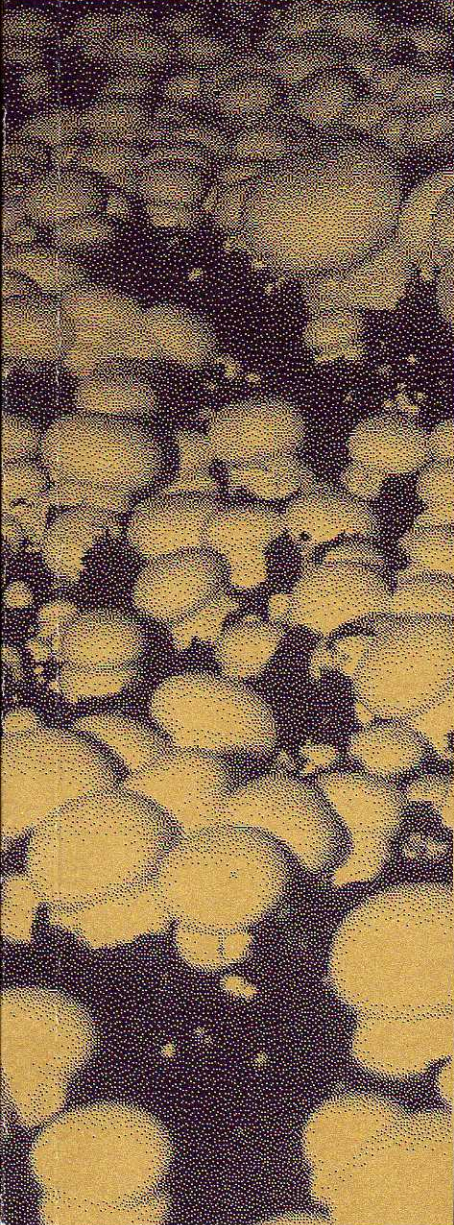


# **Environmental, Agricultural and Industrial Uses**



## **For Spent Mushroom Substrate From Mushroom Farms**

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Spent Mushroom  
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# The Roles of Spent Mushroom Substrate for the Mitigation of Coal Mine Drainage

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Spent mushroom substrate (SMS) has been used widely in coal mining regions of the USA as the primary substrate in constructed wetlands for the treatment of coal mine drainage. Such mine drainage is usually acidic and contains high concentrations of dissolved Fe and, less commonly, Mn. In laboratory and mesocosm studies, SMS has emerged as one of the substrates for mine water treatment, owing to its high organic carbon and limestone content. Processes that are responsible in waterlogged SMS for the successful treatment of acidity and Fe include limestone dissolution, sulfate reduction, and Fe oxidation. Provided the pH of the mine water does not fall below 3.0, SMS can be used in the mitigation plan. However, neither Mn nor dissolved ferric Fe appears to be treatable using reducing SMS wetlands. Care must be taken to create reducing conditions in the SMS wetlands, since if the SMS volume is too low, oxidizing conditions will obtain throughout the profile of the SMS, and eventually the SMS will fail to treat the water. Since after a few years much of the nonrefractive organic carbon in SMS will have been decomposed and metabolized, carbon supplementation can significantly extend the life of the SMS treatment wetland and improve water treatment. Several species of plants thrive in SMS under mine water conditions, but none improve water quality over the short term in excess of the treatment provided by SMS. Nitrogen leakage from SMS wetlands is not problematic after several weeks of operation.

## Introduction

Acidic mine drainage is a serious water pollution problem in coal mining regions, and is especially acute in Pennsylvania, West Virginia, Maryland, Colorado, Kentucky, Tennessee and Ohio, USA (Herlihy *et al.* 1990). Untreated, coal mine drainage can result in deleterious effects upon a wide range of aquatic biota, from benthic invertebrates and fish to vascular plants (Letterman and Mitsch 1978). Therefore, treatment of mine water is imperative, required by state and federal law, and takes a variety of forms. Conventional water treatment involves elevating the often acidic pH of the mine water through the application of chemical bases and exposure to oxygen in the form of a settling pond. The solubility of the two principal metal contaminants of coal mine drainage, Fe and Mn, is pH-dependent. Normally, Fe can be successfully treated by increasing the pH of the mine water to above neutrality; however, Mn treatment requires an excessively high pH (>9.0) in order to precipitate it from solution. Concerns of the mining industry regarding this conventional mode of water treatment primarily relate to cost and disposal. Since mine water generation is often perpetual, in the long run the costs of chemicals and labor are significant. In addition, a metal-laden sludge is generated in the settling pond, and the pond eventually fills with metal oxides and requires disposal. Concerns of the regulating agencies include a possible disruption of water treatment during off-hours, resulting in a discharge of untreated or partially treated mine water into watersheds, leading to ecosystem damage.

In response to the possibility of decreased treatment costs, many coal companies, utilities, and governmental agencies overseeing abandoned mine lands in the above coal mining states began to install constructed wetlands in the hope of providing passive water treatment. This trend began in the early 1980s and has continued to the present date. Most of these wetlands have been implemented in the state of Pennsylvania



(Wieder 1989), and the number in the USA alone has reached about 500 (Kleinmann and Hedin 1993). The success of these wetland treatment systems has varied. Generally, the treatment of Fe at circumneutral pH has been highly successful, the treatment of Fe at an acidic pH ( $<5.5$ ) has been partially successful, and the treatment of Mn has been the least successful (Kleinmann and Girts 1987, Hellier 1989, Kleinmann 1991).

Perhaps the two most important issues surrounding the use of wetlands to treat coal mine drainage pertain to predictability and the effective life span of constructed wetlands. Since these issues are currently under study and largely unknown, the current national regulatory policy in the USA is to deny bond release on sites employing wetland treatment systems, thereby requiring the landowner/mining company to ensure compliance with water quality laws long after the mining and site reclamation is completed. In order to better understand these crucial issues of predictability and longevity, several constructed wetland systems have been monitored over the last few years. In addition, several mesocosm wetland experiments have contributed to our knowledge in these areas.

In this paper, by posing and discussing key questions, we summarize some of the recent laboratory and mesocosm studies in an effort to bring the mushroom industry up to date on the uses and effects of spent mushroom substrate (SMS) on the mitigation of coal mine drainage. This review is by no means exhaustive, and is restricted mostly to studies from Appalachia in the USA.

#### How Does SMS Compare to Other Substrates in the Treatment of Coal Mine Drainage?

In the early 1980s, prior to the recognition of SMS as a viable material for use in water treatment, species of the moss genus *Sphagnum* were used in a variety of experiments. Generally, *Sphagnum* was found to effectively bind Fe and Mn. However, *Sphagnum* plants released  $H^+$  in the process (Gerber *et al.* 1985), thus lowering the pH of the water. In addition, the retention of Fe and Mn was found to be finite, with the end result the death of the plants (Kleinmann 1991). Thus, alternatives to *Sphagnum* were sought, including SMS, sawdust, peat (dead *Sphagnum*), and various manure and topsoil combinations.

A comparison of SMS with wood waste, sewage sludge, and peat at removing metals (especially Fe and Al) revealed that SMS significantly outperformed the other substrates at increasing alkalinity, pH, and supporting sulfate reduction (ref. in Spotts *et al.* 1992). Furthermore, after years of study, the U.S. Bureau of Mines has concluded that "the most successful and inexpensive substrate for the treatment of acidic mine water is spent mushroom compost," owing to its properties that encourage high rates of sulfate reduction and its high limestone component (Kleinmann 1991). While SMS appears to be the best suited substrate produced in large quantities, it is possible to formulate alternative mixtures based on the materials close to the site. Other organic materials will work in lieu of SMS, so long as resident sulfate-reducing bacterial populations are present, adequate supplies of labile carbon are present, and the substratum provides a circumneutral interstitial water pH (Wildeman *et al.* 1994). In severely acidic mine water containing predominantly dissolved ferric Fe ( $Fe^{3+}$ ), even SMS may be unable to sustain compliance water quality. In this regard, a field study in Kentucky compared the substrates *Sphagnum* peat, *Sphagnum* peat-limestone-fertilizer, sawdust, straw-manure, and SMS for capacity to treat mine water at pH 2.89, 119 mg Fe  $L^{-1}$  and 19 mg Mn  $L^{-1}$  (Wieder 1993). Although none of the substrates was found to be suitable for treating this effluent over the long term, researchers found that SMS was the only substrate to accumulate Fe sulfides at depth in the wetlands, accumulated more sul-



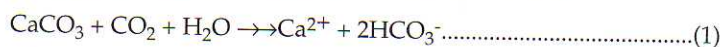
fidic Fe than any other substrate, and was the only substrate tested that did not exhibit biologically-mediated  $\text{Fe}^{3+}$  reduction (Taddeo and Wieder 1991, Vile and Wieder 1993). Fortunately, most coal mine effluents contain predominantly dissolved ferrous Fe ( $\text{Fe}^{2+}$ ), which is addressable using SMS wetlands.

#### What Are the Physical Components of SMS That Make It Useful in Treating Coal Mine Drainage?

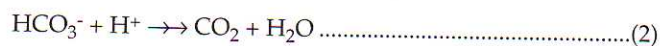
The chemical composition of SMS from central Pennsylvania, USA is relevant, since much of the SMS used in treatment wetlands comes from this region. SMS has a circumneutral pH, which is desirable from the standpoint of neutralizing mine water that more often than not is acidic. In addition, the high organic carbon and calcium contents are notable (Table 1). Perhaps the four most important ingredients in SMS relevant to mine water treatment are limestone, gypsum, organic matter and bulk. Limestone ( $\text{CaCO}_3$ ) assists in the buffering of pH, and is often used in addition to SMS as a wetland base. The dissolution of gypsum ( $\text{CaSO}_4$ ) present in SMS generates dissolved sulfate ( $\text{SO}_4^{2-}$ ), which is integral to the process of sulfate reduction. Both oxidative and reductive processes involved in the retention of metals in SMS wetlands depend in part upon microbial populations that require a source of metabolizable carbon. Thus, the high organic carbon content of SMS provides readily usable carbon to fuel metal oxidation and sulfate reduction reactions. Finally, in order to serve as a repository for metals, particularly metal sulfides, the "bulk" of SMS detains the sulfides, ensuring that movement is restricted.

#### What Are the Processes That Occur in SMS Wetlands That Lead to Fe Retention and pH Elevation, and in What Phase is Fe Deposited in SMS Wetlands?

Processes occurring in SMS wetlands that play a major role in the mitigation of Fe and pH include the dissolution of limestone, sulfate reduction, and Fe oxidation. Dissolution of limestone produces alkalinity (in the form of  $\text{HCO}_3^-$ ) that is probably equivalent to that alkalinity produced by sulfate reduction (Dvorak *et al.* 1992):

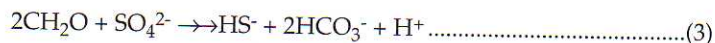


The bicarbonate produced can then consume free hydrogen ions, thus elevating pH in acidic mine water:



When SMS is exposed to acidic mine water,  $\text{Ca}^{2+}$  is leached, and thus appears in elevated concentrations in the effluent relative to the influent water. The difference between the influent and effluent calcium concentrations can be used as an indicator of the amount of alkalinity generated from limestone dissolution (as long as the calcium from the dissolution of gypsum is accounted for).

Sulfate reduction occurs in anaerobic sediments, and may be described by the following overall reaction:



where  $\text{CH}_2\text{O}$  represents the decomposable organic matter present in SMS. If ferrous iron is present in the interstitial water, then the following reaction rapidly takes place:



Thus, the reduction of sulfate ( $\text{SO}_4^{2-}$ ) produces  $\text{HS}^-$ , which combines with ferrous Fe ( $\text{Fe}^{2+}$ ) to produce a solid iron sulfide ( $\text{FeS}$ ). In completely anoxic chambers, the rate of



sulfate reduction was estimated at 377 nmol/cm<sup>3</sup> SMS/day (Dvorak *et al.* 1992). A series of mesocosm experiments in which fresh SMS was exposed to a variety of sulfur and iron compounds has been particularly revealing in this area (Tarutis 1993). Waterlogged SMS is capable of forming an entirely anoxic zone than is amenable to sulfate reduction. Even after adding synthetic mine water to columns of SMS, the pH was effectively buffered. Maintenance of a circumneutral pH after acidification was attributed to (i) sulfate reduction and (ii) limestone dissolution (calcium release) from the SMS. The addition of sulfate to the SMS columns did not affect the rate of removal of Fe or Mn, suggesting that adequate amounts of sulfate are present in the SMS deriving from the dissolution of gypsum. Therefore, sulfate concentrations should not limit sulfate reduction in SMS. The greatest water treatment, as measured by lowest concentrations of interstitial Fe and Mn, occurs near the bottom of the columns of SMS. This region corresponds with the highest sulfide concentrations, again strongly suggestive of sulfate reduction. Similarly, sulfate reduction has been implicated in laboratory tests with SMS, which resulted in successful treatment of Fe, Cu and Zn (Machemer and Wildeman 1992). These findings also pertain in simulated wetlands containing substrates other than SMS (*e.g.*, Calabrese *et al.* 1991). However, it should be noted that researchers found no evidence of biological sulfate reduction in SMS wetlands exposed to mine water containing dissolved ferric Fe (Vile and Wieder 1993).

The phase of the metal that is retained and stored in a treatment wetland is critical to its long term effectiveness, and largely derives from the dominant processes that obtain in SMS wetlands. When Fe or Mn occur in the exchangeable or oxide-bound forms, they may eventually become unstable and enter the water column again as dissolved divalent ions (Tarutis and Unz 1990). However, when these metals occur as a sulfide or in a crystalline form, stability, while not assured, is more likely. Sulfides are preferred to oxides as the repository of wetland metals because sulfides are more stable, do not undergo reduction that liberates ferrous iron in the pore water that may eventually exit the wetland, and occupy less space (Hammack *et al.* 1994). While previous studies employing substrates other than SMS found that most of the Fe in mesocosm wetlands is deposited as an oxide (Wieder *et al.* 1990), recent studies using SMS reached different conclusions.

When SMS is exposed to acidic mine water containing Fe for several weeks and then extracted for determination of Fe phases, more than 65 percent of all retained iron in the lower half of the wetland was bound as a sulfide and/or bound to organic compounds (Stark *et al.* 1995a). These findings are consistent with those of Hedin and Nairn (1993), who reported that 62 percent of the alkalinity generated in field SMS wetlands was traceable to sulfate reduction, and those of Dvorak *et al.* (1992), who found nearly all of the Fe in SMS anoxic chambers was deposited as sulfides.

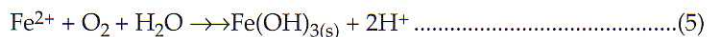
However, at the surface of the SMS,

Table 1.  
Chemical composition of spent mushroom substrate. All units are in percent dry weight except pH, bulk density, porosity, and C:N ratio (from Tarutis 1993).

Parameter	% Dry Weight
pH	7.1 (S.U.)
Bulk Density	0.27 g cm <sup>-3</sup>
Porosity	0.85 (dimensionless)
Aluminum (Al)	0.51
Calcium (Ca)	6.20
Iron (Fe)	0.70
Magnesium (Mg)	0.71
Manganese (Mn)	0.28
Organic Carbon	15.92
Organic Nitrogen	1.55
Phosphorus	0.37
Potassium (K)	1.47
Sodium (Na)	0.13
Sulfur (S)	0.21
Carbon:Nitrogen Ratio	10.27



especially near the wetland inlet, where SMS is first contacted by the raw mine water, the oxidation of iron is an important process:



In addition to ferric oxide ( $\text{Fe}(\text{OH})_3$ ), goethite ( $\alpha\text{-FeOOH}$ ), ferrihydrate ( $5\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ), hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) and crystalline Fe can form (Tarutis 1993, Snoeyink and Jenkins 1980). This results in a mass of iron in a crystalline or amorphous form that accumulates in the upper wetland and surficial zone (Tarutis and Unz 1994a, Faulkner and Richardson 1990). The oxidation of ferrous Fe above can be biologically mediated through the action of *Thiobacillus ferrooxidans*, or formed abiotically.

In SMS wetlands in which an oxic and an anoxic zone exist, Fe may be initially deposited at the surface of the SMS as an oxide, and as burial proceeds, Fe reduction occurs that may eventually result in the formation of sulfides. In an effort to simulate the SMS substrate present in a constructed wetland receiving mine water containing Fe, amorphous Fe oxides and crystalline Fe oxides were added to the surface of the SMS columns, and interstitial Fe was measured in the SMS (Tarutis 1993). Crystalline Fe was found to be much less reactive (reducible and liberating ferrous Fe) than amorphous oxides, probably resulting from a lower surface area (Canfield 1989). Thus, the "yellow-boy" commonly observed on the surface of wetlands (amorphous Fe oxides) gradually reduces with depth in SMS wetlands, producing ferrous Fe in the interstitial water of the wetland. The production of ferrous Fe in this manner (*i.e.*, through Fe reduction) can prove to be advantageous or deleterious to wetland function. In simulation experiments using SMS columns, the ferrous Fe liberated in this fashion quickly combined with sulfide to form a black Fe monosulfide, thus removing Fe from solution. Should, however, conditions not be optimal for sulfate reduction in an SMS wetland, the production of ferrous Fe through Fe reduction of amorphous Fe oxides could result in the release and upward movement of ferrous Fe into the overlying surface water atop the SMS, degrading the water quality further (Vile and Wieder 1993). In field wetlands constructed of SMS, provided the wetland is designed properly and sized according to flow and metal load specifications, most of the beneficial processes outlined above occur (Williams *et al.* 1993, Karathanasis and Thompson 1991).

#### Does SMS Leachate Release Nitrogen Into Solution?

Some concern exists over whether a constructed wetland containing large amounts of SMS will export nitrogen to receiving streams. To address this question, the effluent of SMS wetlands was sampled and analyzed for nitrate-N and ammonia-N. Of the eight SMS wetlands, none exhibited outlet nitrate-N levels in excess of  $10 \text{ mg L}^{-1}$  (the legal limit to discharge), with a range of  $0.02$  to  $9.3 \text{ mg L}^{-1}$ . At the conclusion of the experiment (230 days), the highest  $\text{NO}_3\text{-N}$  was  $0.105 \text{ mg L}^{-1}$ , and all of the outlet concentrations were lower than the source ( $1.63 \text{ mg L}^{-1}$ ). As for ammonia ( $\text{NH}_3\text{-N}$ ), at Day 10, two of the eight wetlands had values in excess of  $1 \text{ mg L}^{-1}$ :  $11.6$  and  $21.2 \text{ mg L}^{-1}$ , respectively. However, on the last two sample dates, all of the eight wetlands had outlet concentrations at undetectable levels ( $<0.005 \text{ mg L}^{-1}$ ). These data indicate that it may be instructive to sample more frequently during the early weeks of a newly constructed wetland in which SMS is used, but that nitrate and ammonia discharges from a wetland containing SMS are virtually nonexistent after a few months (Wuest *et al.* 1992).

#### Under an Oxidizing Regime, How Much Fe, Mn and $\text{H}^+$ Can SMS Retain?

When SMS is exposed under oxidizing conditions to acidic mine water containing  $50 \text{ mg Fe L}^{-1}$  and  $25 \text{ mg Mn L}^{-1}$ , it has a finite capacity to retain these three ions. After



continuous exposure to such mine water at relatively high flow rates in laboratory flow-through chambers, the SMS was found to saturate at  $5.56 \text{ g Fe L SMS}^{-1}$ ,  $0.15 \text{ g Mn L SMS}^{-1}$ , and  $281 \mu\text{eq H}^+ \text{ L SMS}^{-1}$ . That is, one liter of SMS held about 5 grams of Fe, negligible Mn, and 281 microequivalents of hydrogen ions. Once these levels were reached in the SMS, the influent water concentrations of Fe, Mn and  $\text{H}^+$  equaled the effluent water concentrations: it no longer treated the water (Stark *et al.* 1994). These retention maxima are similar to those reported for peat, and have led some scientists to conclude that wetlands constructed of SMS will eventually fail (Wieder 1993).

#### Is It Possible to Extend the Ability of SMS to Treat Mine Water?

Several researchers have demonstrated that it is possible to create an anoxic reducing zone in waterlogged SMS, simulating the reducing zone of natural wetlands (*e.g.*, Dvorak *et al.* 1992, Tarutis and Unz 1994b). Granting that SMS has a finite capacity to retain Fe, Mn and  $\text{H}^+$  ions (the most common pollutants in coal mine drainage) under oxidizing conditions, the question was raised as to what would happen to this same "saturated SMS" if inflow rates were dropped substantially. By lowering the inflow rates to the chambers containing SMS, it was hoped to change the redox profile from one of oxidizing (high Eh) to one of reducing (low Eh), thereby creating an environment conducive to sulfate-reducing bacteria.

When such saturated SMS, laden with Fe, Mn and  $\text{H}^+$  ions, was reexposed to mine water ( $\text{pH } 4.0$ ,  $60 \text{ mg Fe L}^{-1}$ ,  $0 \text{ mg Mn L}^{-1}$ ) under a low flow regime, a gradual transformation of the redox profile occurred. During the first 30 days of this experiment, Fe was flushed from the system, as oxides of Fe were reduced, resolubilized, and then exported from the SMS. However, after 30 days, the SMS began to retain about 50 percent of the Fe it was receiving. In addition, it began to elevate the pH from 4.0 to 6.0. By the end of the 114-day experiment, on a net basis the capacity of the SMS to retain Fe was increased and apparently stable under the decreased flow conditions. Under these experimental conditions, researchers concluded that SMS can retain Fe indefinitely, providing adequate carbon sources are present to fuel bacterial sulfate reduction. This finding contradicted previous assertions that saturated SMS could not be rejuvenated. In addition, it underscored the need for accurate sizing coefficients for constructed SMS wetlands treating mine water: a larger area is equivalent to a lower flow rate (Stark *et al.* 1994).

#### Can a Wetland of SMS Sustain Fe Retention?

The answer here appears to be a cautionary "yes." There is no question that an SMS wetland can sustain Fe retention over the course of an experiment lasting up to a year. At an Fe load of  $5.4 \text{ g Fe m}^{-2} \text{ d}^{-1}$ , which is over seven times the recommended wetland Fe load according to Brodie *et al.* (1988), SMS wetlands retained nearly 100 percent of the Fe. The Fe treatment at this loading was so good, in fact, that researchers had to triple the loading (to  $16.2 \text{ g m}^{-2} \text{ d}^{-1}$ ) in order to detect experimental differences among treatments. Provided that carbon and sulfate are not limiting, and the Fe load is within reason, we have reason to believe that such SMS wetlands can sustain Fe retention indefinitely (Stark *et al.* 1991).

Using a set of 200 L reactors filled with SMS and receiving a constant load of mine water, researchers at the U.S. Bureau of Mines demonstrated that (i) SMS can create anoxic conditions throughout its depth profile, (ii) such an SMS enclosed system is capable of remarkable metal removal efficiencies of nearly 100 percent, and (iii) nearly all of the Fe loaded to the SMS reactors was deposited as Fe sulfides in the SMS (Dvo-



rak *et al.* 1992). Ferric oxides were reduced to ferrous Fe, and pH was elevated from 3.7 to 6.9, with the process of sulfate reduction implicated. As previously mentioned, in very acidic mine water (pH <3.0), the role of sulfate reduction in the treatment of Fe in SMS wetlands is greatly reduced, and it is doubtful if any substrate, including SMS, is capable of sustained Fe retention (Vile and Wieder 1993).

The decomposition of organic matter present in SMS is absolutely critical to the capacity of SMS to retain metals. Since only a thin oxic layer exists on the surface of the substrate when SMS is saturated with water (and the SMS wetland is sized properly), most of the decomposition in SMS is anaerobic. When carbon is not limiting, reducing conditions persist, and amorphous Fe oxides are not abundant in the sediments, anaerobic decomposition and sulfate reduction will proceed. During the initial three years following wetland construction with SMS, anaerobic decomposition will produce sufficient labile carbon to drive sulfate reduction. However, after about three years, mostly refractory organic matter will remain, leaving the SMS dependent upon the decomposition products of plants present in the wetland. Alternatively, some form of carbon supplements can be added to the wetland to fuel sulfate reduction (Tarutis 1993).

#### What Are the Effects of Adding a Supplemental Carbon Source to a Wetland of SMS?

Evidence exists that mine water treatment can be improved in SMS wetlands by supplementing with external carbon and nutrient sources. For example, the carbon-rich supplements dairy whey, brewers' yeast, beet molasses, peach peelings, sodium lactate and polylactic acid are under current analysis for their stimulatory effect on sulfate reduction (Borek *et al.* 1994). In a mesocosm study, fresh sweet cheese whey was selected for study and added near the inlet to SMS wetlands treating mine water. After a period of several weeks, the SMS wetlands receiving the whey were removing Fe and lowering sulfate to a greater extent than unsupplemented SMS wetlands (Stark *et al.* 1991). Furthermore, the effect of adding whey to SMS wetlands was manifested in a significant promotion of both sulfate reduction and iron oxidation in the SMS sediments (Stark *et al.* 1995a).

It is possible that wetland managers may consider using SMS itself as a carbon supplement to SMS wetlands after a few years. Drawbacks to this approach, however, include that SMS takes up more space than a liquid supplement, and would require much more volume than a concentrated liquid alternative like whey. Space is an important consideration since the rate of sediment accumulation at constructed wetlands treating Fe determines in part the longevity of the system.

#### Can a Wetland of SMS Sustain Mn Retention?

The answer here is an equivocal "no." In mesocosm experiments using SMS wetlands, Mn retention has not been sustainable, despite three full-scale attempts (U.S. Bureau of Mines 1993). Mn is retained over the first half of the exposure, but eventually the SMS begins to "leak" Mn, and ultimately the SMS saturates and can hold no more Mn. Under reducing conditions present in mesocosm SMS wetlands, Mn cannot effectively precipitate as an oxide, sulfide, or even as a carbonate, each of which would potentially represent a stable Mn phase. However, laboratory experiments in which SMS is placed under reducing conditions resulted in good Mn retention (Machemer and Wildeman 1992), and bioreactors using SMS exhibit short-term Mn retention under reducing conditions (Dvorak *et al.* 1992). In addition, reports of field wetlands that sustain Mn retention exist, and thus SMS wetlands exposed to oxidizing conditions may exhibit long term Mn retention that is at present less well known (Hedin and



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Nairn 1993). Therefore, additional studies are needed before SMS can be recommended for the treatment of Mn in mine waters.

### What is the Effect of Passing Mine Water through an SMS Wetland on pH, Ca Dissolved Oxygen, Redox Potential Sulfate, Acidity and Alkalinity?

Insofar as creating conditions favorable for the retention of Fe, the effects of SMS on the parameters above are positive. For the sustained retention of Fe in SMS wetlands, reducing conditions are necessary, at least below the surface of the SMS. In order for sulfate reduction to flourish, anoxic conditions are required, including low dissolved oxygen, negative redox potentials, and a circumneutral pH. Upon passing mine water through SMS wetlands at a flow rate and surface water depth low enough to create reducing conditions, the following effects have been repeated several times in the mesocosms. First, the redox potentials become highly negative in the interstitial water. Second, the pH, which is acidic at the SMS surface, becomes elevated to  $>7.0$  in the interstitial water. Third, dissolved oxygen levels in the interstitial water fall to near zero. This combination of pore water conditions provides an ideal habitat for sulfate reduction, and therefore Fe retention (Stark *et al.* 1995b). Concerns about low dissolved oxygen levels exiting SMS wetlands and entering watersheds can be remedied by including an impoundment downstream of the constructed wetland system to oxygenate the water.

Generally, after passage through an SMS wetland in which reducing conditions obtain, acidity, alkalinity, sulfate and sulfide levels will be affected. Owing to the action of sulfate-reducing bacteria in conjunction with limestone dissolution from the SMS, acidity will be decreased and alkalinity will be elevated in the outlet water. Similarly, sulfate will be slightly lowered while sulfide levels may be slightly elevated. With respect to calcium, the usual effect of passing mine water through SMS will be a temporary export of Ca from SMS. This is due to the presence of significant amounts of Ca incorporated in the SMS as gypsum ( $\text{CaSO}_4$ ) and as limestone ( $\text{CaCO}_3$ ). Under acidic conditions, gypsum and limestone dissolve, allowing the dissociated Ca ions to leave the SMS. After some weeks, an equilibrium is reached, whereby inlet Ca is equivalent to outlet Ca.

### When SMS Is Planted With Aquatic/Subaquatic Species of Seed Plants, Is Water Treatment Enhanced?

Three species of plants known to tolerate coal mine drainage, *Typha latifolia* L. (cattail), *Leersia oryzoides* (L.) Sw. (rice cut grass), and *Juncus effusus* L. (common rush), were planted in SMS and exposed to simulated mine water for one growing season. The mine water contained 50-150 mg Fe  $\text{L}^{-1}$  at a pH of 4.0. These species all thrived under the harsh conditions of direct exposure to acidic mine water. By the end of the season, the root masses, especially of *Leersia* and *Typha*, had become so thick that a "root-bound" condition was occurring.

However, the no-plant control wetland consisting only of SMS treated mine water as well as the planted SMS wetlands. Simply by passing mine water through SMS, equivalent Fe retention, sulfate reduction and pH elevation to that in planted SMS were observed over the growing season. At the conclusion of the experiment, the SMS sediments were extracted to see what phase of Fe was retained. Once again, no differences were found between the planted vs. the unplanted SMS insofar as the partitioning of metals and the effects of carbon supplementation. Although cattails are almost exclusively used in the Appalachian region in constructed wetlands treating acidic mine water, *Typha latifolia* exhibited no better water treatment than the unplanted SMS, SMS



with common rush, or SMS with cut grass (Stark *et al.* 1995a).

Despite the negative findings with respect to the effects of plants in SMS on mine water treatment, we must be cautious in dismissing vegetation as having no role in water treatment. First, the positive effects of plants may go undetected in mesocosm experiments conducted for one, or a few, growing seasons. In the long term, a wetland without plants is likely to suffer from inadequate carbon sources to fuel sulfate reduction and biologically mediated iron oxidation. When saturated SMS was reexposed to mine water at a lower flow rate (discussed above), the SMS exhibited characteristics leading researchers to believe that its labile carbon reserves were declining. Furthermore, total vegetative cover was cited as the principal factor in preventing metal release from constructed wetlands during storms in Tennessee (Taylor *et al.* 1993).

### Summary and Recommendations

Spent mushroom substrate has proven to be perhaps the ideal choice for the passive treatment of coal mine drainage using wetlands or chamber treatment methods. It appears to be superior to *Sphagnum* peat, sawdust, and straw + manure systems. Under oxidizing conditions, SMS has a finite capacity to retain Fe, Mn and H<sup>+</sup> ions. This capacity can be extended indefinitely by creating reducing conditions in the SMS. Under reducing conditions, SMS can sustain Fe retention, elevate pH, reduce acidity and produce alkalinity. However, in wetland mesocosms, SMS has not sustained Mn retention. Over the short term period of one growing season, the species or presence of plants in SMS did not affect mine water treatment. Nevertheless, the three species tested exhibited rapid growth in SMS. Supplementation of SMS with whey proved to have beneficial effects on mine water treatment, primarily stimulating sulfate reduction and Fe oxidation. The dominant phase of Fe retained in SMS reducing wetlands is probably of sulfidic origin. Spent mushroom substrate has played a major role in the evolution of constructed wetland treatment systems for coal mine drainage. Especially in Pennsylvania, the availability of SMS has resulted in hundreds of wetlands installed with SMS as a base in which plants are grown. Based upon studies in the laboratory and greenhouse, SMS should continue to serve as a primary base for constructed wetlands treating Fe. However, the treatment of Mn in SMS wetlands needs to be optimized.

### References

- Borek, S.L., D.H. Dvorak, R.W. Hammack and H.M. Edenborn. 1994. Evaluation of organic additives used to enhance bacterial sulfate reduction in mine water treatment systems. p. 404 *In: Proceedings, International Land Reclamation and Mine Drainage Conference and Third International Conference on the Abatement of Acidic Drainage, Vol. 2: Mine Drainage.* Pittsburgh, Pennsylvania, USA.
- Brodie, G.A., D.A. Hammer and D.A. Tomljanovich. 1988. Constructed wetlands for acid drainage control in the Tennessee Valley. p. 325-331 *In: Mine Drainage and Surface Mine Reclamation. Vol. 1: Mine Water and Mine Waste.* Bureau of Mines Information Circular 9183, Pittsburgh, Pennsylvania, USA.
- Calabrese, J.P., A.J. Sexstone, D.K. Bhumbla, G.K. Bissonnette and J.C. Sencindiver. 1991. Application of constructed cattail wetlands for the removal of iron from acid mine drainage. p. 559-575 *In: Sirois, L. (Ed.). The Abatement of Acidic Drainage. Vol. 3.* Montreal, Canada.
- Canfield, D.E. 1989. Reactive iron in marine sediments. *Geochim. Cosmochim. Acta* 53: 619-632.
- Dvorak, D.H., R.S. Hedin, H.M. Edenborn and P.E. McIntire. 1992. Treatment of metal-contaminated water using bacterial sulfate reduction: results from pilot-scale reactors. *Biotech. and Bioeng.* 40: 609-616.
- Faulkner, S.P. and C.J. Richardson. 1990. Iron and manganese fractionation in constructed wet-



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- lands receiving acid mine drainage. p. 441-450 In: Cooper, P.F. and B.C. Findlater (Ed.). *Constructed Wetlands in Water Pollution Control*. Pergamon Press, Oxford, UK.
- Gerber, D.W., J.E. Burris and R.W. Stone. 1985. Removal of dissolved iron and manganese ions by a *Sphagnum* moss system. p. 365-372 In: Brooks, R., D. Samuel and J. Hill (Ed.). *Wetlands and Water Management on Mined Lands*. The Pennsylvania State University, University Park, Pennsylvania, USA.
- Hedin, R.S. and R.W. Nairn. 1993. Contaminant removal capabilities of wetlands constructed to treat coal mine drainage. p. 187-195 In: Moshiri, G.A. (Ed.). *Constructed Wetlands for Water Quality Improvement*. Lewis Publishers, Boca Raton, Florida, USA.
- Hellier, W.W., Jr. 1989. Constructed wetlands in Pennsylvania: an overview. p. 600-611 In: Salley, J., G.L. McCreedy and P.L. Wichlacz (Ed.). *Biohydrometallurgy: Proceedings of the International Symposium*. Jackson Hole, Wyoming, USA.
- Herlihy, A.T., P.R. Kaufman, M.E. Mitch and D.D. Brown. 1990. Regional estimates of acid mine drainage impact on streams in the mid-Atlantic and southeastern United States. *Water, Air, & Soil Poll.* 50: 90-107.
- Karathanasis, A.D. and Y.L. Thompson. 1991. Metal speciation and retention patterns in a high metal load acid mine constructed wetland of southeastern Kentucky. p. 485-498 In: Sirois, L. (Ed.). *The Abatement of Acidic Drainage*. Vol. 2. Montreal, Canada.
- Kleinmann, R.L.P. 1991. Biological treatment of mine water — an overview. p. 27-42 In: Sirois, L. (Ed.). *The Abatement of Acidic Drainage*. Vol. 4. Montreal, Canada.
- Kleinmann, R. and M. Girts. 1987. Acid mine water treatment in wetlands: an overview of an emergent technology. p. 255-261 In: Reddy, K. and W. Smith (Ed.). *Aquatic Plants for Water Treatment and Resource Recovery*. Magnolia Publishing Inc., Orlando, Florida, USA.
- Kleinmann, R.L.P. and R.S. Hedin. 1993. Treat mine water using passive methods. *Pollution Engineering*, Aug: 20-22.
- Letterman, R.D. and W.J. Mitsch. 1978. Impact of mine drainage on a mountain stream in Pennsylvania. *Environ. Pollut.* 17: 53-73.
- Machemer, S.D. and T.R. Wildeman. 1992. Adsorption compared with sulfide precipitation as metal removal processes from acid mine drainage in a constructed wetland. *J. Contam. Hydrol.* 9: 115-131.
- Snoeyink, V.L. and D. Jenkins. 1980. *Water Chemistry*. John Wiley and Sons, New York, U.S.A.
- Spotts, E., T.S. Mitchell, C.T. Hoschouer and W.M. Schafer. 1992. Evaluation of organic substrates for use in wetlands constructed to treat acid mine drainage. p. 170-182 In: *Proceedings, Planning, Rehabilitation and Treatment of Disturbed Lands*. Billings, Montana, USA.
- Stark, L.R., W.R. Wenerick, F.M. Williams, S.E. Stevens, Jr., and P.J. Wuest. 1994. Restoring the capacity of spent mushroom compost to treat coal mine drainage by reducing the inflow rate: a microcosm experiment. *Water, Air & Soil Pollut.* 75: 405-420.
- Stark, L.R., W.R. Wenerick, F.M. Williams and P.J. Wuest. 1995b. The effects of pH, flow rate, and carbon supplementation on manganese retention in mesocosm wetlands. *J. Environ. Qual.*: in press.
- Stark, L.R., W.R. Wenerick, P.J. Wuest, F.M. Williams and S.E. Stevens, Jr. 1991. Adding a carbon supplement to simulated treatment wetlands improves water quality. p. 465-483 In: Sirois, L. (Ed.). *The Abatement of Acidic Drainage*. Vol. 2. Montreal, Canada.
- Stark, L.R., F.M. Williams, W.R. Wenerick, P.J. Wuest and C.A. Urban. 1995a. The effects of carbon supplementation and plant species on iron retention in mesocosm treatment wetlands. *Wetlands* (in press).
- Taddeo, F.J. and R.K. Wieder. 1991. The accumulation of iron sulfides in wetlands constructed for acid coal mine drainage treatment. p. 529-547 In: Sirois, L. (Ed.). *The Abatement of Acidic Drainage*. Vol. 3. Montreal, Canada.
- Tarutis, W.J., Jr. 1993. Iron and Manganese Diagenesis in Constructed Wetlands Receiving Mine Drainage. Ph.D. Thesis, Pennsylvania State University, University Park, Pennsylvania, USA. 143 p.
- Tarutis, W.J., Jr. and R.F. Unz. 1994a. Soil color variations along an iron oxide gradient in a mine drainage treatment wetland. *Wetlands* 14: in press.
- Tarutis, W.J., Jr. and R.F. Unz. 1994b. Iron and manganese dynamics in laboratory wetland mesocosms: implications for coal mine drainage treatment. p. 371-378 In: *Proceedings, International Land Reclamation and Mine Drainage Conference and Third International Conference on the Abatement of Acidic Drainage*, Vol. 1: Mine Drainage. Pittsburgh, Pennsylvania, USA.
- Tarutis, W.J., Jr. and R.F. Unz. 1990. Chemical diagenesis of iron and manganese in constructed wetlands receiving acidic mine drainage. p. 429-440 In: Cooper, P.F. and B.C. Findlater (Ed.).



- Constructed Wetlands in Water Pollution Control. Pergamon Press, Oxford, UK.
- Taylor, H.N., K.D. Choate and G.A. Brodie. 1993. Storm event effects on constructed wetlands discharges. p. 139-145 *In*: Moshiri, G.A. (Ed.). Constructed Wetlands for Water Quality Improvement. Lewis Publishers, Boca Raton, Florida.
- U.S. Bureau of Mines. 1993. Manganese retention in simulated wetlands: an exploration of design parameters. Final Report, Contract No. JO309014, U.S. Department of the Interior, Abandoned Mine Lands Program, Pittsburgh, Pennsylvania, USA. 74p.
- Vile, M.A. and R.K. Wieder. 1993. Alkalinity generation by Fe(III) reduction versus sulfate reduction in wetlands constructed for acid mine drainage treatment. *Water, Air & Soil Pollut.* 69: 425-441.
- Wieder, R.K. 1989. A survey of constructed wetlands for acid coal mine drainage treatment in the eastern United States. *Wetlands* 9: 299-315.
- Wieder, R.K. 1993. Ion input/output budgets for five wetlands constructed for acid coal mine drainage treatment. *Water, Air & Soil Pollut.* 71: 231-270.
- Wieder, R.K., M. Linton and K. Heston. 1990. Laboratory mesocosm studies of Fe, Al, Mn, Ca, and Mg dynamics in wetlands exposed to synthetic acid coal mine drainage. *Water, Air, & Soil Pollut.* 51: 181-196.
- Wildeman, T.R., J. Cevaal, K. Whiting, J. Gusek and J. Scheuering. 1994. Laboratory and pilot-scale studies on the treatment of acid rock drainage at a closed gold-mining operation in California. p. 379-386 *In*: Proceedings, International Land Reclamation and Mine Drainage Conference and Third International Conference on the Abatement of Acidic Drainage, Vol. 2: Mine Drainage. Pittsburgh, Pennsylvania, USA.
- Williams, F.M., L.R. Stark and C. Urban. 1993. Modelling the Dynamics of Metal Retention in Simulated Freshwater Wetlands. Final Report, Project PSU-08. National Mine Land Reclamation Center-Eastern Region. Pennsylvania State University, University Park, Pennsylvania. 41p.
- Wuest, P.J., L.R. Stark, W.R. Wenerick and C.C. Bahler. 1992. Prospective uses of Spent Mushroom compost in Pennsylvania Industries. Final Report, Pennsylvania Department of Agriculture, Harrisburg, Pennsylvania. 56p.