, equalization tank, three influent variable speed influent pumps, two sequencing batch reactors, and effluent decanted to four percolation ponds. The two sequencing batch reactors are filled with a sludge blanket containing various anaerobic and aerobic bacteria, which require a pH of around 7.0 or above to be maintained.

The entering screened influent enters the sequencing batch reactors in a mix/fill step for 15 minutes under anaerobic conditions in an anoxic zone for denitrification to take place. Where oxygen is depleted, heterotrophic bacteria respire nitrate as a substitute terminal electron acceptor. Denitrification generally proceeds through some combination of the following intermediate forms:



The complete denitrification process can be expressed as a redox reaction:



Next, the denitrified influent/fill is mixed in the presence of air for 70 minutes in an oxic zone for nitrification to occur. Nitrification is a microbial process by which reduced nitrogen compounds (primarily ammonia) are sequentially oxidized to nitrite and nitrate. The nitrification process is primarily accomplished by two groups of autotrophic nitrifying bacteria that can build organic molecules using energy obtained from inorganic sources, in this case ammonia or nitrite. In the first step of nitrification, ammonia-oxidizing bacteria, such as Nitrosomonas, oxidize ammonia to nitrite according

to the following equation:



Oxygen is also required to be added to inactivate viruses in wastewater under present Title 22 Health Department recovered wastewater regulations.

Next nitrite-oxidizing bacteria oxidize nitrite to nitrate according to equation:



There is a five minute react stage where no additional influent is added to allow the nitrification step to go to completion. Most carbonaceous BOD removal occurs in the react phase. Further nitrification also occurs by allowing the mixing and aeration to continue, even though the majority of denitrification occurred in the fix/fill phase.

The denitrified/nitrified influent is then allowed to settle for 50 minutes without aeration. To aid in solids settling, polymers may be added.

Approximately one third of the settled treated wastewater is then decanted over 30 minutes in a final step providing a treated decant, which is sent to percolation ponds. An approximately nine foot deep sludge blanket is left in the sequential batch reactors to treat additional wastewater influent.

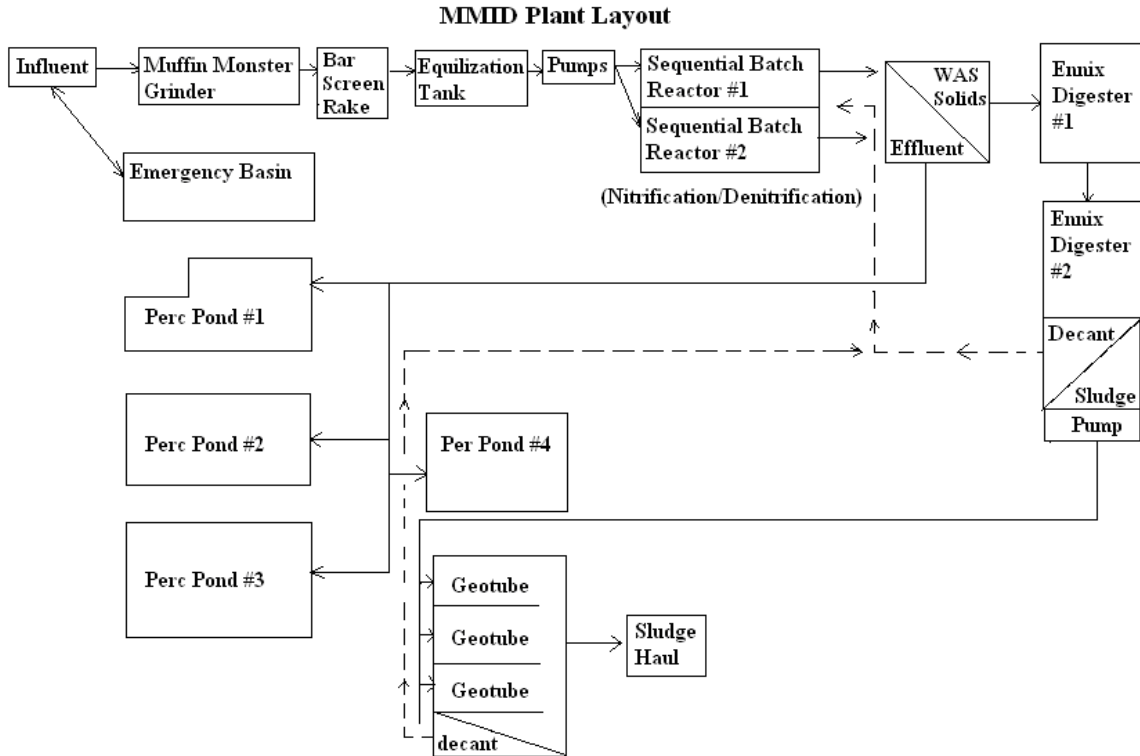
The settled waste activated sludge from the sequencing batch reactors is pumped to a first Ennix Digester, and then to a second Ennix Digester as part of a 30 day guaranteed treatment process to reduce the volume of solids in waste treatment ponds by 40% or more. The sludge from the second Ennix Digester is mixed with additional polymers and pumped into Geotubes placed on a sludge basin for solids separation. To maintain a level and sludge retention time, decant from the second Ennix Digester is pumped back into the sequencing batch reactors. The decant from the Geotubes is pumped back to the sequential batch reactors or the second Ennix Digester. As 200 tons of (18% moisture) of dried sludge from the Geotubes are annually hauled to a disposal site, without Ennix Digestion there would be approximately 330 (200 tns/.6)² tons of sludge per year.

The wet weather plant has a design capacity of 750,000 gallons per day (gpd). An average daily dry weather flow of up to 366,000 gpd was discharged during 1995. Waste sludge is treated onsite by aerobic digestion, and then discharged into lined sludge drying beds with woven polyethylene bags to collect the solids. Treated separated sludge is hauled offsite and disposed of at a legal disposal facility.

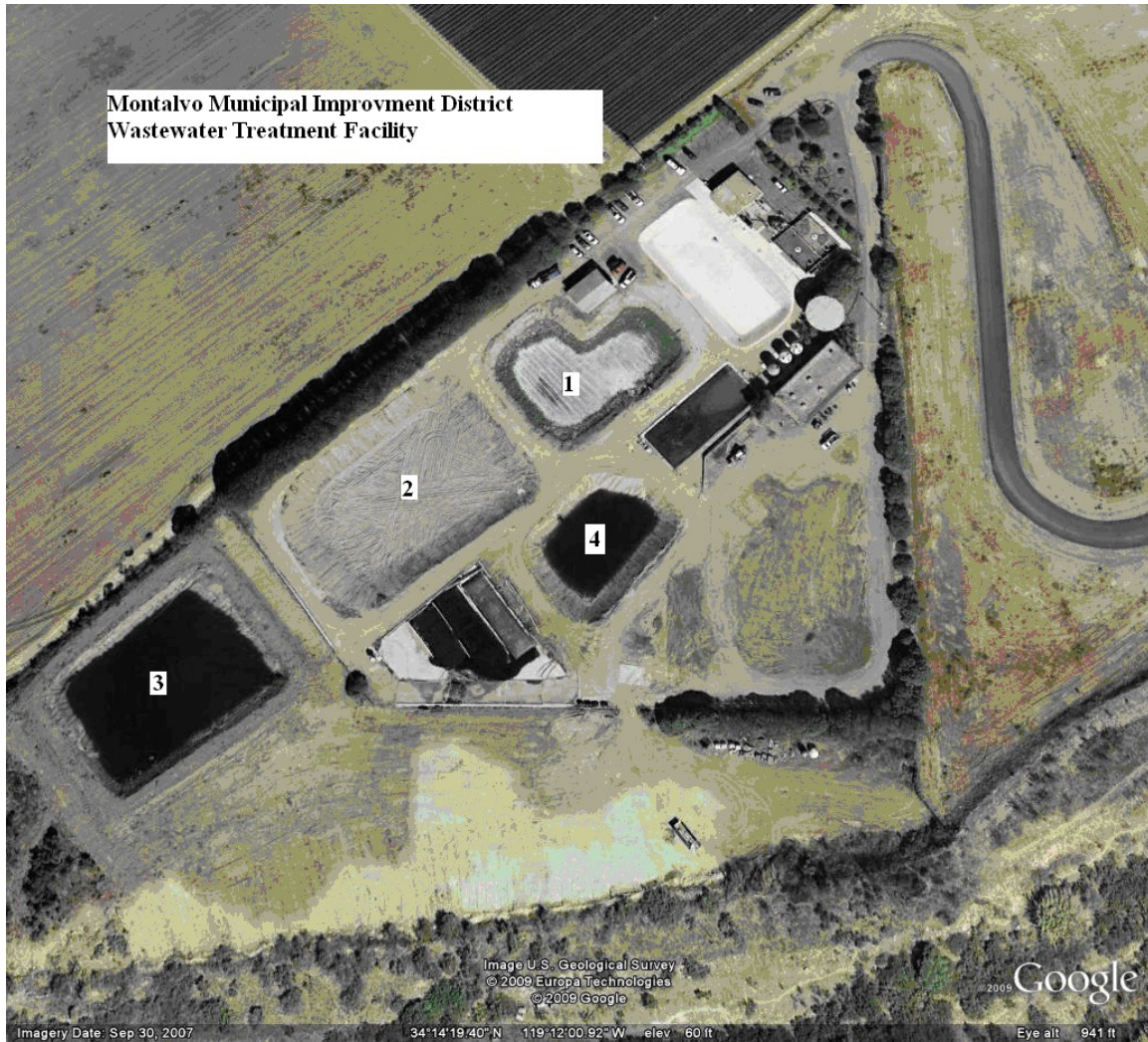
During high flows and/or maintenance of the sequential batch reactor process, a 1,000,000 gallon concrete lined emergency is used to hold influent for later return to the sequencing batch reactors. A standby emergency power generator is at the ready for any

² Conservatively assuming that 130 tons of Ennix reduced sludge is mostly carbon and only produces carbon dioxide rather than more potent methane and nitrous oxide gases, which have in excess of 30 times the affect on uv absorption, this would result in approximately 400 tons of carbon dioxide greenhouse gas emitted by Ennix Digestion per year. (Carbon combines with two oxygen molecules having a greater weight than carbon, so the total amount of carbon dioxide is approximately 3 times this 130 tons, or 400 tons per year. Actual green house gas calculations would be based on field tests of the composite emissions including methane and nitrous oxides). Thus, avoidance of sludge digestion reduces these air emissions to provide carbon credits, and a biofuel for co-firing to provide work and biofuel credits.

power interruption. The drawing below outlines the actual plant layout processing sequence.



The plant utilizes four sequential evaporation/percolation ponds located in Section 20, Township 2N, Range 22W, San Bernardino Base & Meridian. The plant's latitude is 34°14'17"; its longitude 119°11'34". The evaporation/percolation ponds take up over three quarters of the wastewater treatment facility footprint as can be seen from the pond locations shown below. These ponds are 8 to 9 feet in depth, with their bottoms approximately 5 feet above the aquifer, whose ground water level seasonally varies from approximately 180 inches during the summer to approximately 170 inches during the rainy season in February. The ideal would be to reduce the number of evaporation/percolation ponds required for soil aquifer infiltration of the treated wastewater decant.



Percolation Pond #1 (Pond 1) is L shaped approximately 135' x 120' with sloping sides and a depth of approximately 9 feet having a capacity of approximately 1,090,584 gallons, which equals 121,176 gallons/foot depth, or for every inch in increased depth 10,098 gallons is added to the percolation pond. Percolation Pond #2 (Pond 2) is approximately 150' x 240' with sloping sides and a depth of approximately 7 feet having a capacity of approximately 1,429,428 gallons, which equals 204,204 gallons/foot depth, or for every inch in increased depth 17,017 gallons were added to the percolation pond. Percolation Pond 3 (Pond 3) is approximately 174' x 135' with sloping sides and a depth of approximately 7 feet having a capacity of approximately 1,229,936 gallons, which equals 175,705 gallons/foot depth, or for every inch in increased depth 14,642 gallons is added to the percolation pond. Pond 3 is located on very porous soil, which rapidly drains any wastewater added thereto at greater infiltration rates than the other three ponds. Percolation Pond #4 is approximately 120' x 120' with a depth of approximately 8 feet giving it a capacity of approximately 598,400 gallons when filled, or 74,800 gallons/foot, which equals 6,234 gallons for every inch in increased depth.

The SAT system impoundment holding times vary based on the wastewater content, inflow volumes, and the soil porosity. To aid in increasing infiltration rates, it

was proposed to add sulfurous acid to the Montalvo facility treated wastewater to adjust the pH to reduce alkalinity in the wastewater and open up soil pores. The sulfurous acid solution continues to break down bicarbonate/carbonate buildup in the soil via delayed acid release from the bisulfate ionic specie; thereby increasing soil porosity and flow characteristics.

By separating the solids in the sequential batch reactors, the filtered wastewater can pass directly through a sulfurous acid generator without fouling. It was found through testing that sulfurous acid generators, such as the Harmon Systems International, LLC models condition and treat the remaining wastewater solids to self agglomerate into colloidal self adhering solids so that they do not adhere to the surfaces of the sulfur generator and ultimately drop to the bottom of the pond.

Sulfurous acid generators don't add additional acid and water to the wastewater treatment and separation process as is encountered with adding liquid acids to lower the pH. Consequently, the treated wastewater volume is not affected.

For purposes of the ground water penetration tests conducted at the Montalvo Municipal Improvement District, three percolation ponds were used to determine if the addition of acidity compared with the previous the 3R method to condition the percolation ponds so that they can inject roughly 200,000 gallons per day into the ground water. The 3R method sequentially removes the wastewater from a pond, rips approximately 18 inches of the bottom of the pond to break up bicarbonate layers which periodically buildup and seal the bottom of the percolation pond preventing infiltration, and then rests the pond to destroy bacteria and nematodes in the soil.

The Tests

Infiltration tests were conducted at the Montalvo facility beginning March 20, 2009 and continue through the present by injecting sufficient SO₂ into the treated wastewater to form acidified wastewater streams varying in pH from approximately 3 to 7.5 to determine if acidity significantly increases groundwater penetration.³ This additional acidity provided sufficient acid levels to prevent bicarbonates/carbonate deposits from forming, before passing it through a soil aquifer treatment system comprising porous percolation ponds that allowed water to percolate (or seep) through layers of rock and gravel. Sulfurous acid was selected because of cost and it not only removed bicarbonates in the aqueous phase, but provided a delayed release of acid as discussed in the Appendix to open up the soil pores to increase groundwater infiltration. The water is cleaned as it slowly travels downward and eventually reaches an underground aquifer. The purpose of man-made percolation ponds is both to clean the water and to keep the ground from sinking. It also counteracts salt water intrusion near coastal locations.

For the Montalvo infiltration tests, only ponds 1, 2 and 4 were used as they had similar infiltration rates. Approximately 200,000 gallons per day of treated wastewater was then added in differing sequences to each pond, and the ponds acidified with sulfurous acid. The acidity and rates of infiltration were then measured, along with water clarity. To track the rate of infiltration, each pond was adopted with a measuring stick marked in foot/inch increments attached to a cinderblock base, which acted as an

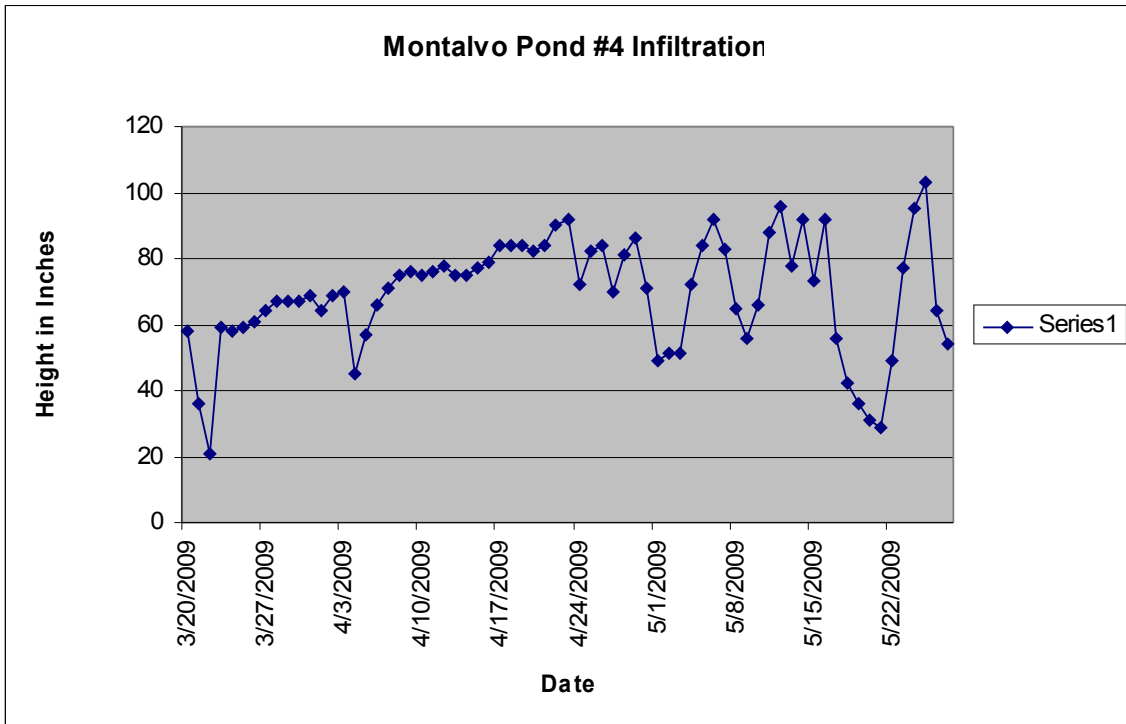
³ Acidity adjustment has long been recognized to affect soil water dispersion; see "Effect of pH on Saturated Hydraulic Conductivity and Soil Dispersion" by D.L. Saurez, J.D. Rhoades, R. Lavado, and C.M. Grieve, *Soil Sci.Soc.Am.J.*, Vol 48, 1984

impromptu Secchi meter to determine water depth clarity. A Harmon Model 10 sulfurous acid generator was positioned at the edge of pond #4 to burn sulfur to create SO_2 to inject into the wastewater taken from a pond and deliver it back into the pond. An inflow line was then placed in the respective pond to be acidified and connected to the sulfurous acid generator, which pumped wastewater from the pond for acidification. A sulfurous acid discharge line was connected to the sulfurous acid generator with its outlet positioned in the middle of the respective pond to add sulfurous acid treated wastewater back into the pond. Rather than move the sulfur burner, the acidified treated wastewater of pond 4 was overflowed and discharged into pond 2.



Testing started using pond 4 in March of 2009. The amount of sulfur burned was varied and the rates of infiltration tracked. For the pond 4 test, approximately 4,250 pounds of sulfur burned and injected into pond #4, which started at an elevation of approximately 58 inches and percolated approximately 200,000 gallons/day of decant.

As the sulfurous acid opened up the soil pores, the rates of infiltration increased. Further, the sulfurous acid agglomerated the suspended solids causing them to drop to the bottom so the water in the pond displayed a crystal clear clarity, which allowed the bottom to the pond to be seen even at a depth of 7 feet as compared with only a 2 feet depth observation of the non-acidified decant. The bottom of the pond for the first time also developed fissures or cracks, which aided in groundwater infiltration. When filled, the acidified Pond 4 also emitted no odor and provided an attractive pond adjacent the main facility. The height of Pond 4 varied as shown below.

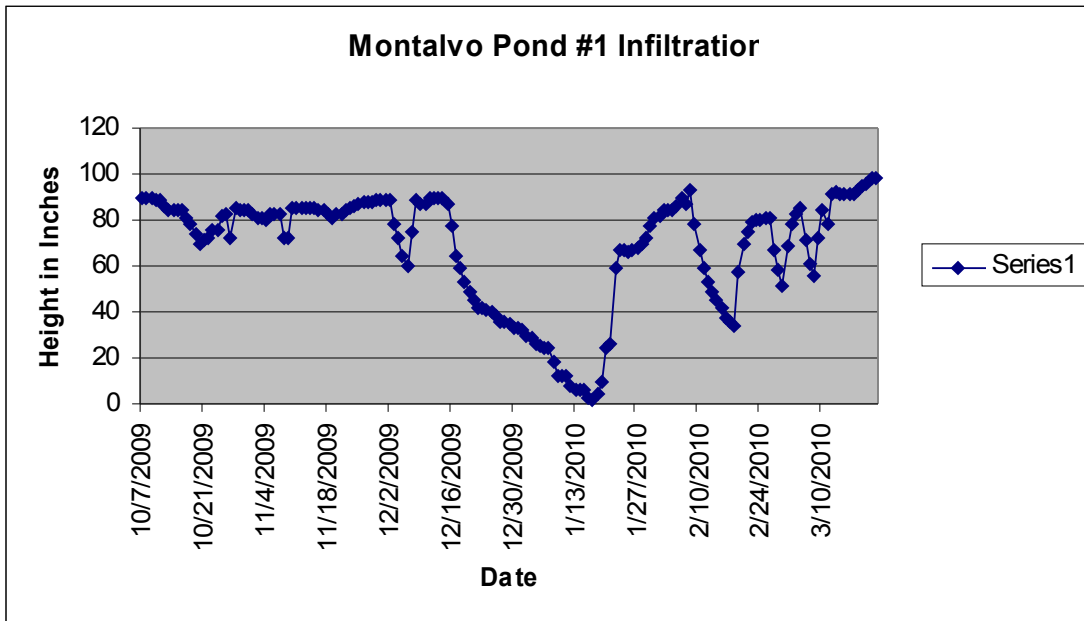


Approximately 10,800,000 gallons of decanted treated wastewater was acidified and entered Pond 4 for infiltration over the test period. From the foregoing, it can be seen that the inflows and infiltration were fairly stable as the entry of 200,000 gal/day decant only slightly increased the level of Pond 4, and was absorbed to lower the pond level to receive more decant the next day. On 12/15/2009 Pond 4 was allowed to percolate and rapidly lowered from 87 inches to 2 feet in three weeks.

This Pond 4 data shows consistent groundwater infiltration in comparison to previous spikes in operational levels, which makes management of the soil aquifer treatment much easier. Assuming a cost of \$.22/lb, the material costs of adding sulfur to increase infiltration of Pond 4 was \$935.00. Even though Pond 4 was acidified last year, it is still draining just as well as Pond 3.

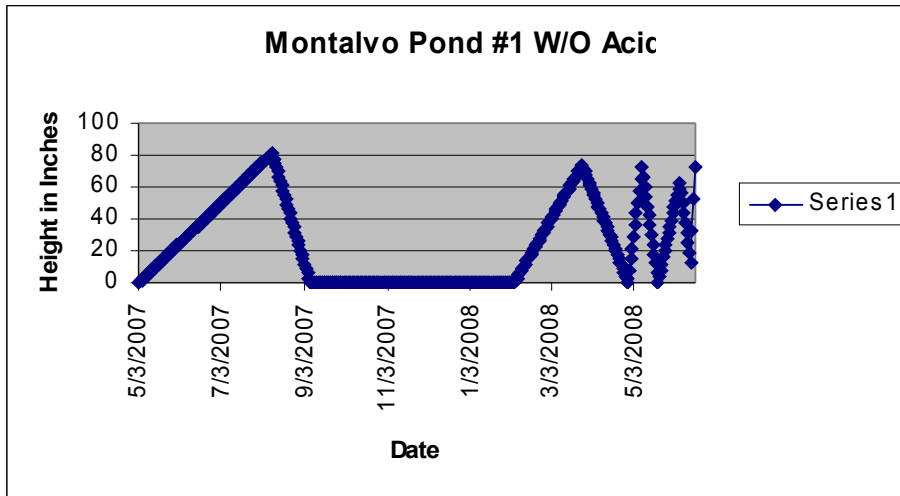
To track the relative effects of the acid addition, the 2009 Pond 1 levels were compared to the 2008 Pond 1 levels. For the pond 1 test, approximately 7,100 pounds of sulfur was burned for a cost of \$1562.00 and injected into the decant entering pond #1, which started at an elevation of approximately 90 inches and percolated approximately 200,000 gallons/day of decant.

The height of Pond 1 is shown below. Again note that the pond levels were fairly consistent as decant was added before Pond 1 was allowed to percolate on 12/15/2009.



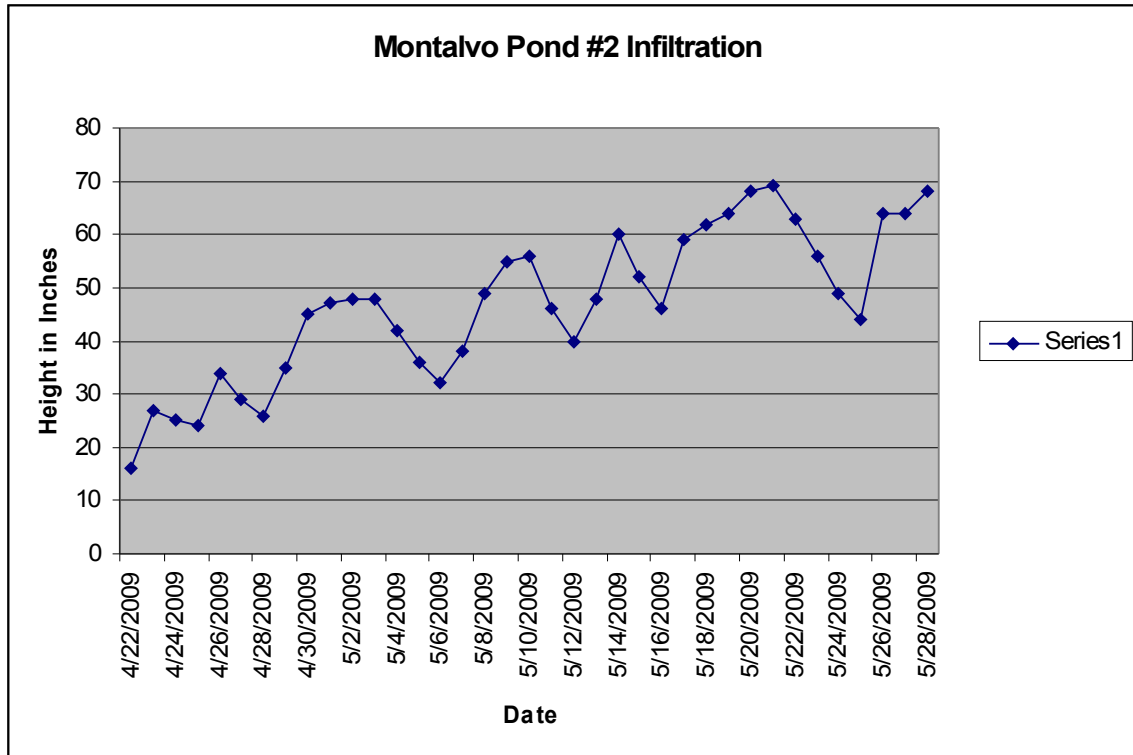
Approximately 14,000,000 (need to check this number) gallons of decanted treated wastewater was acidified and entered Pond 1 for infiltration over the test period. The above levels of infiltration in Pond 1 show that groundwater infiltration was very consistent over the test period. With acidification, the pond consistently drained as soon as the hydraulic head pressure built up to at least 7 feet without the need for ripping.

Comparing the daily infiltration levels of Pond 1 without sulfurous acid treatment for the period May 3, 2007 through June 13, 2008, one can see that the rates of infiltration were not as consistent nor did they daily drain as fast. For example, during the first 90 days, the level of Pond 1 steadily rose an average of 8/10ths of an inch with the daily addition of 200,000 gallons/day rising from 0 inches to 81 inches. At 81 inches, Pond 1 was required to percolate without any additional decant being added for 28 days until September 5, 2007, and then rest until February 4, 2008. Filling recommenced in February 2008, and Pond 1 more rapidly filled and emptied in more volatile accelerating swings reflecting that the ponds were becoming less porous for ground water infiltration as shown below:



For example, after resting beginning February 5, 2008, it took 50 days to fill Pond 1 to a level of 74 inches reflecting that each day on average there was a net increase in the height of the pond of 1.48 inches. Filling was ceased and it took 34 days to drain Pond 1 reflecting an average infiltration per day of 2.176 inches. When filling recommenced on April 29, 2008, it only took 10 days to fill pond 1 to a level of 72 inches. It then took 12 days to drain Pond 1 reflecting an average infiltration of 6 inches. On May 20, 2008, it took 16 days to fill the pond to a level of 63 inches, which subsequently drained over 3 days at an average infiltration of 6.378 inches per day. These swings in infiltration levels make it necessary to continually monitor the ponds to insure that they do not overflow as ground water levels vary.

The levels of Pond 2 were then tracked over a one month period and showed a gradual increase in the level of the pond, even though there was significant amount of decant infiltration as shown below:



Approximately 7,200,000 gallons of decanted treated wastewater was acidified and entered Pond 2 for infiltration over the test period.

For the pond 2 test, approximately 5,250 pounds of sulfur burned and injected into pond #2, which started at an elevation of approximately 16 inches and percolated approximately 200,000 gallons/day of decant. Assuming a cost of \$.22/lb, the material costs of adding sulfur to increase infiltration were \$1,155.00.

The total sulfur costs for treating Ponds 1, 2, and 4 totaled \$3,652.00 (\$935.00 + \$1,562 + \$1,155). This is slightly less expensive than the yearly cost of ripping all the ponds at \$3,800.00 (\$1,720.00 tractor rental for 1 week plus 8 hours labor @ \$65/hr x 4 ponds). If the frequency of ripping the ponds is extended another year as shown by the preliminary data, acidification costs become even more favorable. Data is still being developed regarding the long term affects of adding sulfurous acid to increase infiltration and ripping frequency to resolve this issue. This preliminary cost comparison does not factor in the cost of the sulfur generator equipment depreciation. Nor does it factor in the intangible improvements in pond clarity and odor free condition, as well as freeing up an operator's time to perform other duties instead of taking 4 days per annum to operate ripping equipment vs. 10 minutes per day to monitor pond levels and take pH readings.

Ponds 1 and 2 also displayed the same clarity and fissures and cracks in their bottoms. The liquids and solids also were odorless when acidified. Further, the solids volume left in the bottom of a drained pond appeared to be much less than conventional solids. These light gray solids have a water content less than 10% and curl and crack upon drying when the pond was emptied. As can be seen from the picture below, the sides of the drained ponds were also stratified, which may correspond to the on/off acidification cycle. Again, the ongoing testing will resolve these tentative conclusions.



At the end of the testing in January 2010, only one pond was required to handle the approximately 200,000 gallons/day of decant, leaving three empty. This was fortunate as an extraordinary series of storms occurred beginning January 13 and continuing through January 23. During this 10 day period an average of 6.13 inches of rain was recorded at the Oxnard, California Airport. This resulted in extraordinary additional storm wastewater flows at the Montalvo facility. To handle these emergency storm wastewater flows, the one-million gallon concrete-lined pond was utilized to store untreated wastewater which was then gradually returned to the head works of the plant for treatment. During these emergency flows, the emergency concrete-lined pond collected 3 days of an additional 170,000 gallons per day, and 3 days of an additional 130,000 gallons per day.

The additional storm wastewater flows were treated and then deposited in the three empty ponds by switching from pond to pond. These three ponds were not allowed to rest. Nor was the wastewater decant acidified to chemically dewater the solids under these storm wastewater conditions. Consequently, plugging of the extra ponds' porous sands resulted. This was caused by the heavy non-acidified unconditioned wastewater solids loads and switching into and out of the ponds before the water levels dropped. Without acid conditioning, the suspended solids did not chemically dewater or agglomerate in the same manner as occurred during the test period. Consequently, the same rapid fill/empty cycle was observed with the daily infiltration levels of Pond 1 without sulfurous acid treatment for the period May 3, 2007 through June 13, 2008. The rates of infiltration were not as consistent nor did they daily drain as fast. For example, the non-acidified extra wastewater decant was first used to rapidly fill Pond 1 to a 7 foot level. Then the non-acidified extra wastewater decant was switched to rapidly fill Pond 4

and then Pond 3 so that Pond 1 could rest. However, Ponds 4 and 3 filled so rapidly that Pond 1 was again filled at a 1 to 2 foot level before it had completely drained. Again Pond 1 rapidly filled and Ponds 3 and 4 were then similarly rapidly filled as infiltration was much less than when the flood wastewater decant was acidified. However, because of the extra capacity of these three ponds made available by the prior acidification, these extra flood wastewater flows were handled without incident.⁴

A review of the above data shows that good infiltration occurred not only during the summer dry season, but in the winter wet season when ground water levels were 12 inches higher because of the additional precipitation. In addition, data from the three test wells monitoring the Montalvo site showed that the levels of dissolved oxygen and the pH in the ground water were unaffected by acidification.

Conclusion

It was found that the costs of adding sulfurous acid is similar to the cost of ripping the three ponds, but increased infiltration by approximately double. Only one pond was required for groundwater recharge, resulting in significant land cost savings. The acidity increased the clarity and eliminated the odor of the treated wastewater during pond infiltration. It also reduced non-productive operator ripping time, and provided a reduced volume of dewatered solids left in the bottom of the drained percolation ponds. Further, the ripping cycle to open up the ponds may be extended from an average of 3 months to beyond 6 months, and will be determined by further study. The SO₂ pre-treatment of treated wastewater thus provides a method of extending the effectiveness and maintenance life of SAT systems using acidified reclaimed wastewater. This acidification SAT groundwater recharging wastewater disposal method is particularly useful for disposing of treated wastewater until an end user is located for its use.

⁴ Pond 1 started growing a green algae at the 6 foot fill level in March 2010, which indicated that the treated effluent was high in nutrients sufficient to grow photobiomass. As the level of Pond 1 dropped to 3 feet, the algae combined with the solids formed a greenish brown layer on the side of the pond approximately 1/16 to 1/8 inch thick, which had a similar consistency to dried leaves. After the algae settled, Pond 1 was reacidified and reverted to a crystal clear state. Samples of the greenish brown layer were collected on 2/17/2010 and tested for BTU content. Timpview Analytical laboratories, which showed a BTU content of 4071/lb, and a moisture content of 3.92%--the BTU content was lower than previous samples of chemically dewatered sludges, which was probably due to its 54.2% by weight ash content indicating significant amounts of fine soil particles were contained therein. The greenish brown color was also different than the cinnamon brown color of chemically dried sludges



Chemically dewatered solids



Algae solids layer

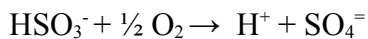
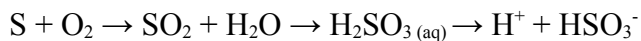
APPENDIX

Sulfurous Acid vs. Sulfuric Acid

The selection of the type of acid to aid in soil aquifer treatment is based on price, the pH and amount of acid required, the number of hydrogen ions added per molecule of acid, avoiding acid components contributing additional unwanted salts to the acidified wastewater, and minimizing of the increase in the volume of wastewater by adding minimal additional volume of liquid acids. Sulfurous acid (H_2SO_3) was selected for soil aquifer treatment at the Montalvo wastewater treatment facility because of its:

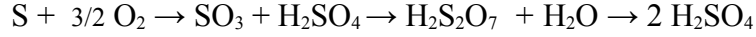
- a. handling safety
- b. mild 6.5 pH required for soil infiltration.
- c. properties aggregating finely suspended solids.
- d. diprotic addition of double concentrated hydrogen ions per molecule.
- e. no increase in wastewater disposal volume.
- f. dissociation into bivalent sulfate anions
- g. lower price than sulfuric acid.

No additional disposal volume is achieved as sulfurous acid is generated on-site with a sulfur generator that first oxidizes elemental sulfur (S) to a +4 gaseous state into sulfur dioxide (SO_2), which is then combined with wastewater to form a weak diprotic acid. The diprotic nature of sulfurous acid creates double concentrated acid than is provided a monoprotic acids such as hydrochloric acid. Sulfurous acid dissociates to release two acidic hydrogen ions (H^+) sequentially or in stages:



It thus ultimately dissociates into bivalent sulfate anions, which avoids the adverse affects monovalent ions such as chlorides and sodium have on plant and soil organisms.

Conversely, sulfuric acid (H_2SO_4) is usually generated off-site with various processes such as first oxidizing sulfur (S) into sulfur dioxide (SO_2); next using pressure, heat, a vanadium catalyst and additional air to form sulfur trioxide (SO_3); which is then dissolved into 98% sulfuric acid to create pyrosulfuric acid ($\text{H}_2\text{S}_2\text{O}_7$) to which water is then added to form sulfuric acid:



Solution Equilibrium Applications

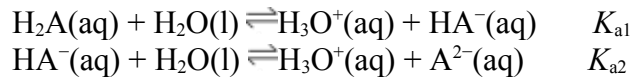
As sulfurous acid is usually delivered and adjusted in the field based on pH readings of the acidified treated wastewater, the amount of acid required for a particular application is dependent upon the system components and whether they are in a gaseous, liquid, or solid phase. This requires an understanding of solution equilibrium vs. soil liquid/solid phase components. For acids and their components in the liquid phase, dissociation constants for strong and weak acids are employed. The dissociation constant is usually written as a quotient of the equilibrium concentrations (in mol/L), denoted by [HA], [A⁻] and [H⁺]:

$$K_a = \frac{[A^-][H^+]}{[HA]}$$

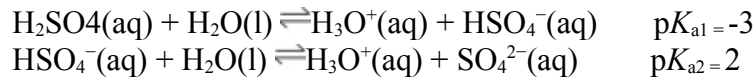
Due to the many [orders of magnitude](#) spanned by K_a values, a [logarithmic](#) measure of the acid dissociation constant is more commonly used in practice. pK_a , which is equal to $-\log_{10} K_a$, may also be referred to as an acid dissociation constant:

$$pK_a = -\log_{10} K_a$$

A diprotic acid such as sulfurous and sulfuric acids (symbolized as H₂A) can undergo one or two dissociations depending on the pH. Each hydrogen ion dissociation release has its own dissociation constant, K_{a1} and K_{a2} .

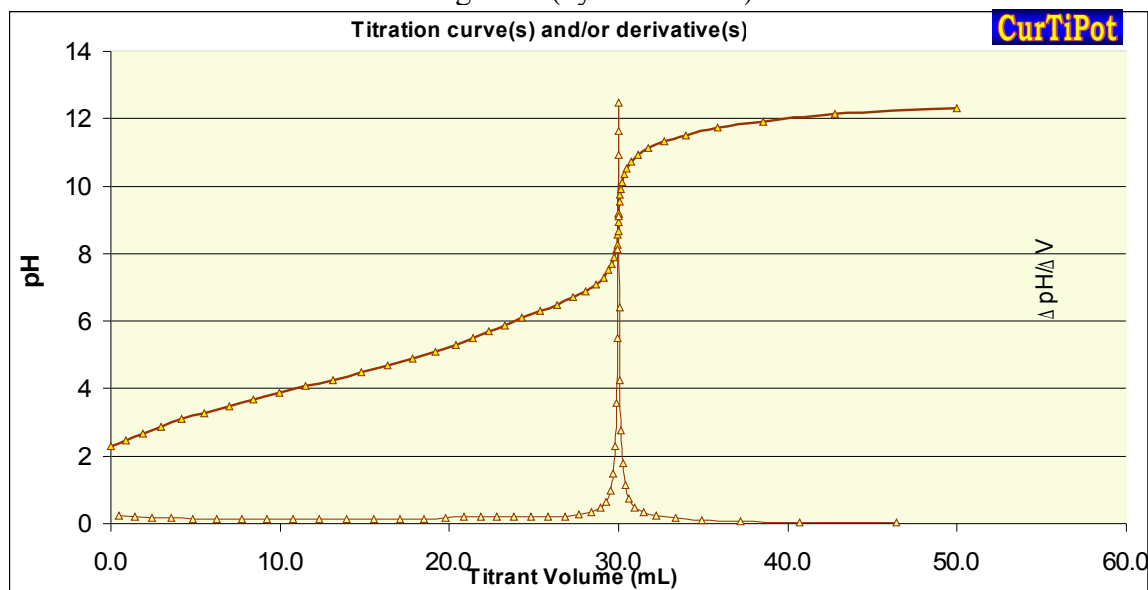


The first dissociation constant is usually greater than the second so $K_{a1} > K_{a2}$. For [sulfuric acid](#) (H₂SO₄) the first proton is donated to form the [bisulfate](#) anion (HSO₄⁻).



As its K_{a1} is very large (10^3), it can donate a second proton to form the [sulfate](#) anion (SO₄)²⁻, wherein the K_{a2} is intermediate strength (10^{-2}). The large K_{a1} for the first dissociation makes sulfuric a strong acid. This can be illustrated by plotting the titration

curve of sulfuric acid with a strong base (hydroxide ion) as shown in the chart below.⁵

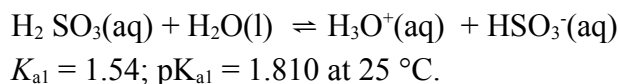


The titration curve of 0.1M solution of sulfuric acid titrated with 0.1 M solution strong base. $pK_{a1} = -3$, $pK_{a2} = 2$. The pK_a s of Sulfuric acid show that while its second proton is much less acidic than the first one, it is strong enough so that both protons get titrated together. Consequently, there is only one steep part of the titration curve as shown.

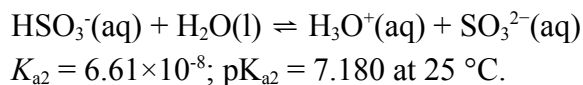
Conversely, weak diprotic acids behave differently. For example, weak unstable [carbonic acid](#) (H_2CO_3) can lose one proton to form [bicarbonate](#) anion (HCO_3^-), which loses a second to form [carbonate](#) anion (CO_3^{2-}). Both K_a values are small even though $K_{a1} > K_{a2}$.

Similarly, sulfurous acid is also a diprotic weak acid with two dissociation constants:

The first is for the rapid dissociation into the bisulfate (hydrogen sulfite) ion:

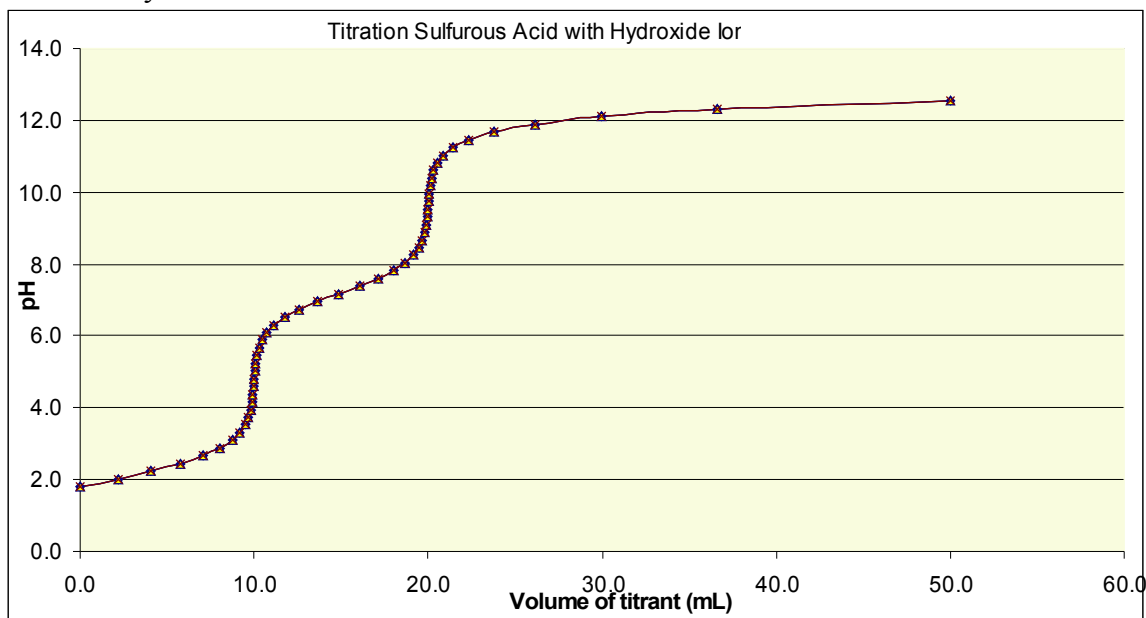


Delayed release of the second hydronium ion provides a buffering action to aqueous sulfurous acid solutions:



⁵Titration curves generated by the Curtiplot program produced by Professor Ivano Gebhardt Rolf Gutz, Instituto de Quimica—Universidade de Sao Paulo, Brazil.

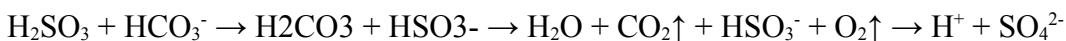
Because the second dissociation constant K_{a2} for HSO_3^- is eight orders of magnitude smaller than K_{a1} for H_2SO_3 , to calculate the initial amount of acid required to produce a given pH at equilibrium in a liquid solution, only the first equation is typically used to approximate the solution hydrogen concentration. This first equation only produces one H^+ , so the amount of weak sulfurous acid required to produce a given pH at solution equilibrium is twice that required of a strong acid such as sulfuric acid, which immediately releases two H^+ . This can be seen by comparing the plot of the above single inflection sulfuric acid titration curve with the dual inflexion titration curve of sulfurous acid with hydroxide ions shown in the chart below.



Vadd (mL)	"pH" simulated	[H]	CHtot = CHcalc	Dill. factor Titrand (sample)	Dill. Factor Titrant (buret)	h1 Sulfurous acid	h2 Sulfurous acid
0.000	1.806	1.563E-02	1.500E-01	1.000E+00	0.000E+00		2.6873
2.157	2.020	9.540E-03	1.354E-01	9.026E-01	9.735E-02		2.5729
4.096	2.235	5.822E-03	1.245E-01	8.300E-01	1.700E-01		2.4501
5.754	2.449	3.553E-03	1.165E-01	7.766E-01	2.234E-01		2.3331
7.077	2.664	2.168E-03	1.108E-01	7.386E-01	2.614E-01		2.2336
8.061	2.878	1.323E-03	1.069E-01	7.127E-01	2.873E-01		2.1568
8.749	3.093	8.073E-04	1.044E-01	6.957E-01	3.043E-01		2.1019
9.210	3.307	4.927E-04	1.027E-01	6.847E-01	3.153E-01		2.0647
9.508	3.522	3.006E-04	1.017E-01	6.778E-01	3.222E-01		2.0403
9.697	3.736	1.835E-04	1.010E-01	6.735E-01	3.265E-01		2.0248
9.817	3.951	1.120E-04	1.006E-01	6.708E-01	3.292E-01		2.0149
9.894	4.165	6.832E-05	1.004E-01	6.690E-01	3.310E-01		2.0086
9.944	4.380	4.169E-05	1.002E-01	6.679E-01	3.321E-01		2.0043
9.982	4.594	2.544E-05	1.001E-01	6.671E-01	3.329E-01		2.0011
10.014	4.809	1.552E-05	9.995E-02	6.664E-01	3.336E-01		1.9981
10.050	5.023	9.474E-06	9.983E-02	6.656E-01	3.344E-01		1.9947
10.098	5.238	5.781E-06	9.967E-02	6.645E-01	3.355E-01		1.9900
10.170	5.452	3.528E-06	9.944E-02	6.629E-01	3.371E-01		1.9829

10.282	5.667	2.153E-06	9.907E-02	6.605E-01	3.395E-01	1.9718
10.457	5.881	1.314E-06	9.850E-02	6.567E-01	3.433E-01	1.9543
10.730	6.096	8.017E-07	9.763E-02	6.508E-01	3.492E-01	1.9270
11.144	6.310	4.892E-07	9.633E-02	6.422E-01	3.578E-01	1.8856
11.748	6.525	2.985E-07	9.450E-02	6.300E-01	3.700E-01	1.8252
12.577	6.739	1.822E-07	9.209E-02	6.139E-01	3.861E-01	1.7423
13.626	6.954	1.112E-07	8.922E-02	5.948E-01	4.052E-01	1.6374
14.824	7.168	6.784E-08	8.615E-02	5.743E-01	4.257E-01	1.5176
16.044	7.383	4.140E-08	8.323E-02	5.549E-01	4.451E-01	1.3956
17.146	7.598	2.526E-08	8.076E-02	5.384E-01	4.616E-01	1.2854
18.041	7.812	1.542E-08	7.886E-02	5.258E-01	4.742E-01	1.1960
18.706	8.027	9.408E-09	7.751E-02	5.167E-01	4.833E-01	1.1295
19.169	8.241	5.741E-09	7.659E-02	5.106E-01	4.894E-01	1.0831
19.478	8.456	3.503E-09	7.599E-02	5.066E-01	4.934E-01	1.0524
19.677	8.670	2.138E-09	7.561E-02	5.041E-01	4.959E-01	1.0325
19.804	8.885	1.305E-09	7.537E-02	5.025E-01	4.975E-01	1.0199
19.886	9.099	7.961E-10	7.521E-02	5.014E-01	4.986E-01	1.0119
19.941	9.314	4.858E-10	7.511E-02	5.007E-01	4.993E-01	1.0067
19.982	9.528	2.965E-10	7.503E-02	5.002E-01	4.998E-01	1.0032
20.018	9.743	1.809E-10	7.497E-02	4.998E-01	5.002E-01	1.0004
20.059	9.957	1.104E-10	7.489E-02	4.993E-01	5.007E-01	0.9977
20.115	10.172	6.737E-11	7.478E-02	4.986E-01	5.014E-01	0.9945
20.200	10.386	4.111E-11	7.463E-02	4.975E-01	5.025E-01	0.9899
20.333	10.601	2.509E-11	7.438E-02	4.959E-01	5.041E-01	0.9829
20.548	10.815	1.531E-11	7.399E-02	4.932E-01	5.068E-01	0.9719
20.896	11.030	9.342E-12	7.336E-02	4.890E-01	5.110E-01	0.9545
21.459	11.244	5.701E-12	7.236E-02	4.824E-01	5.176E-01	0.9274
22.365	11.459	3.479E-12	7.081E-02	4.721E-01	5.279E-01	0.8863
23.818	11.673	2.123E-12	6.846E-02	4.564E-01	5.436E-01	0.8262
26.155	11.888	1.296E-12	6.500E-02	4.333E-01	5.667E-01	0.7436
29.983	12.102	7.906E-13	6.002E-02	4.001E-01	5.999E-01	0.6390
36.644	12.317	4.824E-13	5.296E-02	3.531E-01	6.469E-01	0.5192
50.000	12.531	2.944E-13	4.286E-02	2.857E-01	7.143E-01	0.3973

To approximate the amount of sulfurous acid required to dissolve bicarbonates/carbonates according to the following reaction:

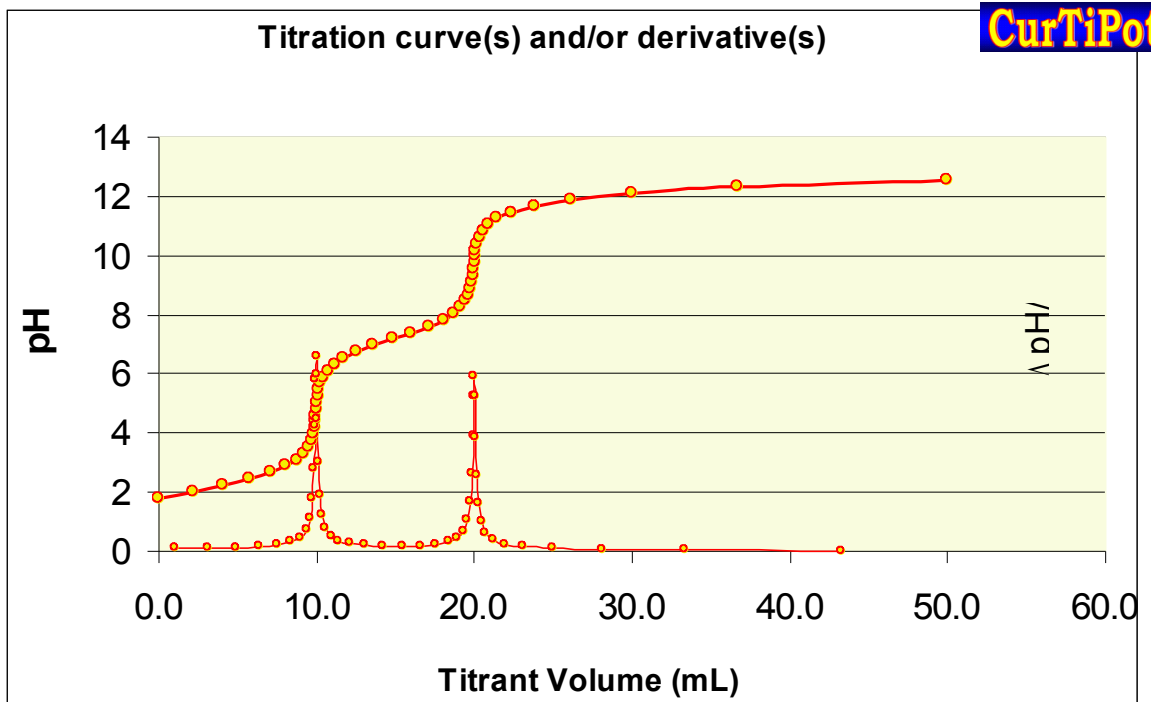


A titration sulfurous acid curve is generated using carbonic acid as the titrant:

Vadd (mL)	"pH" simulated	[H]	CHtot = CHcalc	Dill. factor Titrand (sample)	Dill. Factor Titrant (buret)	h1 Sulfurous acid	h2 Sulfurous acid
0.000	1.806	1.563E-02	1.500E-01	1.000E+00	0.000E+00		2.6873
2.157	2.020	9.540E-03	1.354E-01	9.026E-01	9.735E-02		2.5729
4.096	2.235	5.822E-03	1.245E-01	8.300E-01	1.700E-01		2.4501
5.754	2.449	3.553E-03	1.165E-01	7.766E-01	2.234E-01		2.3331
7.077	2.664	2.168E-03	1.108E-01	7.386E-01	2.614E-01		2.2336

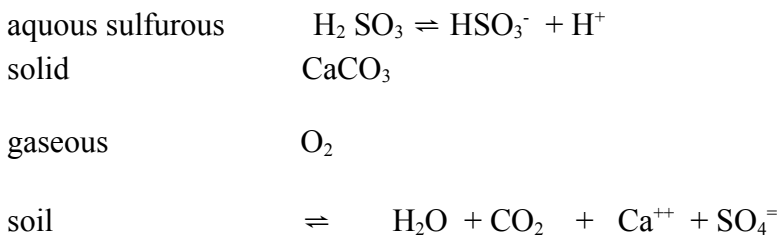
8.061	2.878	1.323E-03	1.069E-01	7.127E-01	2.873E-01	2.1568
8.749	3.093	8.073E-04	1.044E-01	6.957E-01	3.043E-01	2.1019
9.210	3.307	4.927E-04	1.027E-01	6.847E-01	3.153E-01	2.0647
9.508	3.522	3.006E-04	1.017E-01	6.778E-01	3.222E-01	2.0403
9.697	3.736	1.835E-04	1.010E-01	6.735E-01	3.265E-01	2.0248
9.817	3.951	1.120E-04	1.006E-01	6.708E-01	3.292E-01	2.0149
9.894	4.165	6.832E-05	1.004E-01	6.690E-01	3.310E-01	2.0086
9.944	4.380	4.169E-05	1.002E-01	6.679E-01	3.321E-01	2.0043
9.982	4.594	2.544E-05	1.001E-01	6.671E-01	3.329E-01	2.0011
10.014	4.809	1.552E-05	9.995E-02	6.664E-01	3.336E-01	1.9981
10.050	5.023	9.474E-06	9.983E-02	6.656E-01	3.344E-01	1.9947
10.098	5.238	5.781E-06	9.967E-02	6.645E-01	3.355E-01	1.9900
10.170	5.452	3.528E-06	9.944E-02	6.629E-01	3.371E-01	1.9829
10.282	5.667	2.153E-06	9.907E-02	6.605E-01	3.395E-01	1.9718
10.457	5.881	1.314E-06	9.850E-02	6.567E-01	3.433E-01	1.9543
10.730	6.096	8.017E-07	9.763E-02	6.508E-01	3.492E-01	1.9270
11.144	6.310	4.892E-07	9.633E-02	6.422E-01	3.578E-01	1.8856
11.748	6.525	2.985E-07	9.450E-02	6.300E-01	3.700E-01	1.8252
12.577	6.739	1.822E-07	9.209E-02	6.139E-01	3.861E-01	1.7423
13.626	6.954	1.112E-07	8.922E-02	5.948E-01	4.052E-01	1.6374
14.824	7.168	6.784E-08	8.615E-02	5.743E-01	4.257E-01	1.5176
16.044	7.383	4.140E-08	8.323E-02	5.549E-01	4.451E-01	1.3956
17.146	7.598	2.526E-08	8.076E-02	5.384E-01	4.616E-01	1.2854
18.041	7.812	1.542E-08	7.886E-02	5.258E-01	4.742E-01	1.1960
18.706	8.027	9.408E-09	7.751E-02	5.167E-01	4.833E-01	1.1295
19.169	8.241	5.741E-09	7.659E-02	5.106E-01	4.894E-01	1.0831
19.478	8.456	3.503E-09	7.599E-02	5.066E-01	4.934E-01	1.0524
19.677	8.670	2.138E-09	7.561E-02	5.041E-01	4.959E-01	1.0325
19.804	8.885	1.305E-09	7.537E-02	5.025E-01	4.975E-01	1.0199
19.886	9.099	7.961E-10	7.521E-02	5.014E-01	4.986E-01	1.0119
19.941	9.314	4.858E-10	7.511E-02	5.007E-01	4.993E-01	1.0067
19.982	9.528	2.965E-10	7.503E-02	5.002E-01	4.998E-01	1.0032
20.018	9.743	1.809E-10	7.497E-02	4.998E-01	5.002E-01	1.0004
20.059	9.957	1.104E-10	7.489E-02	4.993E-01	5.007E-01	0.9977
20.115	10.172	6.737E-11	7.478E-02	4.986E-01	5.014E-01	0.9945
20.200	10.386	4.111E-11	7.463E-02	4.975E-01	5.025E-01	0.9899
20.333	10.601	2.509E-11	7.438E-02	4.959E-01	5.041E-01	0.9829
20.548	10.815	1.531E-11	7.399E-02	4.932E-01	5.068E-01	0.9719
20.896	11.030	9.342E-12	7.336E-02	4.890E-01	5.110E-01	0.9545
21.459	11.244	5.701E-12	7.236E-02	4.824E-01	5.176E-01	0.9274
22.365	11.459	3.479E-12	7.081E-02	4.721E-01	5.279E-01	0.8863
23.818	11.673	2.123E-12	6.846E-02	4.564E-01	5.436E-01	0.8262
26.155	11.888	1.296E-12	6.500E-02	4.333E-01	5.667E-01	0.7436
29.983	12.102	7.906E-13	6.002E-02	4.001E-01	5.999E-01	0.6390
36.644	12.317	4.824E-13	5.296E-02	3.531E-01	6.469E-01	0.5192
50.000	12.531	2.944E-13	4.286E-02	2.857E-01	7.143E-01	

Plotting the above data, one can easily see that at pH 6.5, the second hydrogen is not yet released in solution equilibrium until at a pH above 8.0 is attained.

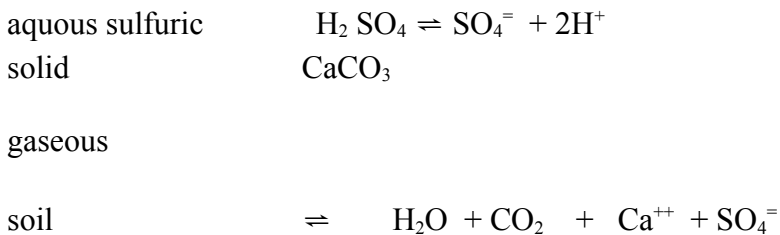


The amount of diprotic sulfurous acid required for land application to reduce bicarbonate buildup at completion is the same as that for diprotic sulfuric acid. This is because carbonate (CaCO_3) buildup in the soil is in a solid form, which interacts with both strong and weak acids driving the following soil reactions to completion.

Sulfurous



Sulfuric



Consequently based on the above pH curves, at solution equilibrium, say at pH 6.5, both hydrogen ions are released from sulfuric acid, whereas only one hydrogen ion is released from sulfurous acid. Hence, if one is applying acid based on a given solution pH at equilibrium, approximately twice as much sulfurous acid is required at pH 6.5 than sulfuric acid. To compensate and add more sulfuric acid to deliver the same acid at completion as sulfurous acid, it would have to be delivered at a lower pH of approximately 2, which can harm some soil plants and microorganisms. Thus, both weak and strong diprotic acid reactions go to completion forming calcium and sulfate ions, water, and carbon dioxide as the end reaction as the amount of calcium carbonate buildup in the soil is overly large and continually reacts with hydrogen ions from any source. Although the speed of reactions vary, ultimately the same amount of diprotic strong sulfuric acid reacts in the same manner as a like amount of diprotic weak sulfurous acid to break down the carbonate buildup and free up the soil.

The cost of double the sulfurous acid produced by SO₂ water injection to deliver delayed acid to break down soil bicarbonates/carbonates is computed as follows:

Assuming 454 grams per pound, and the atomic weight of sulfur as 32 gr./mole, there are 14.2 gram/moles of sulfur per pound. As sulfurous acid is diprotic, this provides 28.4 gr./moles of acid per pound. Assuming the cost of sulfur at \$215/ton/2000lbs/ton = \$0.1075/pound/28.4 gr.moles/lb. = \$0.0037852/mole

The cost of liquid sulfuric acid is computed as follows:

Assuming again 454 gram per lb, and the atomic weight of sulfuric acid is 98 gr./mole, there are 4.6 gr./moles of sulfuric acid per pound acid. As sulfuric acid is also diprotic, this provides 9.2 gr./moles of acid per pound. Assuming the cost of sulfuric acid at \$185.00/ton/2000 lbs/ton = \$0.0925/lb/9.2moles/lb = \$0.0100543/mole.

Thus, the material cost of sulfurous acid generated on site is 1/3 of that of sulfuric acid hauled to the site.

Based on the handling safety and cost advantages of sulfurous acid over sulfuric acid, and its ability to agglomerate and dewater suspended solids, sulfurous acid was selected for the Montalvo Infiltration tests.