PASSIVE TREATMENT OF MINING INFLUENCED WATER: AN OVERVIEW OF AVAILABLE TECHNOLOGIES AND THE PERIODIC TABLE

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INTRODUCTION

There are basically three kinds of passive treatment technologies for treating mining influenced water (MIW):

- **Abiotic, Limestone-based** *methods for treating net-acidic MIW have been effective in adding alkalinity; a subset of this method uses a semi-biological zone to condition MIW for subsequent limestone dissolution.*
- **Biochemical Reactors** *(BCRs) are typically applicable to metal mine drainage with high acidity and a wide range of metals; this technology can function with or without plants.*
- **Aerobic Cells** *containing cattails, other plants, and algae are typically applicable to MIW where iron and manganese and mild acidity are problematic and/or only trace concentrations of heavy metals occur. This method also can be used to polish biochemical oxygen demand (BOD) from BCR effluent and adsorb trace metals on to iron or manganese oxides.*

Most passive treatment systems employ one or more of these cell types. For novice designers, selecting the proper technologies and arranging them in a logical sequence is a problem. This paper should provide baseline guidance. While the primary focus of the article is mining influenced water, the concepts presented may be readily transferable to process waters related to oil and gas operations.

The technical community of regulators and engineers that specializes in passive water treatment should be familiar with the passive treatment "decision tree" that was published by the former U.S. Bureau of Mines about 20 years ago. The decision tree was originally intended to address MIW from coal mines. Since then, however, the breadth of passive treatment has expanded to embrace precious and base metal mines, uranium mines, and even gravel pits. Each MIW has its unique signature, either imposed by the natural geochemical conditions of the ore body and surrounding mine waste, or by resource recovery processes that may include heap leaching or traditional hydrometallurgical technologies. In the context of the elements of the periodic table, the decision tree certainly could be improved, as it was originally developed to focus on coal geology derived MIW, which typically contains acidity/alkalinity, iron, aluminum and

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manganese. For example, the expanded decision tree could consider residual ammonia or nitrates from blasting, cyanide from heap leach pad rinsing, trace amounts of selenium, or other parameters that may require passive treatment at a given mine, coal or otherwise. However, developing an individual decision tree for each MIW element or suite of elements and their species would be a daunting task and would probably introduce more confusion where simplicity is desired.

With apologies to Dmitri Ivanovich Mendeleev, a "Periodic Table of Passive Treatment" could become a useful design tool to satisfy the need to embrace a larger range of MIW chemistries. A single "modified" periodic table was originally presented in an earlier paper (Gusek, 2009); it focused on identifying passive treatment methods that have been observed to work on specific elements or species of elements typically found in MIW. The concept was subsequently revisited (Gusek, 2013) with a closer focus on adsorption phenomena and other processes. This article provides a summary of the two "periodic table" papers and presents the advantages and disadvantages of the various passive treatment components.

In summary, this article is an introduction to the wide range of remediation design options available to practitioners of passive treatment. It also includes a recommended "staged" approach of laboratory-, bench-, and pilot-scale testing protocols which have been shown to support successful designs, especially for MIWs with complex chemistry.

KEYWORDS

sustainability; constructed wetlands; biochemical reactors; heavy metals; radionuclides; acidity; alkalinity; process selection; Mother Nature; geochemistry; oxidation-reduction; adsorption

A SHORT HISTORY OF PASSIVE TREATMENT DEVELOPMENT

Nature has been passively removing dissolved metals from acidic to net alkaline water for eons; examples include pyrite occurrences in coal beds and bog iron ore (limonite) deposits. Wetlands and bogs have long been recognized as nature's method of improving water quality. Contaminant reductions can occur through the precipitation of hydroxides, precipitation of sulfides and pH adjustments and other reactions/processes. Local conditions, oxidation state, and water and substrate chemistries dictate whether these natural reactions will occur under oxidizing (aerobic) or reducing (anaerobic) conditions.

It has been about 35 years since the pioneering work of a group of researchers at Wright State University documented water quality improvements in a natural Sphagnum peat bog in Ohio that was receiving low-pH, metal-laden water (Huntsman et al., 1978). Independently, a group at West Virginia University found similar results at the Tub Run Bog (Lang et al., 1982). In the past, "constructed wetlands" was in common usage but this term carries much regulatory baggage and is not appropriate for many passive treatment unit processes. To paraphrase Gusek (2002):

> ***Passive treatment*** is a process of sequentially removing contaminants and/or acidity in a natural-looking, man-made bio-system that capitalizes on ecological, and/or geochemical reactions coupled with physical sequestration. The process does not require power or chemicals after construction, and lasts for decades with minimal human help.

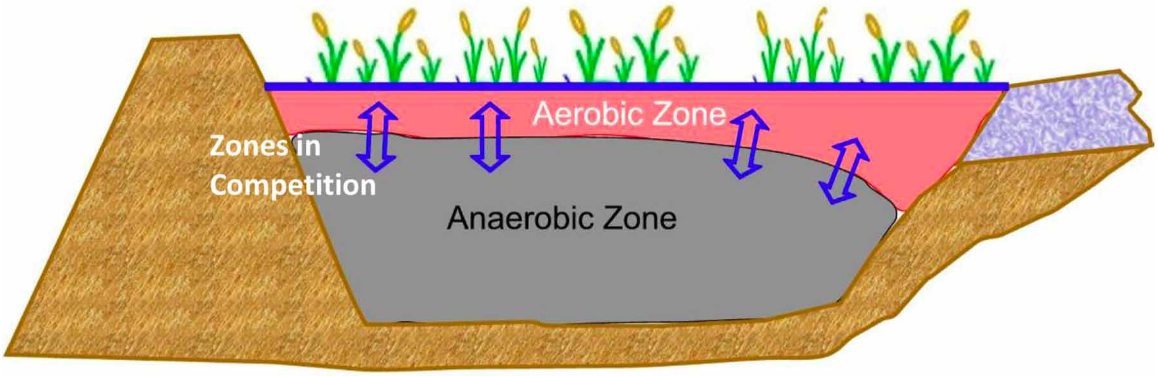
Passive treatment systems are typically configured as a series of sequential process units because no single-treatment cell type works in every situation or with every MIW geochemistry. It is an ecological/geochemical process because most of the reactions (with the exception of limestone dissolution) that occur in passive treatment systems are biologically assisted. Lastly, it is a removal process because the system must involve the filtration or immobilization of the metal precipitates that are formed. Otherwise, they would be flushed out of the system, and the degree of water quality improvement would be compromised.

Man-made passive treatment systems employ the same principles as do natural wetlands, but they are designed to optimize the competing processes occurring naturally in a wetland ecosystem. Aerobic and anaerobic zones "competing" in a natural wetland are shown in Figure 1.

Early passive treatment work was focused on coal geology derived MIW, primarily in the eastern United States. A number of research groups evolved, including: the former U.S. Bureau of Mines; the Tennessee Valley Authority; and various academic communities including Penn State, West Virginia University, and the Colorado School of Mines (Wildeman et al., 1993 and Hedin, 2002). As of 1988, all seemed to agree that there were a number of biogeochemical mechanisms involved in metals removal and water quality improvements in wetland type environments (either natural or man-made), but there was some disagreement on which mechanisms were the most important. For coal mine systems characterized by moderate amounts of iron and manganese, aerobic systems dominated by plants and limestone appeared to be the best means of raising pH (via photosynthesis and neutralization reactions) and precipitating iron through hydrolysis reactions. Researchers out west, primarily Wildeman, Klusman, and Cohen at the Colorado School of Mines, considered sulfate reducing bioreactor (biochemical reactor) systems the most appropriate for metal mine AMD/ARD. According to personal observations by this author, two "camps" had evolved, each thinking that they had the magic bullet.

The American Society for Surface Mining and Reclamation (ASSMR) Conference in Durango, Colorado in 1991 was important, with the different "camps" collaborating for the

FIGURE 1. Natural wetland oxidation-reduction zones.



first time and presenting a short course on passive treatment. Each camp had the opportunity to present its case and view what the other camp's approach had to offer. The course was well attended and many participants stayed after its official end, despite long travels home. It is safe to say that both camps came to recognize the strengths and weaknesses of the two approaches and how the two could be integrated into hybrid systems to treat a variety of AMD/ARD/MIW situations. Subsequently, researchers including Andre Sobolewski (1997), Wildeman and Pavlik (2000), and others have documented the ability of natural wetlands to remediate AMD/ARD; thus, in the past two decades, a number of passive treatment milestones have been achieved (see Gusek and Wildeman, 2002) and a standard passive treatment system (PTS) practitioners' "tool box" has evolved and continues to evolve as new challenges are met and overcome.

THE 2013 PTS PRACTITIONERS' TOOLBOX

The design of passive treatment systems is governed primarily by the chemistry of the water to be treated; thus, MIW characterization is usually the first step in any MIW remediation project. The selection process for specific cell types is summarized in Figure 2, which depicts a "decision tree" type of selection procedure. Figure 2 was originally developed by personnel at the former U.S. Bureau of Mines for coal-geology MIW (Hedin, et al. 1994) primarily containing iron and manganese. It has been updated for the purposes of this article to include a wider range of MIW chemistries. Still, Figure 2 lacks the detail required to consider the breadth of potentially problematic parameters that might be present in a given MIW.

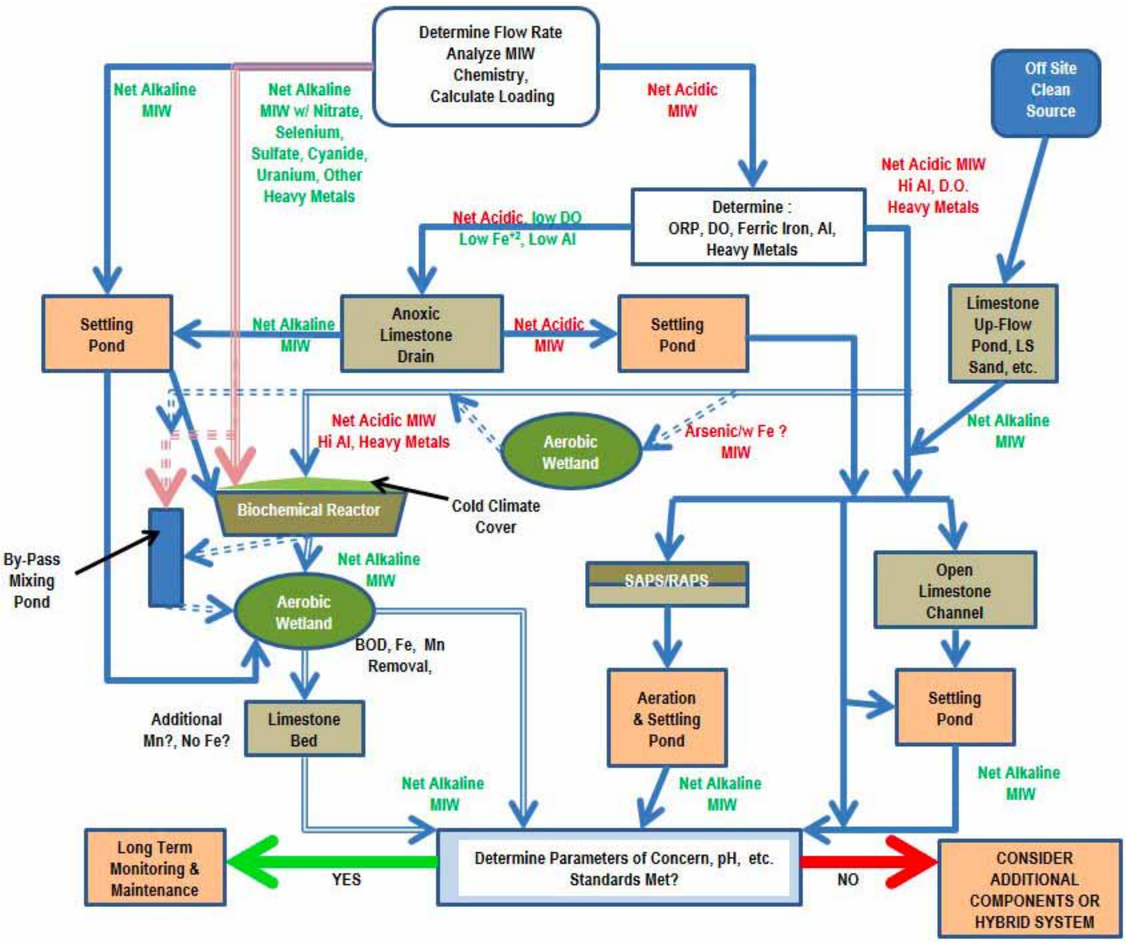
From a PTS designer's perspective, there are three basic "categories" of components available "off-the-shelf," based on the relative contributions of microbes and/or plants.

In many MIW situations, especially in coal geology regions, simple alkalinity addition to neutralize acidity and buffer the MIW is all that is required. Why is adding alkalinity so important? In iron-bearing MIW, the hydrolysis and precipitation of each mole of iron to form oxy-hydroxides yields three moles of hydrogen ions (H^+). Without the buffering bicarbonate alkalinity provided by the dissolved limestone, the pH of the MIW would decrease and iron removal/precipitation rates would slow. Limestone has been found to be the most economical material to add alkalinity and this typically abiotic process can be accomplished in a number of ways as shown in Table 2.

TABLE 1. Summary of PTS Tool Box Components.

Abiotic Components	Semi-Biological Components	Biological Components
• Anoxic limestone drains (ALDs) • Open limestone channels (OLCs) • Limestone Up-flow ponds • Limestone beds • Limestone beds (manganese removal) • Diversion wells • Limestone sand (semi-passive)	• Successive/Reducing alkalinity producing systems (SAPS)/(RAPS)	• Aeration & settling ponds • Aerobic wetlands • Sulfate-reducing bioreactors (Biochemical Reactors (BCRs))

FIGURE 2. 2013 Passive Treatment of Mining Influenced Water Decision Tree.



Once alkalinity is raised in iron-bearing MIW, aeration and settling are required to complete the chemical reactions and avoid discharging the precipitated metals (e.g., iron and aluminum) as total suspended solids. This is shown in multiple places on Figure 2. Aeration and settling ponds are typically colonized by iron-oxidizing bacteria and other microbes (*Acidithiobacillus Ferro-Oxidans*), algae (*leptothrix discophora* & *ulothrix*), and plants (*typha* [cattail], *salix* [willow], carex [sedge], *scirpus* [bulrush], *phragmites* [reed grass], and moss [sphagnum]), which are known to facilitate MIW oxidation and sequester precipitated metals, in particular the typically ubiquitous iron found in most MIW. Thus, aeration and settling ponds are categorized as biological components of passive treatment systems. Several local species of microbes, algae, or plants may favor the conditions at a particular site or even different zones within the same site. Experience has shown that a particular passive treatment system design ecology that is not exactly "tuned" to the local conditions will eventually evolve in response to the influx of native seeds and microbes blown in by the wind or present in the feces of animals that find the new habitat attractive. The adage "if you build it, they will come" certainly applies, but one must know what exactly to build (or be relatively close) to get it right.

TABLE 2. Abiotic and Semi-Biological Limestone Applications for Alkalinity Adjustment.

Component	Function/Situation	Advantages	Disadvantages
Anoxic limestone drains (ALDs)	Add alkalinity to acidic MIW with Fe^{+2} and low aluminum	Easy to build, long-lasting	Cannot tolerate dissolved oxygen or ferric iron; will plug with aluminum; prone to short circuiting
Open limestone channels (OLCs)	Add alkalinity to acidic MIW with Fe^{+3} and moderate aluminum	Easy to build, very cost effective, can be applied on a watershed basis; may function well in removing arsenic and manganese	Limestone armors, lowering efficiency; works best on steep slopes
Limestone up-flow ponds	Adds incremental alkalinity to relatively good water to eventually mix with acidic MIW	Easy to build, very cost effective, can be applied on a watershed basis	Must have good influent water to avoid plugging; alkalinity increases are typically 50 to 80 mg/L
Limestone beds	Adds incremental alkalinity to mildly acidic to relatively good water to eventually mix with acidic MIW	Easy to build, very cost effective, can be applied on a watershed basis	Must have good influent water to avoid plugging; alkalinity gains of 50 to 80 mg/L expected
Diversion wells (semi-passive)	Adds incremental alkalinity to mildly acidic to good water to eventually mix with acidic MIW	Functions in a small footprint; easy to build	Frequent maintenance, small acidity loading capacity; requires good truck access
Limestone sand (semi-passive)	Adds incremental alkalinity to acidic MIW directly or can be added to good water to eventually mix with acidic MIW	Very simple to implement; very inexpensive; can be applied on a watershed basis in remote sites with steep terrain	Frequent (annual?) replenishment; requires good delivery truck access
Successive alkalinity producing systems (SAPS) or Reducing alkalinity producing systems (RAPS)	Add alkalinity to acidic, oxygenated MIW with Fe^{+3} and low aluminum	Organic layer/biotic reactions reduce Fe^{+3} to Fe^{+2} and then the SAPS function like an ALD; can fit in small area; long lasting, can be fitted with automatic flushing for aluminum bearing MIW; some sulfate reduction	Not appropriate for MIW with high acidity and high aluminum; prone to plugging resulting in high maintenance requirements

An anonymous researcher once referred to constructed wetlands as “bioreactors with a green toupee.” This simplistic view is far from correct; the microbiology of biochemical reactors and other plant and algae systems is quite complex. Biological components of passive treatment systems are presented in Table 3.

Recently described iron terraces (Burgos, et al. 2008) would logically fit as a subset under aerobic wetlands. Similarly, recently described tests using chitin as the media (Venot,

TABLE 3. Biological Components of Passive Treatment Systems.

Component	Function/Situation	Advantages	Disadvantages
Aeration & settling ponds	Oxygenate MIW exiting from ALDs, SAPS/RAPS, or biochemical reactors; settle total suspended solids/clarify	Easy to build, long-lasting; iron precipitates can be harvested for beneficial use	Must be periodically cleaned
Aerobic wetlands	Oxygenate MIW to precipitate iron oxy-hydroxides, co-precipitate arsenic, re-oxygenate effluent from BCRs; moderate alkalinity additions; precipitation of manganese oxide facilitated by algae and other biota	Easy to build, very cost effective, low maintenance; iron precipitates can be harvested for beneficial use	Cells subject to freezing; seasonal turnover may create temporary metal (e.g., Fe) spikes as root zone geochemistry fluctuates between oxidizing and reducing conditions
Biochemical Reactors (BCRs)	Reducing environment conducive to de-nitrification, selenium reduction, cyanide destruction, metal sulfide precipitation; uranium oxide precipitation; adds biologically derived alkalinity; hardness and organic concentrations increase which affect metals toxicity; effluent typically can be commingled with bypassed MIW to provide additional treatment	Simple to build, economical, effective in a wide variety of climates and MIW chemistry from net acidic to net alkaline; can treat high levels of aluminum without plugging; infrequent maintenance on the order of decades; temporary overloading survivability is good if designed properly	Ineffective for manganese; may release Mn on startup; effluent may have elevated biochemical oxygen demand; effluent is low in dissolved oxygen and needs polishing with aerobic wetlands or equal; required BCR cell surface area is a function of acidity—high acidity MIW may require pre-treatment in hybrid configuration to fit in restricted space sites. Not efficient for nitrate levels greater than 50 mg/L
Limestone beds (manganese removal)	Microbial facilitated precipitation of manganese oxide	Simple to build, cost effective, low maintenance	Iron levels must be low—aerobic wetland upstream

et al. 2008) would logically fit as a subset under BCRs. When these components stand the test of time and are implemented at multiple sites, they too might advance to become "PTS Tool Box Components." Photos of selected passive treatment components are shown in Figure 3.

COMPONENT SEQUENCING

If testing shows that both aerobic and anaerobic cells are required to produce acceptable effluent quality, is there a preferred sequence of treatment? The sequence is often suggested from MIW quality characteristics such as dissolved oxygen (D.O.) or dissolved constituent levels of concern that favor one type or the other. For example, if D.O. in the feed water is low, it may

FIGURE 3. Examples of Selected Passive Treatment Components.

Aerobic Wetland	Anoxic Limestone Drain
	 photo credit: www.wvu.edu/ ~agexten/ landrec/land
Aeration and Settling Pond	**Sulfate Reducing Bioreactor (Bio-chemical Reactor (BCR))**
	
Successive/Reducing alkalinity producing systems (SAPS/RAPS)	**Open Limestone Channels (OLCs)**
 photo credit: www.wvu.edu/~agexten/landrec/	 photo credit: www.wvu.edu/~agexten/landrec/
Limestone Beds	**Limestone Sand (semi-passive)**
	

be advantageous to preserve the low level and feed the water directly into BCR or an ALD. In some circumstances, however, co-precipitation of difficult-to-remove contaminants such as arsenic and selenium can be effectively removed first (with iron) in an aerobic wetland even though low initial D.O. levels would suggest otherwise. Thus, there is no set sequence of construction for aerobic and anaerobic components.

In summary, the following practical considerations influence component sequencing:

- Oxidation lowers pH, reduction raises pH
- [Aerobic] Fe $(OH)_3$ clogs MIW delivery plumbing
- [Aerobic] Fe must be removed before MnO_2 can be precipitated at circum-neutral pH
- [BCR] FeS does not clog plumbing and BCRs
- [BCR] Aluminum precipitates as a dense, aluminum hydroxy-sulfate
- A BCR cell can efficiently remove all heavy metals except Mn

PHASED DESIGN OF PASSIVE TREATMENT SYSTEM COMPONENTS

If the chemistry of the MIW is somewhat unique, the initial phase of a PTS feasibility evaluation might occur in the laboratory. As with any MIW treatment process design, the chemistry of the water to be treated, the nominal flow rates and seasonal variations, and the target effluent levels must be clearly defined. This data collection effort should be undertaken well in advance of final design.

"Proof of Principal" Testing

Typically, locally-available and plentiful candidate substrate materials for BCR systems are evaluated in the laboratory, involving "proof of principle" testing, utilizing about 30 to 60 grams of different substrate materials in culture bottles immersed in MIW samples. The tests take about six to eight weeks. Aerobic testing is typically conducted simultaneously by monitoring effluent behavior over time under aerobic conditions (algae inoculum) with a gravel rock substrate. Typical algae inoculum may include pond scum or algae growths from natural wetland sites near the project. Indicative measurements during proof of principal testing include pH, oxidation reduction potential (ORP), conductivity, substrate/water color and odor.

Proof of principle studies are static rather than flow-through experiments and are typically developed to:

FIGURE 4. Proof of Principle Testing Setup.

- Test the suitability of the candidate substrate materials or inoculum in a passive treatment component (typically a BCR),
- Determine whether removal of a contaminant by microbial processes in a PTS component with a known substrate composition is possible.

Bench Scale Testing

Next, bench scale tests (see Figure 5), utilizing about 200 pounds (100 kg) of substrate, are operated in the field for at least three months, preferably through a period with a typical range of dissolved metals concentration. These tests constitute a low-cost field demonstration of the principles developed in the laboratory. This approach begins to simulate the typical kinetic chemical reactions that might occur at a larger scale. Site-specific loading factors and substrate hydrology/permeability characteristics are determined during bench scale testing.

FIGURE 5. Bench Scale Testing Setup of Five BCR Mixtures and Aerobic Polishing Cells.

FIGURE 6. Pilot Scale BCR Testing Setups.

Pilot Scale Testing

Successful bench scale testing supports the construction of pilot scale systems utilizing tons of substrate (Figure 6). These systems are typically operated for at least a year before full-scale system design is finalized. If possible, pilot system cells are sized to be integrated into the overall passive system design.

The diversity of pilot BCR construction is apparent in Figure 6. The pilot BCR on the left is an inexpensive, off-the-shelf back-yard swimming pool (5 m dia × 1 m deep) that could be assembled without heavy equipment in under a day. The components of the other pilot cell (roughly 10 m × 10 m square) needed to be more robust. Its pre-fabricated and interchangeable wall and support components needed to be transportable by boat as well since the site lacked direct road access. The shape of the pilot BCRs will vary with the site but the footprints are typically uniform (circular or square) to facilitate construction. Pilot BCRs can also be constructed in geomembrane- or clay-lined earthen excavations.

It is important to note the importance of the laboratory tests to characterize "unique" MIW sources, substrate and their interactive results. A multitude of substrate candidates can be evaluated cost-effectively in proof of principle scale testing. Bench scale testing allows cost-effective determinations of loading factors and system dynamics and thereby improves the likelihood that pilot scale designs will function as expected. This phased approach minimizes risk in determining the applicability of this technology for treating MIW in a wide variety of situations.

PREDOMINANT TREATMENT MECHANISMS IN PASSIVE SYSTEMS

The following treatment mechanisms are thought to prevail in passive systems addressing "traditional" acidic and alkaline MIW. Carbonate alteration (italicized below) is a passive mechanism that has not been specifically addressed by PTS designers.

- Biological sulfate reduction w/alkalinity improvement
- Metal sulfide formation
- Oxidation
- Carbonate dissolution
- Carbonate alteration
- Organic adsorption & complexation
- Plant uptake
- Abiotic adsorption

Conventional wisdom and much research has shown that microbiologically-facilitated reduction and oxidation reactions and carbonate dissolution were the most important removal mechanisms and organic complexation, plant uptake, and adsorption play minor and/or temporary roles; however, another mechanism, carbonate alteration (e.g., conversion of $CaCO_3$ to metal carbonates like $ZnCO_3$ or $FeCO_3$) may see greater utilization.

In addition, the microbiology of passive treatment has become better understood in the past five years and perhaps a "periodic table of microbial activity" might be a logical extension of this article. Ideally, the discussion would focus on the microbial communities most responsible for the removal of parameters of interest in passive treatment system components.

System Longevity

A well-designed passive system should function for many years without a major retrofit to replenish construction materials, periodic visits to conduct "flushing" events, and be able to function without using electrical power. Benning and Ott (1997) described a volunteer passive system outside of an abandoned lead-zinc mine in Ireland that had apparently been functioning unattended for over 120 years. This situation is still likely to be the case 16 years later. Passive treatment system longevity should be at least several decades, but to have it self-sustaining would be the ultimate achievement of passive treatment designers, the true Holy Grail.

Passive treatment system longevity is believed to be limited by the steady effects of metals accumulation and the depletion of key materials/nutrients. Some aerobic components (e.g., aerobic wetlands) could last virtually indefinitely as long as provisions are made to periodically remove and dispose of accumulated iron hydroxides and other precipitates. There may be economic incentives to do this, encouraging some measure of system sustainability. The longevity of limestone-based system components will of course be a function of the limestone "reservoir" and the limestone dissolution/alteration rates which would be affected by armoring. Limestone is typically included in BCR substrate recipes, so its dissolution may govern the longevity of BCR cells.

BCR substrate is typically comprised of organic materials (wood chips, sawdust, hay, manure, etc.) and crushed limestone. Designs based on bench scale tests typically attempt to balance the rate at which the organic matter decays with the rate at which the limestone dissolves so that neither becomes the limiting component in the mix. BCR designs to date take advantage of the observation by Thomas and Romanek (2002) that the consumption of their limestone-buffered organic substrate (LBOS) [organic BCR substrate] progressed from the top-downward in their top-fed columns. Thus, BCR substrate longevity can be extended with increasing cell depth/mass. The oldest BCR known, the West Fork system in Missouri, reached its 17-year milestone in the summer of 2013. While it does not appear to be running out of "fuel" nor plugging with metal precipitates, it may require some maintenance.

When the issue of passive system longevity was first considered by Wildeman et al. in 1993, the depletion of carbon in the substrate appeared (on paper) to be the limiting BCR longevity criteria. Estimates involving typical BCR cell loading, carbon content, and dimensions suggested that a typical BCR cell could last about 30 years without the addition of fresh organic material. Natural vegetation on the surface of the cell had the potential to extend the effective cell life span somewhat, but to make a cell large enough to be self-sustaining with respect to carbon levels was deemed to be impractical at the time. This is still believed to be the case.

Longevity of Manganese Beds and Iron Terraces

Both of these design components have natural analogues whose existence suggests that PTSs that include them could be nearly self-sustaining. Iron terrace deposits are found just north of the Summitville Mine in southwest Colorado (elevation 11,400 ft./3,475m & Lat./Long.: 37.431°N ,106.605°W). These deposits probably started to form shortly after the conclusion of the last ice age. Similarly, "manganocrete" deposits that likely pre-date mining activities occur in Pinal Creek, north of Miami, Arizona. Clearly, Mother Nature seems to favor these types of metal sequestration processes and design engineers should consider mimicking them if the MIW chemistry is appropriate.

PERIODIC TABLE(S) OF PASSIVE TREATMENT

Certainly, treating some MIW parameters is considered "easy," such as systems that address iron and hydrogen ion (the basic unit of acidity). These parameters have been the focus of typical coal geology derived MIW treatment since the early 1980s. In comparison, "difficult" parameters such as common anions (e.g., sodium, chloride, and magnesium and other components of total dissolved solids [TDS]) are conserved in traditional passive treatment systems; passive treatment is not considered an appropriate technology. Next are the elements associated with traditional metal mining: iron (again), copper, lead, zinc, cadmium, mercury, and arsenic. These elements are typically found in metal mine ores and wastes as sulfides and passive treatment designers typically focus on creating conditions favorable to sulfide precipitation, such as those found in biochemical reactors (BCRs). Fortunately, ARD formation involving pyrite evolves sulfate needed in BCRs; but sulfate in and of itself can become an MIW issue. Aluminum and manganese are special cases worthy of focused consideration. The compounds associated with MIW that do not receive much attention from a passive treatment perspective include:

- Ammonia and nitrate (residue from blasting agents),
- Selenium,
- Uranium and radium,
- Cyanide and cyanide complexes, and
- Thallium.

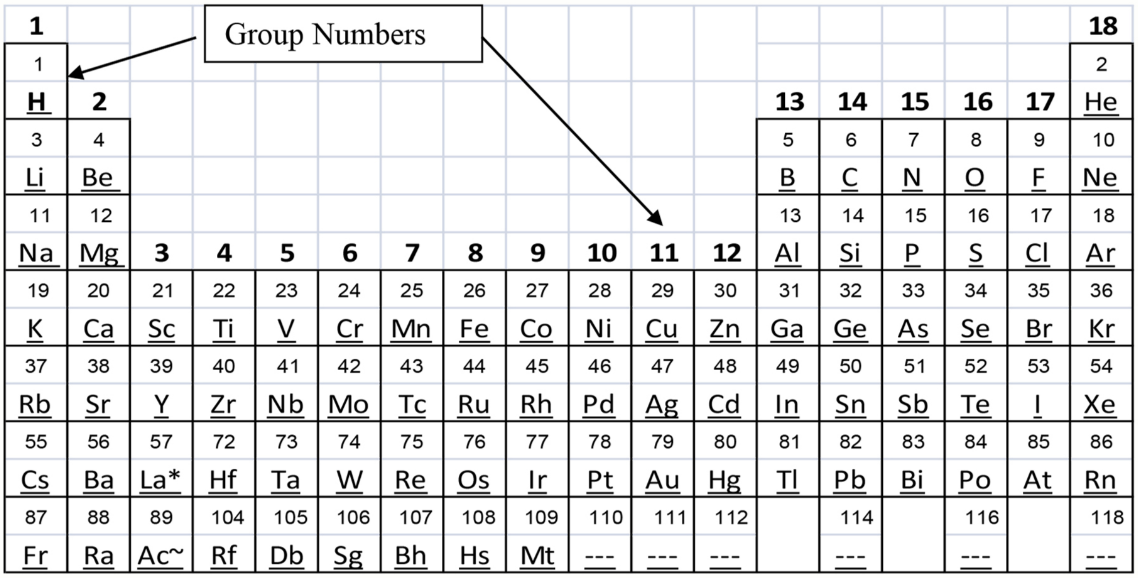
The definition of MIW may be driven by regulations. Coal mines typically need to meet effluent standards for pH, aluminum, iron, and manganese; however, it has been this author's experience that coal geology derived MIW typically contains other heavy metals including nickel, copper, zinc, and cobalt which are usually removed in lime-dosing treatment systems installed at active mines but may not be included in the permit limits. The MIW chemistry from the abandoned Fran Coal Mine in Clinton County, Pennsylvania has much in common with the chemistry of the Berkley Pit MIW in Montana. Fortunately for Pennsylvania, the volume of MIW involved at the Fran Mine is many orders of magnitude less. Regardless, in designing a BCR for the Fran Mine, the non-regulatory parameters needed to be considered because the BCR sizing depends on acidity, aluminum, and iron plus the concentrations of zinc and other dissolved metals. Placing these parameters in proper perspective has been a design challenge for the past 20 years. How can parameters be grouped to streamline the design process? Revisiting Mendeleev's Periodic Table of Elements (since revised) might be a good place to start.

Periodic Table of Elements Review and Typical MIW Related Elements

Oriented horizontally, the PTE (Figure 7) is organized into seven periods or rows of elements and the Lanthanide and Actinide Series (omitted in Figure 7). Oriented vertically, there are 18 groups, or columns, of elements. The noble gases are found on the right side of the table; the hydrogen and the anions such as lithium, sodium, and potassium are found on the left side of the table. The elegance of this organization is that the elements of a single group tend to behave similarly in chemical reactions and that applies to behavior in passive treatment systems as well. Why this happens is typically not a concern to passive treatment system design engineers but the fact that it does may need to be more fully embraced.

For the sake of simplicity, the focus of the discussion will be elements and compounds that are problematic or "interesting" ones associated with MIW as summarized in Table 4.

FIGURE 7. Simplified Periodic Table of Elements sans Lanthanide and Actinide Series.


Group Numbers

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac~	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 ---	111 ---	112 ---		114 ---		116 ---		118 ---

TABLE 4. Elements and Species of Interest in Passive Treatment Systems.

Group	Elements	Common Species/Associated Parameters
1	Hydrogen (H), Sodium (Na), and Potassium (K)	TDS, Acidity
2	Magnesium (Mg), Calcium (Ca), Barium (Ba), Radium (Ra)	TDS, Ra-226
3	No traditional MIW elements or compounds	N/A
4	No traditional MIW elements or compounds	N/A
5*	Vanadium (V) and Uranium (U) [*Actinide Series]	V_2O_6, U_3O_8
6	Chromium (Cr), Molybdenum (Mo)	Cr^{+6}, Cr^{+3}, Mo^{+5}, Mo^{+6}
7	Manganese (Mn)	Mn^{+2}, Mn^{+4}, Acidity
8	Iron (Fe)	Fe^{+2}, Fe^{+3}, Acidity
9	Cobalt (Co)	Co^{+2}, Acidity
10	Nickel (Ni)	Ni^{+2} , Acidity
11	Copper (Cu), Silver (Ag), Gold (Au)	Cu^{+2}, Ag^{+2}, AgCN complex, Au-Chloride? AuCN complex, Acidity
12	Zinc (Zn), Cadmium (Cd), Mercury (Hg)	Zn^{+2}, Cd^{+2}, Hg^{+2}, Hg^{+1} (organic), Acidity
13	Aluminum (Al), Thallium (Tl)	Al^{+3}, SO_4^{-2} Tl^{+1}, Tl^{+3}, Acidity
14	Carbon (C), Lead (Pb)	HCO_3^-, TOC, BOD_5, Pb^{+2}, Pb-carbonate complex
15	Nitrogen (N), Phosphorous (P), Arsenic (As), Antimony (Sb)	NH_3, N_2, NO_2, NO_3, PO_4, As^{+3}, As^{+5}, multiple As-complexes/ionic species
16	Oxygen (O), Sulfur (S), Selenium (Se)	O_2, SO_4, Selenite, Selenate
17	Fluorine (F), Chlorine (Cl)	TDS
18	Noble Gases, No traditional MIW elements or compounds	N/A

Periodic Table of Passive Treatment for MIW—Oxidation/Reduction Controls

From a passive treatment system designer's perspective, there are eight basic components available "off-the-shelf":

- Sulfate reducing bioreactors [compost wetlands, SRBRs, vertical flow ponds, and biochemical reactors (BCRs)]
- Aerobic wetlands,
- Anoxic limestone drains,
- Limestone up-flow ponds,
- Limestone diversion wells,
- Aeration & settling ponds,
- Successive alkalinity producing systems (SAPS), and
- Open limestone channels & limestone beds.

There may be two more to add to the list: sulfide sequestration cells and iron terraces, which might be considered a sub-set of aerobic wetlands.

Each component has its own expected geochemical or biogeochemical capability with respect to mitigating MIW; however, some of these components could exhibit capabilities that have heretofore not been considered within the context of the Periodic Table of Passive Treatment as first introduced in Gusek (2009).

In Gusek (2009), the oxidation/reduction potential (ORP) was the principal condition that would control whether or not a given MIW parameter would be addressed. This admittedly preliminary approach did not include adsorption phenomena or the displacement/replacement of the calcium ion in calcium carbonate by a metal. The same substitution process may be occurring with the carbonate ion when displaced by fluorine to form fluorite (CaF_2).

The pH of the MIW will control the formation of metal precipitates. Some metal species are almost fully pH-dependent; aluminum is an example as it can precipitate in both oxidizing and reducing conditions. Attempting to fully understand the variety of competing reactions, biological activity, and metal and ionic removal phenomena can be a very daunting task and may require modeling using geochemical software. While these models typically do not include biological inputs, some can generate pH-Eh diagrams that can be quite useful in projecting the stability of various metal precipitates in a wide range of geochemical conditions. In an attempt to simplify matters to a level that will fit the proposed Periodic Table of Passive Treatment, it is assumed that the oxidation reduction potential (ORP) conditions prevailing in the off-the-shelf components will typically control the bio-geochemical reactions that occur there.

Oxides and hydroxides will typically form in aerobic zones and reducing conditions that are favorable for the formation of oxides (e.g., uranium), hydroxides (e.g., chromium and aluminum), and other reduced species such as sulfides. Table 5 characterizes each component with respect to prevailing ORP conditions. The color coding, when applied to the periodic table, should show at a glance how various elements and groups of elements might be treated passively.

When the general ORP categories introduced in Table 5 are applied to the PTE based on the author's experience and the available literature, the guidelines in Figure 8 are the result.

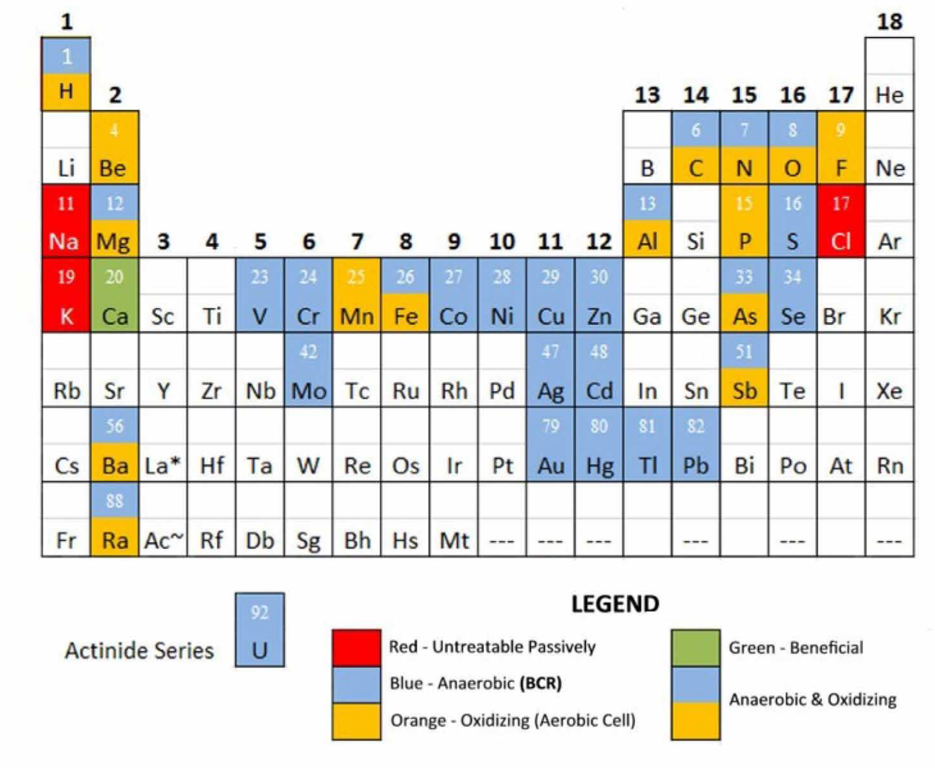
In Figure 8, the red-shaded elements (Na, K, Cl), which may be associated with elevated TDS, are not affected by the off-the-shelf passive treatment processes. Calcium, which is also conserved or involved in the generation of hardness, is a beneficial ion and it is therefore color coded in green. There are specialized situations where elevated fluorine (as fluoride) has been a component of MIW. Being a halide immediately above chlorine, passive fluoride removal

TABLE 5. Oxidation Reduction (ORP) Conditions Prevalent in Conventional Passive Treatment System Components.

Passive System Component	Aerobic (ORP > zero mV) Oxidizing Conditions	(ORP < zero mV) Reducing Conditions
Biochemical bioreactors (BCRs)	X (upper 1–2 cm)	X (most of the cell mass)
Aerobic wetlands & aeration/settling ponds	X	
Oxidation & settling ponds	X	
Anoxic limestone drains		X
Reducing Cell (RAPS) component in a Successive Alkalinity Producing System (SAPS)	X (upper 1–2 cm)	X (most of the cell mass)
Open limestone channels and limestone beds	X	

Note: Table 5 above does not include emerging technologies that hold promise but may still be under development. Also, while an anoxic limestone drain may exhibit mildly reducing conditions, it is sole design goal is to add alkalinity, not remove metals. Thus it should not be inferred that ALD's are appropriate for the precipitation of certain metals beyond their ability to remove aluminum and iron. ORP values assume standard hydrogen electrode.

FIGURE 8. Periodic Table for Passive Treatment of MIW—ORP Controlled.

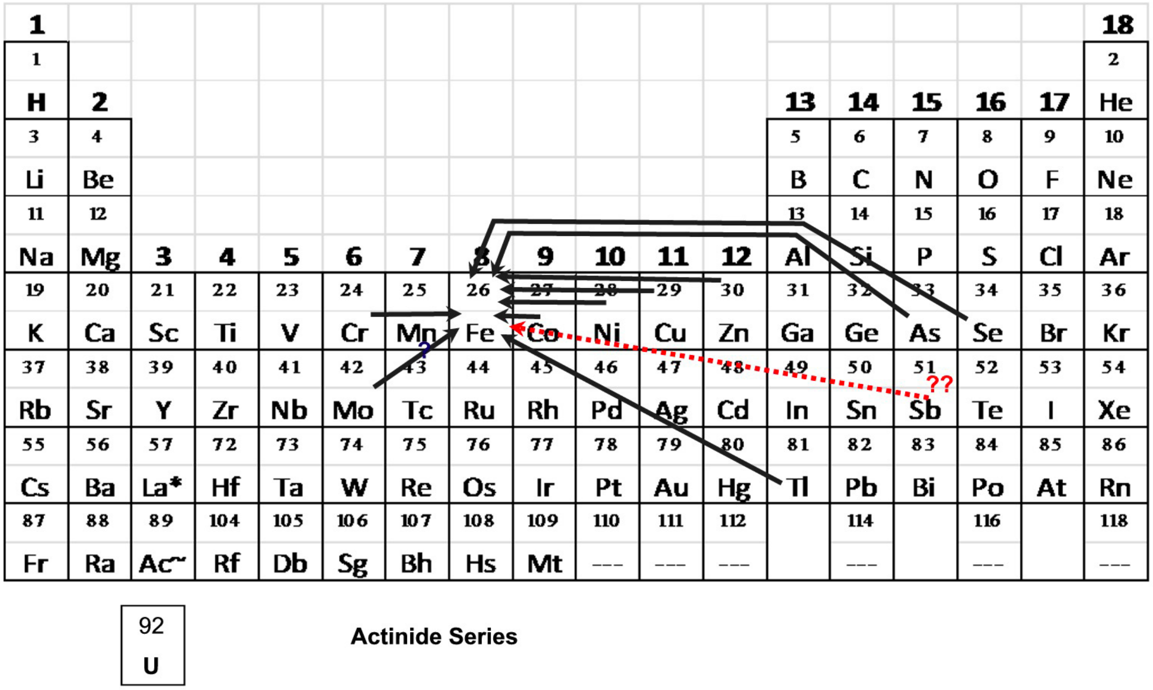


is not straightforward with respect to ORP conditions; however, other mechanisms such as adsorption and ion exchange appear to be appropriate as subsequently discussed.

Periodic Tables of Passive Treatment of MIW—Adsorption and Other Processes

Early research (Wildeman et al. 1993) suggested that adsorption processes contributed a small percentage of the overall divalent metal removal performance of passive treatment systems.

FIGURE 9. Periodic Table for Passive Treatment of MIW—Iron Adsorption Tendencies.



Work by Tebo et al. (2004) and others suggest otherwise. For example, provided that interferences are addressed in pretreatment steps or are not present at all, many divalent metals and other MIW parameters will adsorb to manganese oxide (MnO_2) at neutral pH. Arsenic adsorption to iron oxyhydroxide ($Fe[OH]_3$) has been observed by many practitioners, including unpublished work by this author. Both phenomena have been found to be microbially facilitated (by Tebo, et al. 2005 in the case of manganese and LaBlanc et al (1996) in the case of iron oxyhydroxide). See Figures 9 and 10 for graphical summaries of this process for iron and manganese, respectively. Evidence of antimony adsorption to iron was not readily apparent in the technical literature. However, as antimony is in the same group as arsenic, one might infer that an MIW that yielded $Fe(OH)_3$ would scavenge dissolved antimony if it were present. The presence of arsenic in the same MIW may be an interference that would need to be verified in bench or pilot testing.

Calcium Carbonate Alteration

The author suspected non-sulfate-reduction mechanisms were responsible for metal removal in one of two pilot-scale BCR cells at the Brewer Mine which were described in Gusek (2000). Sulfate, calcium, and divalent metal mass balance calculations (unpublished) suggested that calcium present in the limestone portion of the BCR substrate was being displaced by some of the divalent metals present, including copper, iron, and zinc. This topic was addressed by Railsback (2010) who provides a thermodynamic stability/solubility plot of some carbonate minerals of divalent cations and an insightful discussion of the effects of atomic radii on this phenomenon. This topic is worthy of modeling investigations by geochemists followed by laboratory and field demonstrations. A summary of calcium-related processes with respect to passive MIW treatment is provided graphically on Figure 11.

FIGURE 10. Periodic Table for Passive Treatment of MIW—Manganese Oxide Adsorption Tendencies.

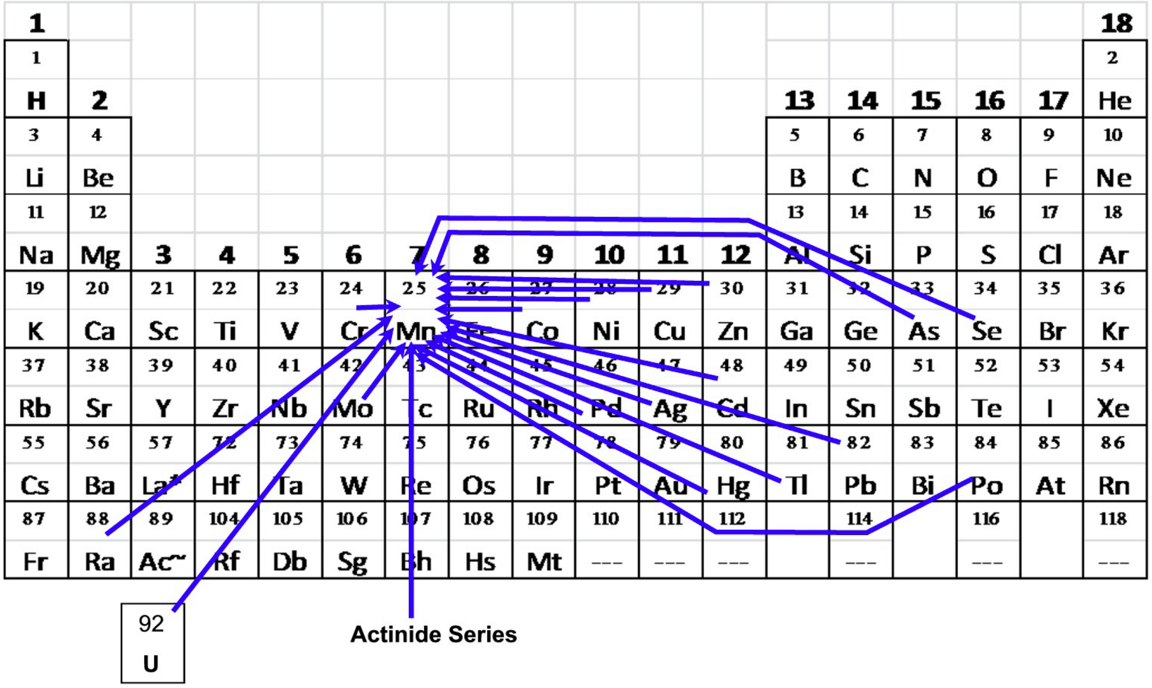
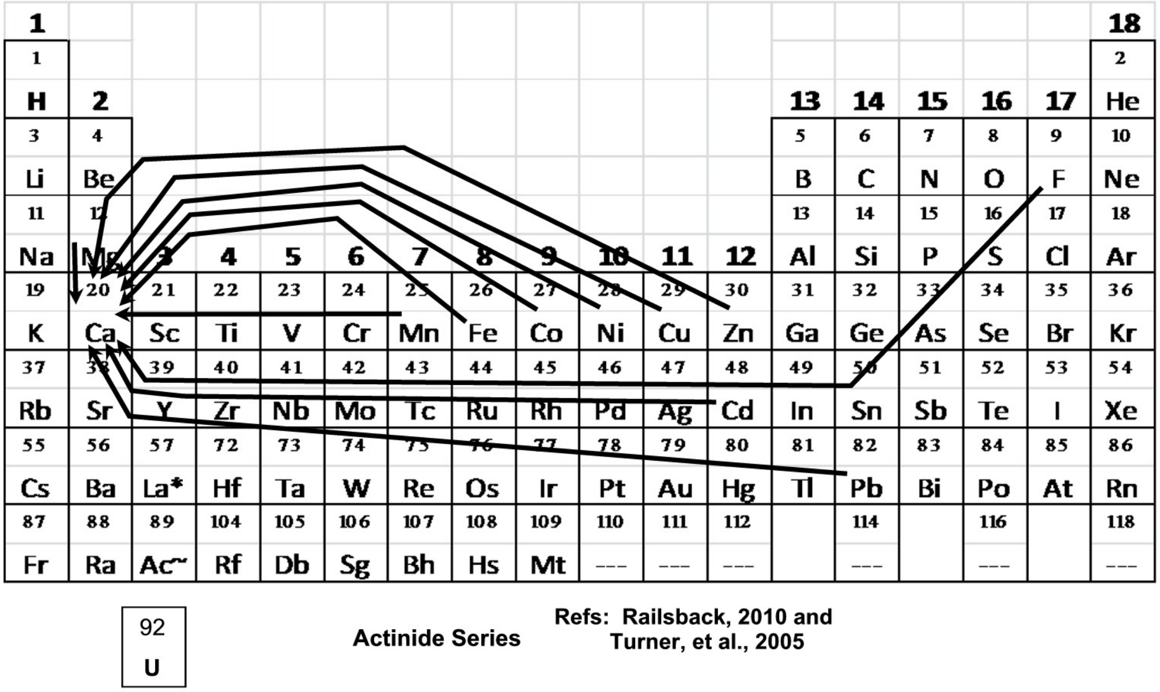


FIGURE 11. Periodic Table for Passive Treatment of MIW—Calcium Replacement/Calcite Alteration.



Refs: Railsback, 2010 and Turner, et al., 2005

An additional calcite/limestone alteration/replacement mechanism is discussed by Turner et al (2005) for the sequestering of fluorine. Those authors note that some geochemical models (PHREEQ) are ill-equipped to handle this situation because both adsorption and precipitation mechanisms are involved. This process could be used in conjunction with anoxic limestone drains, limestone up-flow ponds, open limestone channels, or limestone diversion wells. Equation 1 shows the alteration of calcite to the zinc carbonate mineral smithsonite in the presence of a neutral MIW containing dissolved zinc ions.

$$CaCO_3\,(\textit{calcite}) + Zn^{+2} \rightarrow ZnCO_3\,(\textit{smithsonite}) + Ca^{+2} \qquad (1)$$

A similar replacement reaction (equation 2) may be responsible for the alteration of calcite to the mineral fluorite.

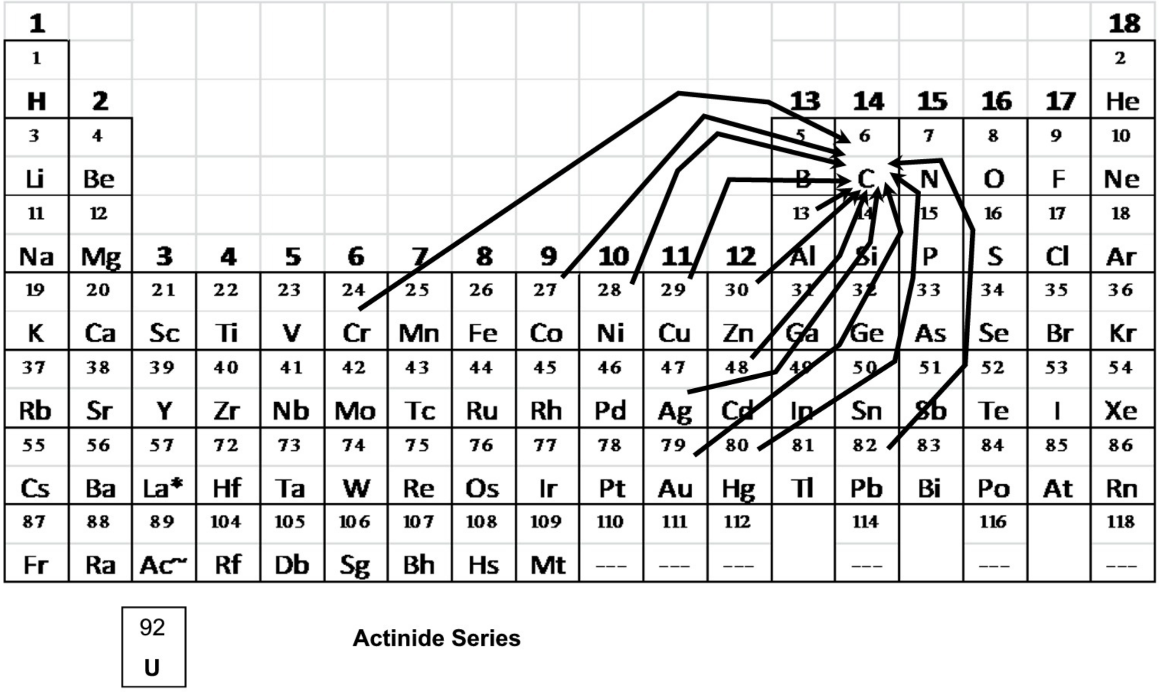
$$CaCO_3\,(\textit{calcite}) + 2F^{-1} \rightarrow CaF_2\,(\textit{fluorite}) + CO_3^{-2}(aq) \qquad (2)$$

Column tests by Turner et al (2008) suggest that pH control is essential for optimizing fluoride removal and that the effects of some interfering ions (e.g., sodium) appear to diminish with time. Also, increased partial pressure of CO_2 (1 atm) in the MIW (e.g., spent pot liner leachate from an aluminum smelting process) also improved the process efficiency. The results were supported by geochemical modeling (PHREEQ) and the process was considered appropriate for designing a permeable reactive barrier.

Carbon and Organic Complexation Processes

Figure 12 summarizes the potential elements that can adsorb to activated carbon or carbon-based substrates like peat (Eger, et al., 2008). Some of these processes can also work with

FIGURE 12. Periodic Table for Passive Treatment of MIW—Carbon Adsorption and Complexation.



natural vegetation but the results could be reversible. Peat has been long-recognized for its ability to sequester metals. Pelletized peat, however, appears to improve on the inherent properties of the natural material and it could further polish MIW that had been treated/conditioned with other processes. The ability of activated carbon to sequester precious metals and mercury in cyanide circuits is well known.

In Figures 9 through 12, tendencies of various elements associated with MIW to adsorb to, co-precipitate with, or complex with iron, manganese, calcium, and carbon, are indicated by arrows. Due to space restrictions, it is not possible to address the many pre-conditions, interferences, and adsorption sequences that could be involved with these generalized relationships. Probably the most important precondition in most (but not all) adsorptive situations is circum-neutral pH. This is most certainly true in the case of manganese, where the virtual absence of dissolved iron is an essential precondition. The partial pressure of carbon dioxide, P_{CO_2}, and the presence of competing cations are important preconditions with respect to the kinetics and products of calcite replacement/alteration, respectively.

Due to space restrictions, specific references supporting the suspected or documented adsorptive relationships of selected MIW parameters are not included. The multiplicity of mechanisms for a given element suggests that competitive adsorption/replacement/alteration tendencies could make precise predictions with geochemical models difficult. This situation would be further compounded with potential interfering or enhancing conditions. Elevated P_{CO_2} is one example of an enhancing condition with respect to limestone dissolution or alteration. Oxidation reduction potential (ORP) is another.

Turner et al (2008) employed elevated P_{CO_2} conditions in their work on fluoride removal. Sibrell, et al. (2000) employed a similar strategy in enhancing the dissolution of limestone for generating alkalinity. It may be possible to take advantage of this phenomenon with respect to improving passive treatment system designs. Perhaps deep (>33 m) limestone diversion wells could be used to enhance the kinetics of carbonate replacement/alteration reactions at elevated P_{CO_2} ($P > \sim 3$ atm). Maintaining these deep wells would involve periodically exhuming depleted limestone and replacing it with fresh material. Air lift pumping technology could be used to flush-out depleted media. Industrial foams might also be considered for flushing and tremmie placement of fresh media (Masloff 2013).

The discussion will now progress through the elements remaining in the various groups as shown in Table 4. The references are provided to provide guidance for cursory additional research and are not intended to be all-inclusive.

SUMMARY

The state of the art of passive treatment has advanced in the past 30-plus years with a number of important milestones which have been achieved through the cooperation of practitioners, researchers, and engineers in government, academia, and private industry. The 2013 Passive Treatment Practitioner's Toolbox as discussed has room for expansion, but its basic organization has basically remained constant over the years and will likely remain so for quite a while.

The proposed Periodic Table(s) of Passive Treatment offer a different perspective of the sometimes complicated picture of conflicting priorities in treating MIW passively. As suggested earlier, this perspective is a good starting point for a more complete understanding of the complicated bio-geochemistry behind the passive treatment design process. It should be considered a logical expansion of the passive treatment decision trees, and like Mendeleev's

TABLE 6. Passive Treatment of Typical Elements and Species in MIW.

Group	Element or Species	Suspected or Documented Mechanisms & Passive System Components	Reference
1	Hydrogen ion	H^+ can be addressed aerobically and anaerobically: limestone dissolution in ALDs, OLCs, BCRs and SAPS and microbial bicarbonate alkalinity in BCRs or SAPS	Conv. wisdom (multiple refs)
2	Magnesium	Mg has been observed being removed by the replacement of calcium in limestone to form suspected dolomitic limestone in a pilot BCR in Slovakia; this may occur aerobically as well	Gusek, et al. 2000; Railsback, 2010
2	Barium	Dissolved barium can be precipitated aerobically or anaerobically as the insoluble barium sulfate by comingling with slightly-elevated sulfate bearing MIW	Conv. wisdom
2	Radium	Ra 226 was observed being removed in a BCR pilot in 1993, probably as $RaSO_4$ with barite	Unpublished BCR data & Wanty et al. 1999
5	Vanadium & Uranium	V and U occur naturally in uranium roll front deposits which form in reducing conditions prevalent in BCRs	Whitmer and Saunders 2000
6	Chromium	Reduction to Cr^{+3} with hydrolysis/precipitation of chromium hydroxide in BCRs	Ozawa et al. 1995
6	Molybdenum	Molybdenum removal in a bench BCRs was observed in 2008	Unpublished data
7	Manganese	Precipitation of MnO_2 facilitated by bacteria and algae; oxidizing conditions required; presence of limestone is recommended but not required; $MnCO_3$ (*rhodochrosite*) formation suspected in over-loaded BCRs	Conv. Wisdom; Robbins & Ziemkiewicz 1999, & other refs
8	Iron	Fe precipitation as ferric oxy-hydroxide in aerobic wetlands, OLCs, oxidation ponds, and the surface zone of BCRs; iron sulfide (FeS) precipitation in BCRs and reducing zone of SAPS	Conv. wisdom (multiple refs)
9	Cobalt	Cobalt sulfide formation in BCRs, adsorption to MnO_2	Eger 1992 & Tebo, et al., 2004
10	Nickel	Nickel sulfide formation in BCRs, adsorption to MnO_2	Hammack and Edenborn 1991 & Tebo, et al., 2004
11	Copper	Copper sulfide formation in BCRs, adsorption to MnO_2	Wildeman et al., 1990; Tebo, et al., 2004
11	Silver	Silver sulfide formation in BCRs; adsorption to peat	Conv. wisdom
11	Gold	Native gold precip. in BCRs is possible but undocumented; adsorption to carbon	?
12	Zinc	Precipitation of *sphalerite* (ZnS), also sorbs to ochre and MnO_2	Wildeman, et al. 1990; Tebo, et al., 2004

(continued on next page)

TABLE 6. (continued)

12	Cadmium	Cd removal in a pilot BCR suspected to be as *greenockite* (CdS) observed in 1994; adsorption to MnO_2	Unpublished data (BCR) & Tebo, et al., 2004
Group	**Element or Species**	**Suspected or Documented Mechanisms & Passive System Components**	**Reference**
12	Mercury	*Meta-Cinnabar* (HgS) in BCRs—some uncertainty of Hg methylation in BCRs	Unpublished data (BCR): Tebo, et al., 2004
13	Aluminum	Al hydroxide (*gibbsite*) precipitates at pH > 5 in well-buffered MIW in aerobic wetlands, OLCs, SAPS, ALDs; aluminum hydroxysulfate precipitation in BCRs	Conv. wisdom & Thomas 2002
13	Thallium	Tl sulfide co-precipitation with FeS in BCRs; adsorption to $Fe(OH)_3$ or MnO_2	Blumenstein, et al. 2008; Tebo, et al., 2004
14	Cyanide	CN degradation anaerobically in BCRs	Cellan, et al. 1997
14	Cyanide	CN degradation aerobically by UV light in aerobic wetland	Wildeman, et al. 1994
14	Biochemical Oxygen Demand	By-product of BCRs—polished with aerobic wetlands	Conv. wisdom (multiple refs)
14	Lead	PbS (*galena*) precipitation in BCRs; adsorption to MnO_2	Wildeman, et al. 1993; Tebo, et al., 2004
15	Ammonia	NH_3 is oxidized to nitrate in aerobic wetlands and is also utilized by plants	EPA 1988
15	Nitrate/ Nitrite	NO_3 and NO_2 are denitrified in BCRs to N_2	EPA 1988
15	Phosphate	Plant uptake in aerobic wetlands	EPA 1988
15	Arsenic	Removal in aerobic conditions adsorbing to iron oxy-hydroxide and anaerobic (BCR) conditions as sulfide	Wildeman et al. 1994; Tebo, et al., 2004
15	Antimony	*Stibnite* (Sb_2S_3) formation in hot springs environments may be similar to conditions in a BCR—removal data lacking; could adsorb to $Fe(OH)_3$ similar to arsenic behavior	?
16	Oxygen	Depressed dissolved oxygen from BCRs is polished with aerobic wetlands; oxygen is required in aerobic wetlands and other situations to precipitate iron.	Conv. wisdom (multiple refs)
16	Sulfate	Sulfate is removed by microbial conversion to sulfide in a BCR	Conventional wisdom (multiple refs)
16	Sulfide	Sulfide is scavenged by sacrificial metals such as zero valent iron	Conv. wisdom (multiple refs)
16	Selenium	Selenium is removed by microbial conversion to elemental selenium or iron selenide precipitates in a BCR; adsorption to $Fe(OH)_3$ or MnO_2	Conv. wisdom (multiple refs)
17	Fluoride	Replacement of carbonate in calcite to form CaF_2	Turner et al., 2005; Tebo, et al., 2004

original work over 130 years ago, should be the focus of future enhancement. This might consist of geochemical modeling, investigations into the speciation of precipitate formation in different passive treatment cell types or zones within those types, and studies that might identify specific microbiological suites associated with or that have adapted to given elements.

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