A PERIODIC TABLE OF PASSIVE TREATMENT FOR MINING INFLUENCED WATER[1]

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Abstract. 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 US Bureau of Mines about 14 years ago. The decision tree was originally intended to address mining influenced water (MIW) from coal mines. But since then, 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 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. The revised, color-coded table presented in this paper focuses on identifying passive treatment methods that have been observed to work on specific elements or species of elements typically found in MIW that is based on the author's experience or other practitioner's of the technology. The author offers it as a starting point that could be enhanced with further study, to include geochemical modeling and speciation investigations in existing passive treatment systems.

Additional Key Words: MIW, acid rock drainage treatment, metal, coal

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Introduction

The Periodic Table of Elements (PTE) was first introduced by the Russian chemist Dmitri Ivanovich Mendeleev in 1869. Fifty-seven of the elements had been discovered prior to that date, and the rest discovered since then. The scientific and industrial revolution of the 18th and early 19th centuries yielded most of the rest of the elements that Mendeleev categorized. Mendeleev's contribution to science was monumental; he organized the elements into similar groups which we now know are governed by how their atomic structures are arranged. For a more in-depth approach to the PTE from different perspective, the reader is referred to "An Earth Scientist's Periodic Table of the Elements" (Railsback 2004).

The concept of "mining influenced water" was first introduced by Schmiermund and Drozd (1997). It covers the breadth of solutions ranging from what might be termed traditional acid rock drainage (ARD) and neutral mine drainage to the mining process solutions that may be very alkaline such as NaCN solutions used in the recovery of Au or Ag in heap leaching or milling operations. The multiplicity of MIW sources compounds the problems facing engineers charged with designing MIW treatment systems. Consequently, every treatment system, whether active or passive, seems to require some site-specific customization. Before passive treatment approaches to various groups in the PTE can be discussed, it is appropriate to consider the accepted definition of the term "passive treatment". 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.

Certainly, treating some MIW parameters is considered “easy”, such as systems that address Fe and hydrogen ion (the basic unit of acidity). These parameters have been the focus of typical coal geology derived MIW treatment since the early 1980’s. In comparison, “difficult” parameters such as common anions (e.g., Na, Cl, and Mg 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: Fe, Cu, Pb, Zn, Cd, Hg, and As. 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 Mn are special cases worthy of focused consideration.

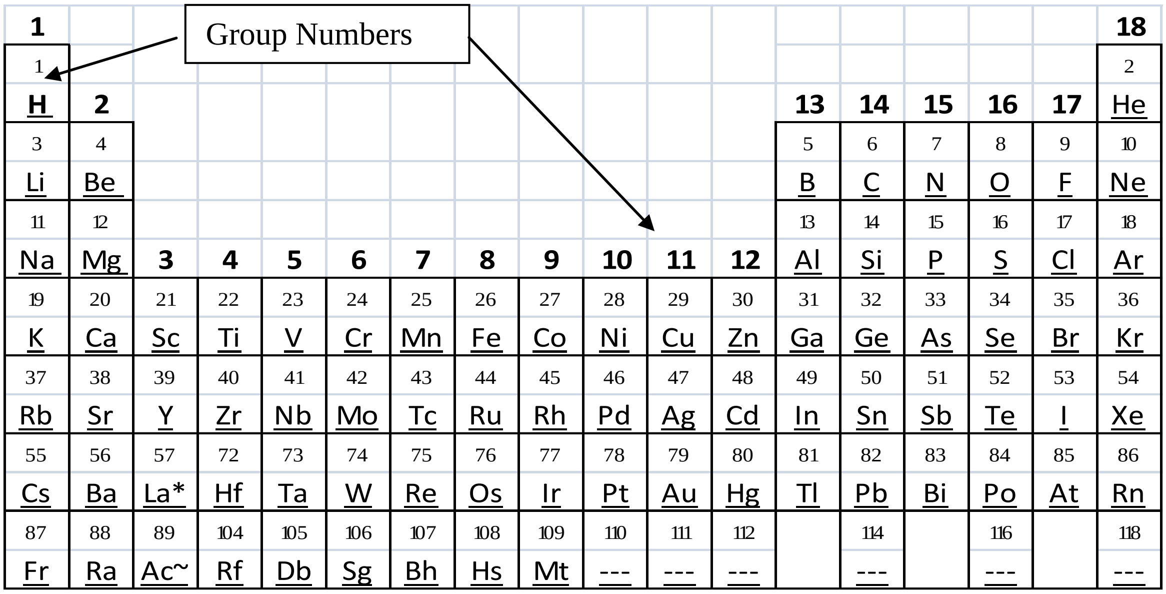
The compounds associated with MIW that do not receive much attention from a passive treatment perspective might include:

- Ammonia and NO_3^-sidue from blasting agents),
- Selenium,
- Uranium and Ra
- Cyanide and CN complexes, and
- Thallium.

The definition of MIW may be driven by regulations. Coal mines typically need to meet effluent standards for: pH, Al, Fe, and Mn. However, it has been this author’s experience that coal geology derived MIW typically contains other heavy metals including nickel, Cu, Zn, and Co 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, Al, and Fe *plus* the concentrations of Zn, et al. 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 (Fig. 1) is organized into seven periods or rows of elements and the Lanthanide and Actinide Series (omitted in Fig. 1). Oriented vertically, there are 18 groups or columns of elements. The noble gases are found on the right side of the table; the H and the cations such as Li, Na, and K 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.



Group Numbers

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

Figure 1 – Simplified Periodic Table of Elements sans Lanthanide and Actinide Series

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 1 below.

Table 1 – Elements and Species of Interest in Passive Treatment Systems

Group	Elements	Common Aqueous 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

Predominant Treatment Mechanisms in Passive Systems

The following treatment mechanisms have been thought to prevail in passive systems addressing “traditional” acidic and alkaline MIW.

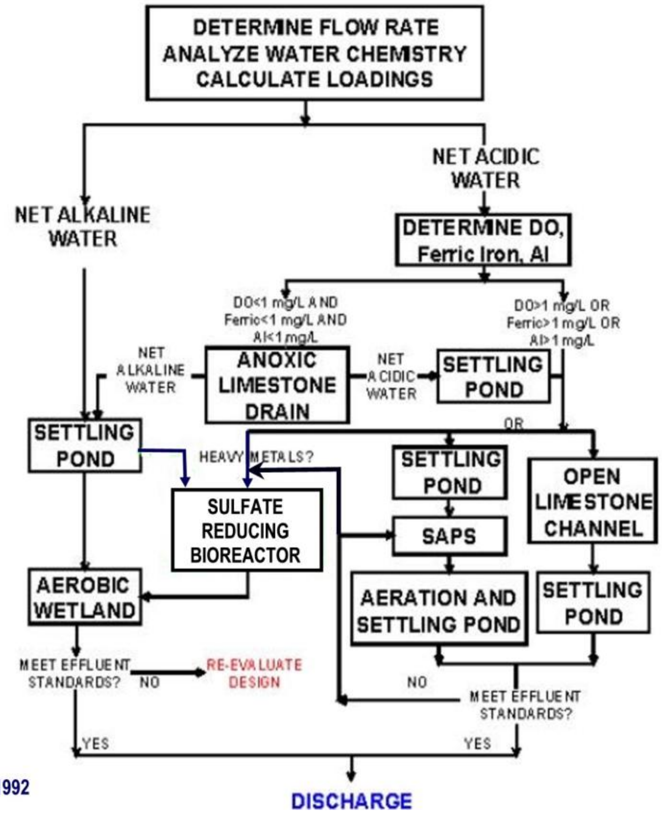
- Biological sulfate reduction with accompanying alkalinity improvement
- Metal sulfide formation
- Oxidation
- Carbonate dissolution
- Organic complexation
- Plant uptake
- Adsorption

Conventional wisdom and much research has shown that micro-biologically facilitated reduction and oxidation reactions and carbonate dissolution are the most important removal mechanisms and organic complexation, plant uptake and adsorption play minor and/or temporary roles. 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 paper. Such a paper would link the microbial communities most responsible for the removal of parameters of interest in passive treatment system components.

Periodic Table of Passive Treatment for MIW

From a passive treatment system designer’s perspective, there are several basic components available “off-the-shelf” as shown on the traditional passive treatment “decision tree” as shown in Fig. 2.

- Sulfate reducing bioreactors,
- Aerobic wetlands,
- Anoxic limestone drains,
- Aeration & Settling ponds,
- Successive alkalinity producing systems (SAPS), and
- Open limestone channels & limestone beds (not shown).



After Hedin & Nairn, 1992

Figure 2 – Traditional Passive Treatment Decision Tree

Recently, the SO_4^{2-} reducing bioreactor has evolved into a more universal MIW passive treatment role. The evolution of the name for this specialized passive treatment unit has included over the years:

- Compost wetland,
- Anaerobic cell or wetland,
- Sulfate reducing bioreactor (SRB or SRBR),
- Vertical flow pond, and most recently,
- Biochemical reactor (BCR).

Many practitioners agree that the “BCR” moniker captures many facets of the technology because it acknowledges both the biotic and abiotic processes involved. BCRs have been known to treat MIW and similar waters for a wide range of contaminants to include the typical suite of heavy metals, and CN, NO_3^-, SO_4^{2-}, Se, and several radionuclides. References to guide the interested reader in how these behave in BCRs are provided in Table 3.

The pH of the MIW will control the formation of metal precipitates; some metal species are almost fully pH-dependent; Al 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 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 form typically in aerobic zones and reducing conditions are favorable for the formation of oxides (e.g., U), hydroxides (e.g., Cr and Al), and other reduced species such as sulfides. Table 2 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.

Table 2 – Oxidation Reduction Conditions Prevalent in Conventional Passive Treatment System Components

Passive System Component	Aerobic (ORP > zero mV) Oxidizing Conditions	Anaerobic (ORP < zero mV) Reducing Conditions
Biochemical bioreactors	X (upper 1-2 cm)	X (most of the cell mass)
Aerobic wetlands	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 2 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 Al and Fe. ORP values assume standard hydrogen electrode.

When the general ORP categories introduced in Table 2 are applied to the PTE based on the author's experience and the available literature, the following guideline results:

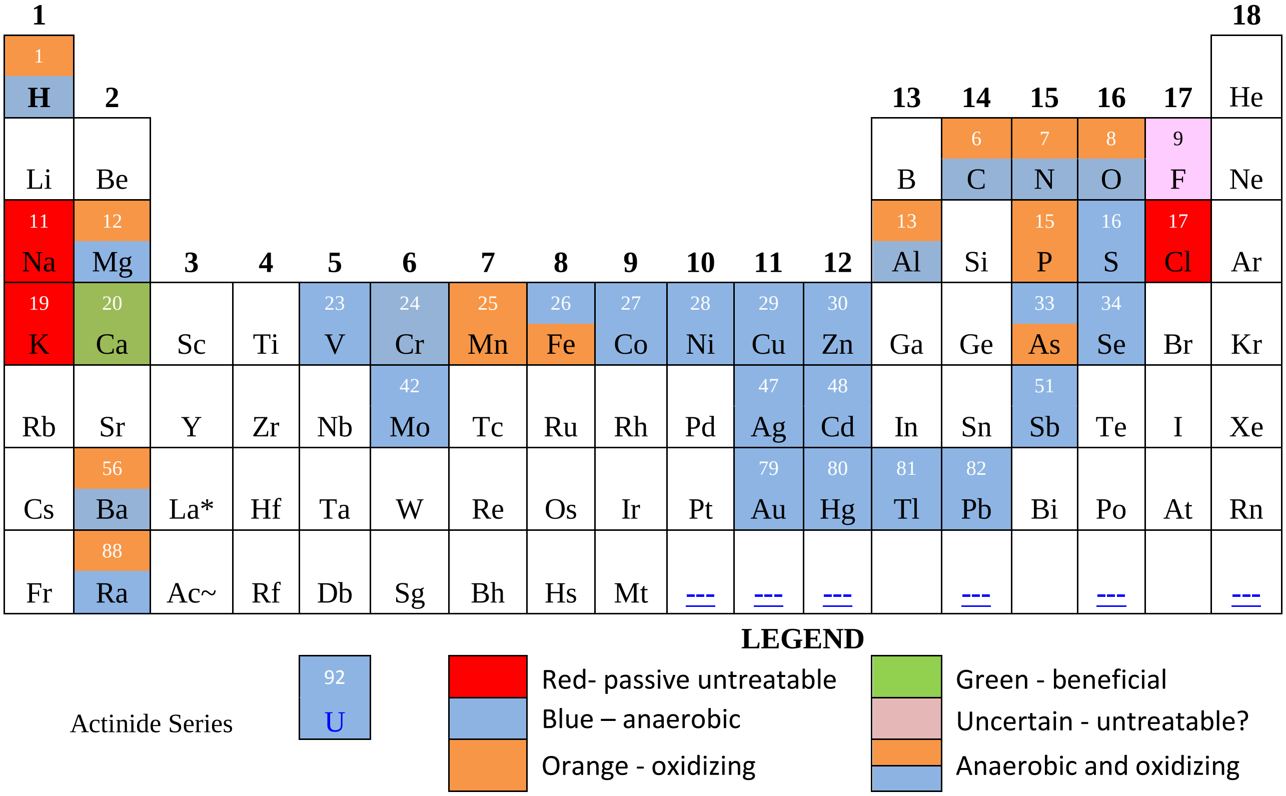


Figure 3 – Proposed Periodic Table for Passive Treatment of MIW

Discussion

In Fig. 3, 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 F^-) has been a component of MIW. Being a halide immediately above Cl^-, passive F^- removal is not straightforward. In acidic MIW, F^- solubility is known to be sensitive to pH, but a solid precipitate can be formed only in a very restricted pH range. This condition may be difficult to maintain in a passive treatment system; fluorine is thus color coded a shade of pink.

The discussion will now progress through the elements remaining in the various groups as shown in Table 3. The references are provided to provide guidance for cursory additional research and are not intended to be all-inclusive.

Table 3 – 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	Conventional 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
2	Barium	Dissolved barium can be precipitated aerobically or anaerobically as the insoluble barium sulfate by comingling with slightly-elevated sulfate bearing MIW	Conventional 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 pilot BCR was observed in 1994	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	Conventional 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	Conventional Wisdom (multiple refs)
9	Cobalt	Cobalt sulfide formation in BCRs	Eger 1992
10	Nickel	Nickel sulfide formation in BCRs	Hammack and Edenborn 1991
11	Copper	Copper sulfide formation in BCRs	Wildeman et al., 1990

Group	Element or Species	Suspected or Documented Mechanisms & Passive System Components	Reference
11	Silver	Silver sulfide formation in BCRs	Conventional Wisdom
11	Gold	Native gold precip. in BCRs is possible but undocumented	?
12	Zinc	Precipitation of *sphalerite* (ZnS), also sorbs to ochre	Wildeman, et al. 1990.
12	Cadmium	Cd removal in a pilot BCR suspected to be as *greenockite* (CdS) observed in 1994	Unpublished data
12	Mercury	*Meta-Cinnabar* (HgS) in BCRs – some uncertainty of Hg methylation in BCRs	Unpublished data
13	Aluminum	Al hydroxide (*gibbsite*) precipitates at pH >5 in well-buffered MIW in aerobic wetlands, OLCs, SAPS, ALDs; aluminum hydroxysulfate precipitation in BCRs	Conventional Wisdom & Thomas 2002
13	Thallium	Tl sulfide co-precipitation with FeS in BCRs	Blumenstein, et al. 2008
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 (BOD)	By-product of BCRs – polished with aerobic wetlands	Conventional wisdom (multiple refs)
14	Lead	PbS (*galena*) precipitation in BCRs	Wildeman, et al. 1993
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
15	Antimony	*Stibnite* (Sb_2S_3) formation in hot springs environments may be similar to conditions in a BCR – removal data lacking	?
16	Oxygen	Depressed dissolved oxygen from BCRs is polished with aerobic wetlands; oxygen is required in aerobic wetlands and other situations to precipitate iron.	Conventional 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	Conventional wisdom (multiple refs)
16	Selenium	Selenium is removed by microbial conversion to elemental selenium or iron selenide precipitates in a BCR	Conventional wisdom (multiple refs)

Summary

The proposed Periodic Table of Passive Treatment (PT^2) offers another view of the sometimes complicated picture of conflicting priorities in treating MIW passively. In some instances, the author has no specific experience with a particular element (e.g., Sb) and was not successful in finding a reference in the over 3,000 technical papers found in the combined proceedings of the American Society of Mining and Reclamation (ASMR), International Conference on Acid Rock Drainage (ICARD), the West Virginia Acid Mine Drainage Task Force Symposia, and the Tailings and Mine Waste Conferences.

As suggested earlier, the proposed PT^2 is a starting point to a more complete understanding of the complicated bio-geochemistry behind the passive treatment design process. It should be considered a logical expansion of the former USBM passive treatment decision tree and like Mendeleev's 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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