Recovery of Rare Earth Elements (REEs) from Coal Mine Drainage

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ABSTRACT:

The rare-earth elements (REE) are essential for many high technology products such as permanent magnets, lamp phosphors, catalysts, rechargeable batteries, etc. With China producing more than 90% of the global REE and its increasingly tight export quota, the rest of the world is facing a REE supply risk. The shortage of rare earths stimulates the search for new deposits. It also stimulates research on the recycling of rare earths from End-of-Life consumer goods and other sources The fundamental processes used for recovering and recycling REE from industrial wastes are similar to those utilized for REE raw ore. Generally, these processes include acid leaching of feedstock material, removal (e.g. precipitation) of undesirable minerals, and extraction and purification of REE products using solvent extraction.

Acid mine drainage (AMD) often contains considerable concentrations of rare earths as REE is released in low pH conditions (Merten and Buchel, 2004; Biennemans, et al., 2013). During AMD treatment, REEs are likely adsorbed onto the Fe–Al–Mn oxide/hydroxide colloids forming co-precipitates, or precipitating directly as $RE(OH)_3$, thereby resulting in the REE scavenging from AMD (Zhao et al., 2007). Some studies reported the possibility of other metal recovery from AMD by ion-exchange resins or by biosorption (Biennemans, et al., 2013). However, no information is available on the potential to recover rare earths from AMD sludge. A USGS (2011) study by Cravotta and our preliminary research indicate AMD sludge could be an important feedstock for REE.

REE in Appalachian Coal Mine Drainage. In the Appalachian Basin, coal mine drainage (CMD) is produced in vast quantities at both abandoned and current coal mining and preparation facilities. Unfortunately, there are no accurate data identifying the volume of CMD produced in the Appalachian Basin.

Currently active coal operations are obliged by the Federal Clean Water Act sec. 402 to obtain permits that specify pollutant discharge limits. The majority of mines thus require treatment systems consisting of acid neutralization, oxidation and solids precipitation to remove transition metals and acidity. Precipitated solids are captured in settling basins or clarifiers prior to disposal. Addition of alkalinity to AMD results in an increase in pH and the formation of metal hydroxides which form the bulk of the precipitated mass. Depending on the type of mine and its local geology, CMD can range from acidic (acid

mine drainage or AMD) to alkaline. In 2011 Cravotta (2008a, b and 2011) sampled CMD from over 186 mine discharges in Pennsylvania. In the 2011 study, samples were taken upstream and downstream of treatment systems. These samples were analyzed for various metal concentrations, and the dataset included the majority of REEs. Analysis of pre and post treatment chemistries indicated that TREE concentrations were highest at a pH less than 3 and were essentially absent from solution at pH > 4.5 (Figure 1). This indicates that REEs precipitate with the more plentiful transition metals and concentrate in AMD sludge.

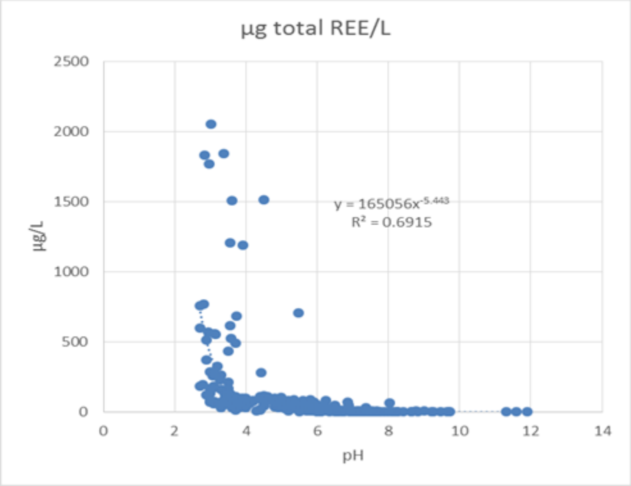

Figure 1. The aqueous concentration of REE in coal mine drainage decreases with increasing pH. Data are drawn from 233 samples collected by USGS in 1999 and 2011.

This relationship held for both untreated (raw) AMD and treated AMD. By comparing raw and treated concentrations of REE we estimated its mass in the AMD sludge. The relationship between discharge rate and concentration indicated the mass of sludge and REE per unit time which are expressed as load (kg/yr). Note that the discharge volumes were based on single samples and most were taken during summer/fall, low flow conditions. So these would be low estimates of annual production. It is also important to note that most AMD treatment sites have been accumulating large volumes of AMD sludge in impoundments, drying cells and underground mine voids for decades so partial recovery of these reserves is possible.

Major sludge components include Fe, Al, Mn hydroxides plus silicates and gypsum. Thus it is possible to approximate the proportion of TREE and major ions in the resulting sludges (Table 1). This element-by-element analysis can then be extended to approximate the total value (i.e. potential revenue) of the REEs present in the sludges. The data in Table 1 not only indicates that the total revenue from individual treatment sites can be significant, but more subtly, these data indicate that 49.8% of the REE mass and a majority of the revenue (52.8%) is derived from elements which have been classified as “critical” by DOE (Nd, Eu, Tb, Dy, and Y). This unique elemental distribution amplifies the attractiveness of sludge-based REE sources when compared to traditional ores where the majority of the revenue is derived from the more abundant elements, such as Lanthanum and Cerium (Molycorp, 2013).

Table 1. REE production at fifteen PA AMD treatment sites ranked according to their estimated value. Estimated values do not account for transportation costs, only (price-processing cost) x mass/year. Critical REEs are shaded.

		Average 15 PA AMD treatment sites			
	price*	production		est. value	
REE	$/kg	kg/yr	% TREE***	$/yr	% total
Eu	1600	5.46	1.3%	$ 8,742	18.8%
Y	44	126.82	29.3%	$ 5,580	12.0%
Dy	170	23.35	5.4%	$ 3,969	8.5%
Tb	900	4.39	1.0%	$ 3,955	8.5%
Gd	150	23.69	5.5%	$ 3,554	7.6%
Ho	750	4.38	1.0%	$ 3,288	7.1%
Yb	325	8.77	2.0%	$ 2,850	6.1%
Ce	30	84.81	19.6%	$ 2,544	5.5%
Sm	130	19.35	4.5%	$ 2,515	5.4%
Lu	1800	1.30	0.3%	$ 2,349	5.1%
Nd	42	55.59	12.8%	$ 2,335	5.0%
Tm	1500	1.45	0.3%	$ 2,178	4.7%
Er	100	11.79	2.7%	$ 1,179	2.5%
La	30	31.77	7.3%	$ 953	2.1%
Pr	38	12.50	2.9%	$ 475	1.0%
Sc**	?	17.36	4.0%	?	?
total		432.78	100.0%	$ 46,464	100.0%

* UGSS, 2009

** no price given for Sc

*** no data available for Pm

REE concentrations in AMD and AMD treatment sludge. Mineral value is strongly dependent on concentration in the process feedstock. Our feedstock will be AMD treatment sludge. There are very few reports of REE concentrations in AMD sludge so we estimated REE concentrations over 47 coal mine discharges and their rate of production (kg/yr) using the Cravotta 2011 data set.

This required estimation of two independent variables: 1) The mass of TREE precipitated per unit time in a given AMD sludge and 2) the mass of sludge produced per unit time during AMD treatment. The former was estimated by subtracting the TREE load in step 1, Figure 2 from the TREE load in step 4. The latter is estimated by calculating the major ion load (Ss). However, the sludge mass Ss consists of more than just the major ions. It also includes hydroxyl ions and hydration water. Based on the data in table 2, we estimated that a multiplying major ion load by a correction term of 3.34 yielded a Ss value that was equal to the measured values in the two sludge samples.

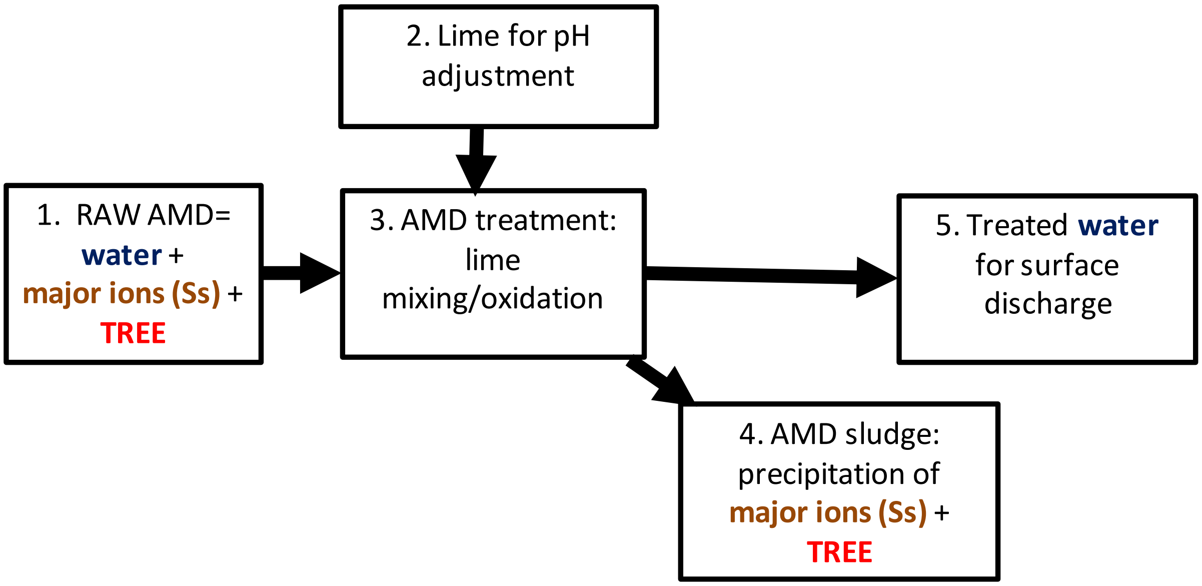

Figure 2. Schematic diagram showing a typical AMD treatment process and its separation of sludge containing major ions and TREE from discharge quality water.

To verify our estimates we sampled two AMD sludges, one from a Freeport/Kittanning refuse facility and another from a Kittanning surface mine. Those results (Table 2) indicate that the summation of aqueous, major ion concentrations accounted for about 30% of the actual sludge solid mass while accounting for hydroxides in the metal precipitates more than doubled the estimated sludge mass leaving about 30% that was likely hydration water. Since hydroxide and hydration corrections would be constant across the REEs and major sludge ions, a factor of 3.34 was included in the estimation of TREE concentration (formula 1). Aqueous chemistry, coupled with discharge volume can, thus, estimate the annual production of TREE, AMD sludge and the grade of AMD sludge as a process feedstock.

Table 2. REE concentrations in two West Virginia AMD sludges. Site A is a combined Freeport/Kittanning refuse facility at an underground mine while Site B is a Kittanning surface mine.

	AMD sludge (mg/kg)	
REE	site A	site B
Ce	26.0	160.0
Dy	9.0	34.0
Er	5.0	19.0
Eu	2.0	6.0
Gd	9.0	34.0
Ho	2.0	7.0
La	8.0	59.0
Lu	0.6	2.0
Nd	16.0	90.0
Pr	3.0	19.0
Sc	6.0	9.0
Sm	5.0	23.0
Tb	2.0	6.0
Tm	0.6	2.0
Y	54.0	230.0
Yb	4.0	14.0
TREE actual	152.2	714.0

	AMD sludge (mg/kg)	
Ss	site A	site B
SO4	8,870	40,210
Al	13,400	79,000
Ca	128,000	8,200
Si	19,700	34,700
Fe	98,200	51,800
Mg	20,700	63,600
Mn	8,500	24,200
Ss	297,370	301,710
TREE/Ss	512	2,367
Correction factor	3.36	3.31
Avg. correction factor		3.34
TREEc	153.3	708.8

$$TREEc = \Sigma(\Delta REE)/(Ss \times 3.34) \times 10^{6} \qquad (1)$$

Where: TREEc = estimated TREE concentration in treated AMD sludge (mg/kg)

ΔREEa = change in AMD REE concentration: pre and post-MAD treatment (mg/L)

Ss = sludge solids: sum of major ions in raw AMD feed water: Ca, SO4, Si, Fe, Mg, Mn (mg/L)

*For untreated AMD sources, the downstream REE values can be set at zero.

Many AMD treatment sites have been accumulating large volumes of sludge in impoundments and drying cells for decades so in some circumstances it may be possible to recover these resources to supplement current AMD sludge production.

We found that 46% of sites in the USGS dataset had TREEc sludge concentrations greater than 300 mg/kg while 31% exceeded 1,000 mg/kg. AMD sludge, thus, represents a concentration factor averaging 15,000x over raw AMD. Table 3 shows fifteen of the richest AMD sludge sources.

Table 3. AMD treatment sludges with the highest TREEc in the USGS 2011 sampling. The far right column indicates the concentration factor in sludge vs. untreated AMD (TREEc/Ss).

AMD	Ss	AMD		TREEc	Conc.
treatment plant	mg/L	mg/L	kg/yr	mg/kg	factor
SaxmanRun	67	0.69	2.7	3073	4478
Racic	93	0.77	92.0	2495	3232
Thomas	12	0.09	17.5	2169	24585
CaledoniaPike	42	0.28	80.0	1997	7144
Nittanny	339	2.07	180.6	1824	883
Morris2	111	0.61	292.8	1663	2707
RogersMill	43	0.23	20.1	1595	6949
Nittanny	360	1.85	117.5	1535	831
McVillePile	364	1.83	641.3	1510	823
MtMorris	14	0.07	3.9	1500	21566
PotRidge2	114	0.55	110.2	1462	2635
PotRidge2	119	0.56	13.4	1408	2507
Antrim	72	0.33	467.4	1371	4173
Keener	156	0.71	50.6	1359	1921
HallTallent	26	0.09	5.0	1032	11413

Environmental Benefits. Acid mine drainage is the second most important source of stream impairment in the Appalachian Basin. Most is the result of untreated, pre-law mining. Development of an REE recovery industry around pre and post-law mines will incentivize capture of these drainage sources, treatment of AMD and discharge of clean water. For active mining and treatment operations, it will provide a byproducts market that does not currently exist. It is anticipated that after REE have been recovered, the residual AMD sludge can be either used for beneficial purposes or disposed in deep mines through the SDWA/UIC program exactly as treated sludge is currently disposed. Other environmental benefits to this approach include the use of existing mining operations as essentially heap leach facilities and the AMD treatment systems as primary concentrators. Neither of these require additional mining or waste disposal sites. The waste products will be acidified but neutralization of these materials is straightforward and could be accomplished by simply adding lime to the effluent stream as is currently done with AMD though much lower volumes would require treatment since sludge solids constitute roughly 1% of raw AMD. AMD sludge is not a RCRA subtitle C waste and it is not radioactive as are many REE ores; therefore, waste streams are expected to be non-hazardous.

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