

BIOCHEMICAL REACTOR MEDIA CHARACTERIZATION STUDY¹

Tom Rutkowski², Jacob Waples, Jim Gusek, and Brad Shipley

Abstract. Biochemical reactors (BCRs) are frequently used to effectively treat acid rock drainage (ARD). The subject of this study was a vertical-flow pilot BCR with treatment media consisting of, by weight, 40% co-gen fuel, 29% limestone chips, 10% hay, 10% rice hulls, 10% cow manure, and 1% ash. The pilot operated at a flow rate of about 3.8 Liters per minute for 26 months and treated low pH ARD with high concentrations of aluminum, iron, and zinc.

BCRs, also known as sulfate-reducing bioreactors (SRBRs), are generally considered low maintenance passive treatment systems which require neither electricity nor continuous chemical inputs. In order to remain effective, the substrate from BCRs must be removed and replaced every so often as the organic matter and limestone are consumed. Substrate from a pilot scale BCR at the Golinsky Mine near Lake Shasta, California was studied upon decommission of the pilot test. The study examined geochemical stability of the substrate, in particular with respect to metals, in order to evaluate appropriate disposal options for the substrate. The study included elemental and mineralogical analyses, as well as different types of short-term leach tests. In addition, several zones, such as an oxide and sulfide zones, were identified vertically within the pilot cell substrate where different metals accumulated, depending on removal mechanisms. The stability of metals in the substrate appears dependent on the removal mechanism for the metals. For example, metals that appear removed as solid metal sulfides are susceptible to remobilization under oxidizing conditions, indicating the substrate should not be disposed of under surface conditions. Disposal options may vary by zone.

Additional Key Words: removal mechanism, passive treatment, sulfate- reducing bioreactor, BCR, substrate disposal

¹ Paper was presented at the 2010 National Meeting of the American Society of Mining and Reclamation, Pittsburgh, PA *Bridging Reclamation, Science and the Community* June 5 - 11, 2010. R.I. Barnhisel (Ed.) Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502.

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Proceedings America Society of Mining and Reclamation, 2010 pp 888-913

DOI: 10.21000/JASMR10010888

<http://dx.doi.org/10.21000JASMR10010888>

Introduction

The Golinsky Mine is an abandoned underground base metal mine near Lake Shasta, located in Shasta County, California in the Shasta-Trinity National Forest (see Fig. 1) in rugged, mountainous terrain. The mine was last active in the early part of the 20th century (SHN, 2004) when copper and zinc and minor amounts of the precious metals were recovered. The geochemistry of the Golinsky Mine ore was dominated by sulfide mineralization, including pyrite. From July 2004 to October 2006, Golder Associates Inc. (Golder), under contract with the United States Department of Agriculture Forest Service (USFS) Region, operated a pilot biochemical reactor (BCR) to treat acid rock drainage (ARD) from the Golinsky Mine. Golinsky Mine water is characterized by depressed pH (2.1 to 4.2 standard units (s.u.)) and elevated average concentrations of Fe (73 mg/L), Al (23 mg/L), Cu (12 mg/L), Zn (37 mg/L), Cd (0.47 mg/L), and Mn (0.85 mg/l).

The pilot BCR was a vertical-flow cell with treatment media consisting of, by weight, 40% co-gen fuel, 29% limestone chips, 10% hay, 10% rice hulls, 10% cow manure, and 1% ash. These materials were mixed during construction to form the treatment media which was placed inside the pilot BCR cell which

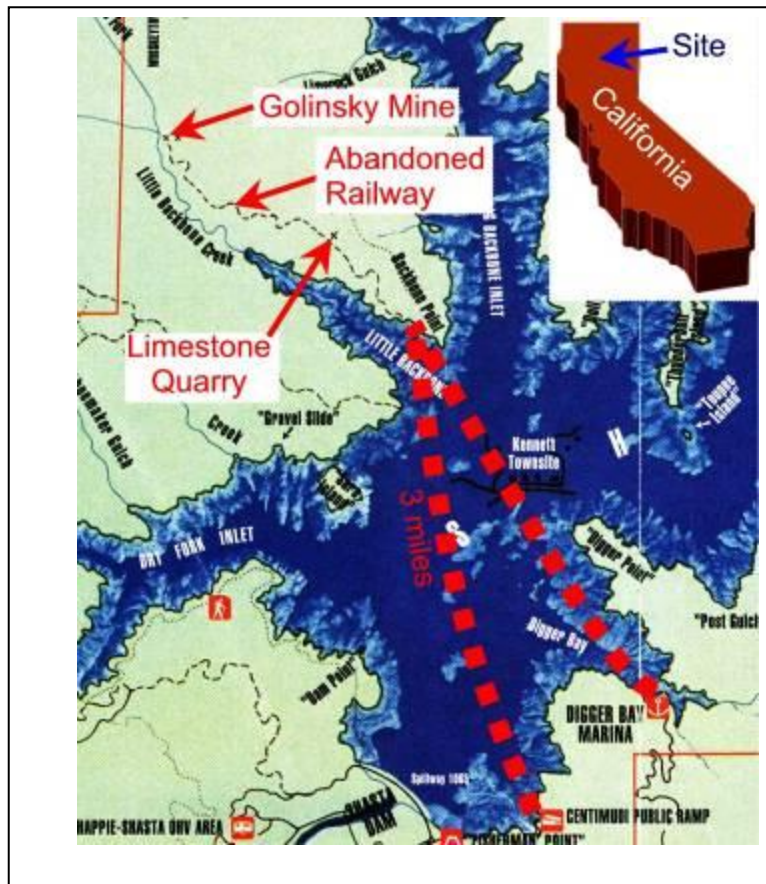


Figure 1. Site vicinity

measured 10 m wide by 10 m long by 1 m deep (32 ft by 32 ft by 3.2 ft). During the course of the 26-month long treatability test of the BCR technology, approximately 5,700 m³ (1.05 million gal) of mine effluent was passively treated at an average flow rate of about 3.8 L/min (1 gpm). The BCR effluent pH was typically circum-neutral and about 99 % of the non-manganese metals load was removed and sequestered as oxide, sulfide, and hydroxy-sulfate mineral phases in various vertical zones of the BCR.

Upon pilot cell decommissioning, Golder tested the BCR media to investigate disposal options, estimated media longevity, and metal precipitation zones within the media. This paper presents the results of this evaluation.

BCR Media Characterization Approach

The three goals of the media characterization were as follows.

Substrate disposal stability. BCR substrate should be properly disposed of when it eventually becomes depleted. Data collected focused on identifying the potential for release of hazardous components, specifically metals leaching or acid generation, from the used media, including change in the potential with time.

Substrate Longevity. The principal components of the substrate are limestone and organic carbon. Ideally, both are consumed at about the same rate. When either of these become depleted, the bioreactor substrate should be renewed either by amendment or replacement with depleted components(s).

Metal precipitation zones. Metal accumulation horizons for four metals (Al, Cu, Fe, Zn) were investigated by analyzing substrate at multiple depths for total metals content. The location of metals precipitation can provide evidence of metal removal pathways and suggest bioreaction kinetics data required for system scale-up design and may influence disposal options.

BCR Media Samples

Media samples were collected over the course of a four-year period. Two initial substrate samples were collected in July 2004 during pilot construction. Eighteen samples were collected during pilot decommissioning in October 2006. Post-decommissioning samples included one sample collected after one year (November 2007), two samples collected after two years (November 2008), and two samples collected after three years (November 2009) from the media disposal pile. Decommissioning samples were collected at four locations in the bioreactor (T-1 through T-4) as shown in Fig. 2 and at up to five distinct horizons at each location (0"-6" below surface (BS), 6"-12" BS, 12"-18" BS, 18"-24" BS, 24"-30" BS).

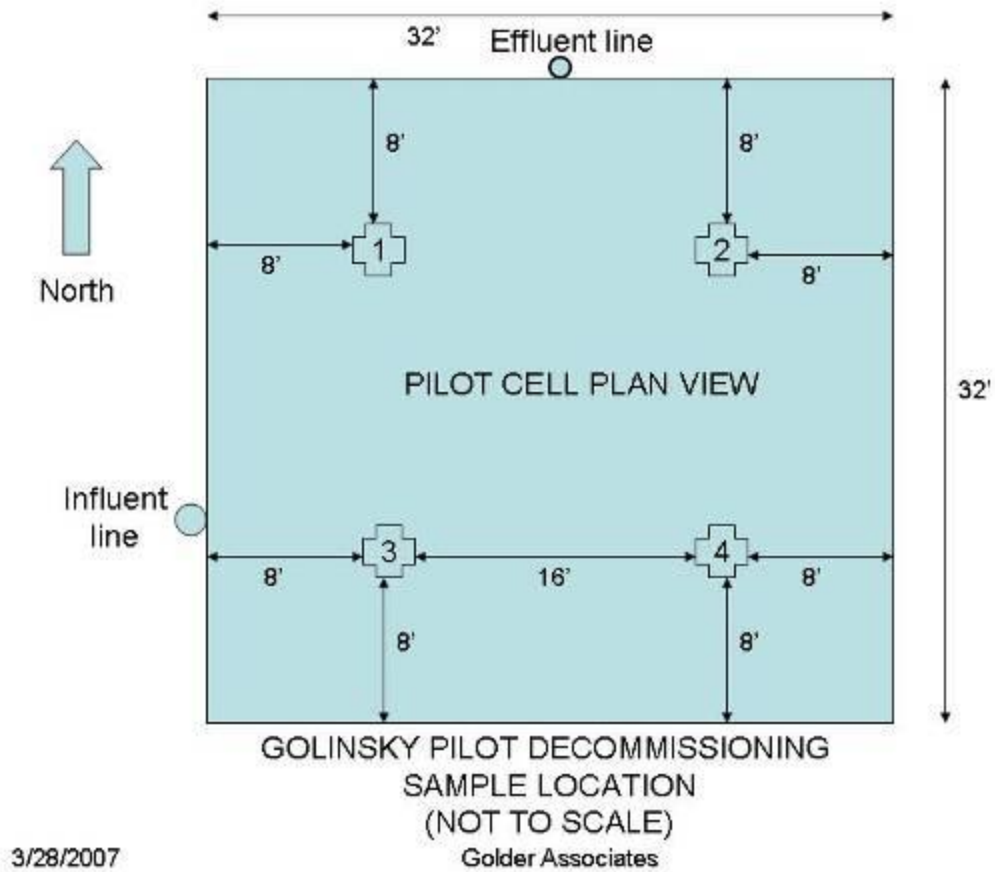


Figure 2. Pilot cell plan view with sample locations

The frequency, locations, and sample numbers were not selected to satisfy any particular statistical criterion. The sampling effort was developed to provide indications of gross medium changes that may have occurred during the 26-month test interval. During decommissioning, all of the pilot media was placed in a disposal pile on site approximately 70 m (230 ft) from the pilot BCR location. In the process of decommissioning, hauling, and dumping, the media was thoroughly mixed. Decommissioning photos are shown in Fig. 3 and 4. As such, the disposal pile is considered a homogenous mixture of all of the media horizons that formed during the pilot test. Post-decommissioning samples were collected from uppermost 12 in. of the disposal pile.



Figure 3. Pilot BCR after being drained and before decommissioning.



Figure 4. Decommissioning of pilot BCR

BCR Media Characterization Methods

The suite of laboratory analytical methods used in this study is provided in Table 1. Notes for specific pertinent methods are provided below.

- Acid base accounting (ABA) includes sulfur forms and neutralization potential (NP), as determined using the standard Sobek methods. These tests allow evaluation of acid generation potential by comparing total NP in a sample to total acid potential (AP) based on sulfide oxidation. In addition, the NP was used to evaluate substrate longevity.
- Toxicity Characteristic Leaching Procedure (TCLP) is a short-term leach test using a dilute acetic acid lixiviant that is routinely used to evaluate and classify waste materials for proper disposal.
- Net Acid Generation (NAG) tests involve leaching a sample with a strong oxidant (hydrogen peroxide) designed to oxidize all sulfides present in the sample. The resultant pH and acidity generated provides an indication as to the acid generation potential of the sample (Miller et al. 1997). In addition, analysis of the leachate can provide information as to a “terminal,” worst-case effluent resulting from complete and instantaneous sulfide oxidation and concurrent buffering.

The initial and decommission samples were analyzed for the full suite of analytes shown in Table 1. The one-year sample was analyzed for TCLP metals only and the two- and three-year samples were analyzed for TCLP metals, NAG leachate metals, and neutralization potential only due to budget constraints.

Evaluation of Substrate Disposal Stability

Substrate disposal stability was evaluated to help determine an appropriate disposal method for the pilot substrate and to help plan for future passive treatment systems at the site. The media in a full-scale treatment system at the site may need to be replaced every 10 to 20 years or perhaps longer, depending on final installed substrate thickness.

To address potential concerns over substrate disposal options with respect to metals leaching potential, the pilot substrate was evaluated with two short-term leach tests: the toxicity characteristics leaching procedure (TCLP) and the net acid generation (NAG). The nature of

these two tests is quite different. The TCLP test simulates leaching by a mild acidic solution, specifically the organic acetic acid. The NAG test includes an aggressive leach solution of hydrogen peroxide, a strong oxidant intended to oxidize sulfides. While intended to evaluate acid generation potential due to sulfide oxidation, acid generation, and concurrent buffering (Miller et al. 1997), it may also provide insight into metals release due to sulfide oxidation and acid generation. To address potential concerns over acid generation, materials were evaluated using the NAG test and ABA results.

Table 1. List of laboratory methods

Purpose	Analysis	Method
TCLP	TCLP Extraction	M 1311
TCLP	TCLP Metals (As, Ba, Cd, Cr, Pb, Se, Ag)	M 6010B ICP
TCLP	TCLP Mercury	M 7470A
Substrate Disposal Stability	Net Acid Generation Procedure	Sequential NAG - EGI 2002
Substrate Disposal Stability	NAG Metals (Zn, Cu, Cd, Pb)	M 6010B ICP
Limestone Content	Neutralization Potential as CaCO ₃	M600/2-78-054 3.2.3
Substrate Longevity	Carbon, TOC	ASA No. 9 29-2.2.4
Substrate Longevity	Organic Matter	EPA 600 3.2.14
Substrate Longevity	Moisture Content	M209F
Sulfate, sulfide precipitation	Sulfur forms (for ABA)	M600/2-78-054 3.2.4
Metals precipitation location	Environmental Total	M3050B
Metals precipitation location	Environmental Total Metals (Ca, Fe, Al, Cu, Zn)	M 6010B ICP
	Paste pH	USDA No. 60 (21A)

TCLP Results

TCLP testing is used to determine whether waste material is classified as a hazardous waste. Hazardous waste material can only be disposed of in designated hazardous waste landfills. The results of the TCLP testing for decommissioned, one-year, two-year, and three-year samples as well as the applicable RCRA standard (e-CFR Title 40 Part 261.24) are shown on Table 2.

For decommissioned samples, TCLP results for six of the seven metals are either below detection or well below the RCRA standard. The exception is cadmium for the T-1 0-6" sample at the time of decommissioning, which is 1 mg/L, equal to the RCRA standard. The Cd results for the other three samples stratigraphically beneath it are below the Cd detection limit.

The TCLP metals concentrations for the one-, two-, and three-year samples are less than the RCRA standards for all metals. The decommissioned samples were collected from a specific horizon in the pilot cell whereas one-, two-, and three-year samples were collected from the well-mixed disposal pile. As such, the two sets of results cannot be directly compared. A more accurate comparison would be possible if a disposal pile sample had been collected at the time of decommissioning in 2006; unfortunately, such a sample was not collected. Regardless, the three sets of results show some similarities, including consistent low level releases of barium and cadmium. Arsenic appears to be released in the one and two year samples; however the difference in detection limits between the one and two year samples and the decommissioning samples limits evaluation of this result.

In addition, the one-year and two-year results indicate that concentrations of arsenic, barium, and cadmium released appear to be increasing with time between 2007 and 2008. However, this increasing trend did not continue into 2009, as released concentrations decreased or remained the same as those in 2008.

Table 2. TCLP Results for decommissioned, one-year, two-year, and three-year samples.

Sample Date	Sample Name	Arsenic mg/L	Barium mg/L	Cadmium mg/L	Chromium mg/L	Mercury mg/L	Selenium mg/L	Silver mg/L
RCRA std. ¹		5.0	100.0	1.0	5.0	0.2	1.0	5.0
10/10/2006	T-1 0-6"	<0.2	0.21	1.0	<0.05	0.0003	<0.2	<0.05
10/10/2006	T-1 6-12"	<0.2	0.33	<0.03	<0.05	0.0003	<0.2	<0.05
10/10/2006	T-1 12-18"	<0.2	0.56	<0.04	<0.05	0.0004	<0.2	<0.05
10/10/2006	T-1 18-24"	<0.2	0.52	<0.05	<0.05	<0.0002	<0.2	0.12
11/10/2007	Grab	0.05	0.206	0.119	<0.05	<0.0002	<0.2	0.02
11/24/2008	Grab	0.1	0.475	0.393	<0.05	<0.0002	<0.2	<0.05
11/24/2008	Grab	0.1	0.507	0.368	<0.05	<0.0002	<0.2	<0.05
11/9/2009	Grab	<0.1	0.469	0.17	<0.02	<0.0002	<0.1	<0.02
11/9/2009	Grab	<0.1	1.0	0.37	<0.02	<0.0002	<0.1	<0.02

Note:

< - a less than sign indicates the value was below the minimum detection limit given.

¹ RCRA standards, e-CFR Title 40 Part 261.24 Toxicity characteristic.

During decommissioning in 2006, samples were collected from discrete horizons. Samples collected from media waste pile in 2007, 2008, and 2009 were grab samples collected from the top 12" horizon of the pile.

ABA Results

Acid base accounting results are summarized in Tables 3 and 4, which also provides standard ABA calculations derived from the modified Sobek NP and the AP (calculated from total sulfur). These calculations include the net neutralization potential (NNP; = NP minus AP) and the neutralization potential ratio (NPR; = NP to AP). There are various methods and criteria for evaluation of these values. For example, the classification provided by Price (1997) considers samples with NPR values < 1 as having possible acid rock drainage properties, samples with NPR values between 1 and 2 are possibly acid generating, samples with NPR values between 2 and 4 have low acid generation potential, and NPR values > 4 indicate a sample is non-acid generating. For NNP, EPA (1994) provides a classification system that defines uncertain behavior by NNP values between -20 and 20 tCaCO₃/kt, with values less than -20 tCaCO₃/kt as potentially acid generating and above 20 tCaCO₃/kt as non-acid generating.

The ABA results indicate that all of the media tests are classified as non-acid generating using the classifications described above, with the exception of T1 0-6", which would be classified as uncertain following EPA (1994) or possibly acid generating following Price (1997).

Table 3. T-1 Neutralization Potential Results

Sample Date	Sample ID	pH, Saturated Paste	Acid	Acid	Net Neutralization Potential	Neutralization Potential as CaCO ₃
			Neutralization Potential (calc)	Generation Potential (calc on S total)		
		s.u.	t CaCO ₃ /Kt	t CaCO ₃ /Kt	t CaCO ₃ /Kt	%
Jul-04	Initial Substrate	NA	226	5	221	22.6
Oct-06	T-1 0-6"	5.8	38	23	15	3.8
Oct-06	T-1 6-12"	6.8	89	16	73	8.9
Oct-06	T-1 12-18"	6.8	92	14	78	9.2
Oct-06	T-1 18-24"	6.8	93	13	80	9.3
Oct-06	T-1 24-30"	6.8	91	14	77	9.1

Note:

During decommissioning in 2006, samples were collected from discrete horizons. Samples collected from media waste pile in 2007 and 2008 were grab samples collected from the top 12" horizon of the pile.

Table 4. T-4 Neutralization Potential Results

Sample Date	Sample ID	pH, Saturated Paste	Acid	Acid	Acid-Base	Neutralization Potential as CaCO ₃
			Neutralization Potential	Generation Potential (cal)	Potential (calc on S)	
		s.u.	t CaCO ₃ /Kt	t CaCO ₃ /Kt	t CaCO ₃ /Kt	%
Jul-04	Initial Substrate	NA	226	5	221	22.6
Oct-06	T-4 0-6"	6.2	81	18	63	8.1
Oct-06	T-4 6-12"	6.8	90	19	71	9
Oct-06	T-4 12-18"	6.9	89	13	76	8.9
Oct-06	T-4 18-24"	6.9	91	14	77	9.1
Oct-06	T-4 24-27"	6.8	89	11	78	8.9
Nov-08	Grab	NS	NS	NS	NS	6.4
Nov-08	Grab	NS	NS	NS	NS	6.2
Nov-10	Grab	NS	NS	NS	NS	4.8
Nov-10	Grab	NS	NS	NS	NS	8.3

Note:

During decommissioning in 2006, samples were collected from discrete horizons. Samples collected from media waste pile in 2007, 2008, and 2009 were grab samples collected from the top 12" horizon of the pile.

NAG Results

To further address concerns over substrate disposal stability, NAG testing was performed to determine how substrate would react in an oxidizing environment. While a bioreactor is in operation, the substrate is typically submerged and anoxic which allows metals to precipitate as metal sulfides. However, depleted substrate could potentially be disposed of in an oxidizing environment such as a land application at a disposal site. An oxidizing environment could potentially reverse the sulfide precipitation process that occurred in the functioning bioreactor and cause the substrate to become a source of potentially acidic metal-laden water.

The NAG testing was performed to evaluate how substrate might behave if it is disposed of in an oxidizing environment. However, it is important to note that the NAG test is an aggressive test resulting in instantaneous oxidation of sulfides. The kinetics of this reaction in the field situation are expected to occur over a much longer time period. In addition, the presence of residual unreacted organic matter in depleted substrate will likely delay oxidation of sulfides. It is anticipated that the organic matter would need to decay completely before sulfide oxidation would become significant.

None of the four NAG test results were positive for acid generation, consistent with the ABA results. NAG leachate results are summarized in Table 5. Detectable concentrations of Cd, Cu, and Zn were measured in leachate from the four decommissioned samples analyzed. The highest Cu and Cd concentrations were in leachate from the surface sample T-1 0-6" while highest zinc concentrations were in leachate from a sub-surface sample (T-1 6-12"). Concentrations of Cu and Zn were detected in the two- and three-year samples while cadmium was not. One-year samples were not analyzed for NAG. Cadmium was detected in the TCLP leachate, but is generally absent from the NAG leachate. These tests indicate that cadmium release is less sensitive to oxidation and may be more sensitive to the acidic pH of the TCLP test. This provides insight into the removal mechanism for Cd, which may be as hydroxide precipitation or sorption, rather than sulfide precipitation. Lead concentrations in all samples were below the detection limit. Changes in leachability by the NAG test do not change significantly with time, though as the disposal pile material remains at the surface, available sulfides are expected to be depleted.

Table 5. NAG results from decommissioned and two-year samples.

Sample Date	Sample ID	Dissolved Cadmium mg/L	Dissolved Copper mg/L	Dissolved Lead mg/L	Dissolved Zinc mg/L
10/10/2006	T-1 0-6"	0.106	10.5	<0.04	3.5
10/10/2006	T-1 6-12"	<0.005	0.03	<0.04	6.27
10/10/2006	T-1 12-18"	<0.005	0.01	<0.04	0.11
10/10/2006	T-1 18-24"	<0.005	<0.01	<0.04	0.03
11/24/2008	Grab	<0.005	0.25	<0.04	0.14
11/24/2008	Grab	<0.005	0.32	<0.04	0.13
11/9/2010	Grab	<0.005	0.03	<0.04	0.06
11/9/2010	Grab	<0.005	0.07	<0.04	0.03

Note:

< - values below the minimum detection limit are preceded by a '<' and entered as the minimum detection limit.

During decommissioning in 2006, samples were collected from discrete horizons. Samples collected from media waste pile in 2007, 2008, and 2009 were grab samples collected from the top 12" horizon of the pile.

Discussion of Substrate Stability and Recommended Disposal Protocol

The two leaching tests indicate that metals, specifically Cd, Cu, and Zn are released from the 26-month substrate (i.e., decommissioned samples). Barium, Hg, and As were also released during leach testing, but at relatively low concentrations, well below RCRA standards, indicating these metals are not a concern. Cadmium, the only constituent leached at RCRA standards, was predominantly leached from the upper surface sample (T-1 0-6"), which contains both oxide and sulfide removal zones (described further below). Cadmium removal in the BCR likely occurs due to sorption to iron oxide and possibly precipitation as sulfides. Leaching by the mildly acidic TCLP lixiviant may have caused desorption of cadmium or iron oxide dissolution and subsequent cadmium release. Leaching with an oxidant in the NAG test may have resulted in sulfide oxidation or dissolution of the iron oxides (from localized acid generation), again resulting in Cd release. Similar removal and release mechanisms for Cu are expected. Zinc was leached in greatest concentrations from a subsurface sample (T-1 6-12") in the NAG test. The horizon of the greatest Zn release and that it was released by the NAG oxidant, implies that Zn was released from a sulfide form.

Leaching of metals may be due to one of several changing geochemical conditions occurring as the decommissioned pile has remained exposed on the surface. Oxidation of sulfides in the materials would result in release of metals previously sequestered as sulfides. Oxidation of iron sulfides may also result in some localized acid generation that may release metals. Finally, aging of iron oxides (e.g., from amorphous ferrihydrite to more crystalline forms like hematite or goethite) may also be occurring, which may result in reduction of sorption surface area and subsequent metals release.

When considering how substrate from a full-scale bioreactor that has operated for 15 years or more would fare in TCLP test, there are three important factors to consider.

- Based on the low TCLP concentrations for six of the seven TCLP metals, Cd is the only metal approaching RCRA standards in the TCLP leachate.
- The main difference between the pilot substrate, which operated for 27 months, and 15-year old substrate would be a greater amount of metal precipitates in the older substrate. This could lead to higher TCLP results.
- As the substrate “depletion front” migrates deeper into the cell, the upper layers may actually have depleted metals and an elevated metal horizon might develop elsewhere in the cell mass. TCLP samples are typically collected as a composite sample of all the substrate horizons rather than focused samples such as the ones evaluated in this study. A composited sample of all substrate layers would likely have a lower TCLP result for Cd in this case, given the observed uneven distribution of metal precipitates in the substrate.

In addition, based on the NAG results, oxidizing environment disposal of depleted substrate is not recommended as metals in addition to Cd may be released. However, TCLP results suggest that landfilling depleted substrate may be appropriate if Cd persists in Golinsky ARD. Operational protocols of full scale BCR cells may need to be developed so that the medium is replenished at the point where the total composited mass is below the TCLP hazardous threshold. Alternatively, cadmium-rich horizons may require special handling or processing.

Substrate Longevity

Limestone Longevity

Two methods were used to determine limestone longevity: neutralization potential (NP) testing of substrate and a calculation of limestone dissolution based on influent and effluent calcium concentrations.

Neutralization Potential Testing

The longevity of the limestone in the substrate was estimated by NP testing. Results for initial, decommissioned T-1 samples are provided in Table 3; initial, decommissioned T-4, two-year, and three-year sample results are provide in Table 4. The initial substrate sample contained an NP value of 22.6% which corresponds with the initial substrate recipe of 29% limestone on an as-received weight basis. The NP value is slightly less because it is measured on a dry basis and limestone typically contains some impurities. The average NP value for location T-1 was 8.1% which is a reduction of 64% from the initial substrate. This assumes that the initial substrate had the prescribed proportion of limestone. The average NP value at T-4 was 8.8% which is a reduction of 61% from the initial substrate. At the T-1 sample location, the top layer of substrate (0"-6") contained significantly less NP than the other layers. One would expect to see the greatest limestone depletion at the surface of the bioreactor where incoming acidic water is buffered. Based on an NP reduction of about 60% during the 27 months of pilot operation, the pilot cell would have been depleted of limestone after an additional 45 months or about 3.8 years of operation. This is not consistent with the limestone longevity estimates developed using other methods as described below and is predicated on the assumption that the limestone content of the substrate used was as specified, i.e., 30% by as received weight. On average, two-year and three-year results (Table 4) show a decrease in NP compared to the average NP of 8.8% of the decommissioned T-4 samples.

Limestone Dissolution Rate

The limestone dissolution rate was calculated using influent and effluent Ca concentrations and flow rate. The dissolution rate (grams/day) was calculated for each sampling event by subtracting the effluent calcium concentration from the influent concentration, multiplying by the flow rate, and converting to the equivalent mass of limestone (CaCO_3). The average dissolution rate for pilot cell was 2,073 grams of limestone per day. Multiplying this rate over the lifetime of the pilot cell (27 months or 824 days) provides a total limestone dissolution mass of 1,708 kg.

The limestone quantity specified in the initial pilot construction was 11,268 kg. Assuming an initial mass of limestone of 11,268 kg and a dissolution rate of 2,073 grams per day yields a limestone longevity of about 15 years. This value agrees with the bench scale test results upon which the pilot cell design was based.

Field Measurements of Limestone

Field measurements of limestone were conducted to provide another method of estimating the limestone content of the pilot cell upon its decommissioning. A substrate sample was collected from each six-inch layer in a sixteen ounce soil jar. The limestone was separated from the organic substrate on site using a gold pan. The limestone samples were transported back to Denver, CO and air-dried and weighed at the Golder Soils Laboratory. The results of these field measurements are presented in Table 6.

Table 6. Field Measurement of Limestone Content

Sample Date	Sample ID	Limestone Content per 473 ml (16 fl. oz.) of Substrate, Dry
		Weight grams
Jul-04	T-4 0-6"	62
Oct-06	T-4 6-12"	84
Oct-06	T-4 12-18"	124
Oct-06	T-4 18-24"	124
Oct-06	T-4 24-27"	124

The amount of limestone present in each layer increased with increasing sample depth. The bottom three layers all contained the same amount of limestone. These findings support the theory that limestone is preferentially dissolved in the uppermost layers as acidic water is introduced at the top of the cell. This phenomenon has been described as a rolling front of limestone dissolution (Thomas 2002) that slowly migrates vertically downward as the limestone in each layer is consumed. Limestone that is below the front is undissolved and should be similar to the amount of limestone contained in the initial substrate (Thomas 2002). These

results are consistent with the decrease in NP in the T-1, 0-6" sample. The field measurements of limestone contradict the large NP decrease between 'initial' and decommissioned substrate samples which implied that significant limestone dissolution had occurred through all layers of the substrate.

Limestone Longevity Summary

The two limestone longevity estimates range from 3.8 years according to the NP testing to 15 years according to the calculated limestone dissolution rate. The field measurement of limestone contradicts the NP results and indicates that limestone dissolution has been limited to the upper two layers of substrate (0"-6", 6"-12"). This is consistent with the longer dissolution rate longevity estimate. When considering the large difference between 'initial' and decommissioned NP values, it is important to consider that the 'initial' sample was prepared specifically for this report and was not actually collected from the pilot cell at startup. It is possible that the substrate that was mixed and placed in the pilot contained less limestone than was specified. If the actual original substrate contained less limestone than the 'initial' substrate sample, then the actual NP reduction would be proportionately less and the limestone longevity based on NP testing would more closely agree with the limestone dissolution rate estimate. Another possible explanation for the low NP values in the decommissioned samples is laboratory analytical error. The physical evidence and experience at other sites/situations support the longer estimate.

Organic Carbon Longevity

Organic carbon is the vital source of energy for the bacterial community of an BCR (Wildeman and Updegraff 1997). The lifespan of an BCR is thus linked to a steady supply of organic carbon. The carbon longevity of the pilot cell was also calculated by two separate methods: one method based on sulfate reduction and the other based on Total Organic Carbon (TOC) measurements of substrate samples. The measure of TOC does not indicate the amount of bio-available carbon (cellulose) compared to the relatively low-biodegradable carbon (lignin) (Place et al. 2006). This analysis assumes that 15% of the initial substrate was lignin and is therefore not available as a carbon source.

Carbon longevity based on sulfate reduction

The longevity of the organic substrate is based on the amount of carbon required to support the sulfate reduction occurring in the bench cells. By assuming typical moisture contents, a typical loss on ignition value for the hay, a laboratory loss on ignition value for the co-gen fuel,

and 15% lignin content, Golder estimated the initial carbon content of the pilot cell. The bacteria-mediated reduction of sulfate to sulfide requires two moles of carbon for every mole of sulfate or 24 grams of carbon for every 96 grams of sulfate. Using the design sulfate reduction rate of 0.3 moles per day per cubic meter of medium, Golder estimated a carbon longevity of about 25 years based on the available carbon and the carbon consumption rate to sustain the sulfate reduction rates.

Carbon longevity based on TOC measurements

An 'initial' and a decommissioned substrate sample from location T-2 were analyzed for TOC. The results are presented on Table 7. The 'initial' TOC value of 23.2% decreased to an average TOC value of 14.4% in the decommissioned samples. This is equivalent to a 38% decrease in TOC during the 27 months of operation. Based on this assumed steady-state rate of decrease of TOC, the pilot cell would be depleted of TOC in an additional 71 months or about 6 years of operation. This rapid decrease in TOC was likely caused by the loss of significant amounts of organic matter in the first six months of operation due to flushing of labile organic matter from the cell. Indeed, visual inspection of the decommissioned medium (see photos 17 to 20) revealed a dearth of hay and rice hulls, which combined comprised 20% by weight of the initial mass of substrate. BCRs typically have high effluent biochemical oxygen demand (BOD) levels at startup when manure and labile organics such as hay and rice hulls are biodegraded and partially flushed from the cell. These labile organics are designed to kick start the bacterial community by provided readily available organic carbon. After startup, BOD levels decrease dramatically and the bacteria begin degrading the long-term carbon sources (i.e., co-gen fuel). It is likely that the substrate TOC decreased significantly during this period which would explain the large drop in TOC between the 'initial' and decommissioned samples. Assuming this rapid decline of TOC will be sustained is not appropriate.

Carbon Longevity Summary

The two methods of estimating carbon longevity yielded significantly different values. The sulfate reduction method yielded a carbon longevity estimate of 25 years while the TOC analysis yielded an estimate of about six years. The TOC longevity estimate is considered to be too low because it was based on the observed rate of TOC depletion that was artificially high due to the large flush of BOD from the cell at startup. Ideally, TOC analysis could be performed before startup, after 6 months of operation, and at regular intervals thereafter to gain a better

understanding of organic matter depletion rate in BCR's. The abundance of unreacted wood chips in the media (Fig. 5) anecdotally suggests that a carbon longevity is likely longer than six years.

Table 7. Total Organic Carbon Results

Sample ID	Carbon, total organic (TOC)
	%
Initial	
Substrate	23.2
T-2 0-6"	13.7
T-2 6-12"	13.6
T-2 12-18"	13.6
T-2 18-24"	16.6



Figure 5. Media profile with tape measure showing depth from top of media.

Metal precipitation ZONES

Preferential metal precipitation zones were identified by analyzing selected substrate samples for Al, Cu, Fe, and Zn content.

Field Observations

The following distinct layers were observed in the substrate at decommissioning:

0"-1" BS – As seen in Figures 6, 7, and 8, a 1 inch-thick layer of iron hydroxide deposits were present on the entire surface of the BCR cell. This zone has been referred to as the oxide zone because iron hydroxide precipitates indicate oxidizing conditions (Thomas 2002)



Figure 6. Edge of bioreactor substrate with thin ferric hydroxide coating.



Figure 7. Sample location T-2.



Figure 8. Disturbed substrate sample with top of substrate on the left.

1"- 8" BS – As seen in Fig. 9, a 7 inch-thick dark black layer exists at this depth. This zone may be black due to sulfide deposits. Although sulfate reducing bacteria are probably not active in the area due to a depressed pH, it is possible that hydrogen sulfide gas, generated in the transition zone (8"-10" BS) or in the sulfide zone (14" – 30" BS), diffused upwards and formed iron sulfide (pyrite) at this depth (Thomas 2002).



Figure 9. 0" – 14" depth showing iron hydroxide zone (0" – 1"), black sulfide zone (1" – 8") and aluminum zone (8" – 14")

1. 8" – 14" BS – This gray 6 inch-thick layer, also observed by Thomas (2002), probably contains aluminum hydroxysulfate precipitates (Fig. 9) but lacks black metal sulfides that would otherwise darken the medium's appearance as in the 1"-8" BS zone. This has been referred to as the transitional zone because it creates a boundary between the oxide zone and the reducing conditions of the sulfide zone (Thomas 2002). It may also be a zone where colloidal sulfides precipitated higher in the bioreactor find conditions favorable for deposition/accumulation.

14" – 30" BS – This zone of black substrate is the sulfide zone and is likely where the majority of sulfate reduction is occurring (Thomas 2002).

Substrate Metals Analysis

Substrate samples from locations T-1, T-2, and T-4 were analyzed for aluminum, copper, iron, and zinc (Tables 8, 9, and 10). Background metals concentrations of the initial substrate were not analyzed. The following conclusions can be drawn.

Table 8. T-1 Total Metals Analysis

Sample ID	Average depth	Aluminum, total	Copper, total	Iron, total	Zinc, total
		mg/kg	mg/kg	mg/kg	mg/kg
Initial					
Substrate	NA	3880	17	4140	75
T-1 0-6"	3"	19900	8350	38300	3730
T-1 6-12"	9"	6950	32	8500	6330
T-1 12-18"	15"	5060	16	8270	225
T-1 18-24"	21"	5800	15	9220	48
T-1 24-30"	27"	8960	36	12600	63

Table 9. T-2 Total Metals Analysis

Sample ID	Average depth	Aluminum, total	Copper, total	Iron, total	Zinc, total
		mg/kg	mg/kg	mg/kg	mg/kg
Initial					
Substrate	NA	3880	17	4140	75
T-2 0-6"	3"	14300	3900	22100	8320
T-2 6-12"	9"	6000	20	9650	528
T-2 12-18"	15"	5030	14	6790	42
T-2 18-24"	21"	5620	15	7040	48
T-2 24-28"	26"	4390	22	10600	87
T-2 0-6"					
DUP	3"	16500	4530	25000	4960

Table 10. T-4 Total Metals Analysis

Sample ID	Average depth	Aluminum, total mg/kg	Copper, total mg/kg	Iron, total mg/kg	Zinc, total mg/kg
Initial					
Substrate	NA	3880	17	4140	75
T-4 0-6"	3"	25300	12100	21500	2560
T-4 6-12"	9"	6090	20	8400	6880
T-4 12-18"	15"	9080	19	11700	155
T-4 18-24"	21"	5180	13	6950	53
T-4 24-27"	25.5"	6060	15	8410	60

Aluminum – The highest Al concentration were measured in the 0”-6” layer. Consistent Al concentrations were detected in the lower four layers.

Copper – The vast majority of Cu was contained in the uppermost layer. This indicates that the Cu may have been sorbed to the iron (0”-1” BS) or Al precipitates or precipitated as a sulfide in the 4”- 6” BS zone. Copper removal also likely occurs via partitioning to organic matter (Thomas 2002).

Iron – The largest Fe concentrations were detected in the uppermost layer which is consistent with highly visible orange iron hydroxide deposits. Iron was detected at significant concentrations at every layer. High levels of iron were also detected towards the bottom of the cells (sulfide zone) where colloidal iron pyrite precipitated higher in the reactor encountered conditions favorable for deposition/accumulation.

Zinc – The vast majority of Zn was removed in the top two layers of substrate. Zinc removal is likely due to coprecipitation with iron hydroxides and sorption to organic matter. (Thomas 2002). Zinc removal as zinc sulfide in the 1”-8” BS layer is also possible.

Metal Precipitation Pathways

The field observation and total metal analyses are similar to those documented by Robert Thomas in his doctoral thesis (Thomas 2002). Thomas has carried out the most detailed investigation of BCR removal mechanisms to date. The precipitation of zinc and copper in the upper one foot of substrate is qualitative indicator of cell longevity. As the limestone in the top layer dissolves and the rolling front of limestone dissolution migrates downward through the cell, some fraction of the metals will likely redissolve and reprecipitate at lower depths. The concentration of Cu and Zn in the uppermost layers of the cell indicates that there was significant remaining vertical capacity in the cell.

Conclusions

The goal of this decommissioning study was to determine substrate disposal stability, substrate longevity, and examine metal precipitation trends. The results of this study should provide the basis for proper design and disposal of BCR media for future passive treatment systems at the site.

- The TCLP metals results did not exceed the RCRA hazardous waste standards, although the Cd concentration in one sample did equal the RCRA standard. These results indicate that the overall pilot substrate would not be classified as a hazardous waste and could be disposed of in municipal landfill. Samples collected from the well-mixed media disposal pile show increasing leachate concentrations of As, Ba, and Cd for the first two years following decommission, but the trend did not extend to the third year. To date, no sample has exceeded the TCLP limits which would render the media a hazardous waste and only Cd is within an order of magnitude of the RCRA leachate standards.
- The NAG results indicate that decommissioned substrate does not have acid generation potential. However, the NAG leachate did contain detectable concentrations of Cd, Cu, and Zn, with elevated Cu and Zn. This implies that Cu and Zn sulfides may be oxidized by the NAG test. As such, Golder does not recommend disposal in an oxidizing environment. Two-year samples contained copper and zinc concentrations that were consistent with decommissioned samples; the concentrations from the two-year samples of well-mixed media were less than highest decommissioning samples and greater than the lowest decommissioning samples. The leachate results indicate that decommissioned substrate may release aqueous metals if the substrate is allowed to oxidize (given enough time to do so), though may deplete with time. For long-term management of the substrate, Golder

recommends incorporating the pilot substrate into future BCR cells at the site or disposing of the substrate at a municipal landfill.

- The two methods of calculating limestone longevity gave significantly different results. The NP results indicate that more than half of the limestone has been dissolved. These results are inconsistent with the dissolution rate longevity estimate and field measurements of limestone. The dissolution rate estimate of limestone longevity is fifteen years.
- The two methods of estimated organic carbon longevity also yielded significantly different results. The large decrease in TOC is likely due to typical flushing of labile organic matter at cell startup. The carbon longevity based on sulfate reduction is 25 years.
- The metal precipitation zones throughout the cell and the cell stratification into an oxide, transitional, and sulfide zone are consistent with the research of successful BCR cells (Thomas 2002). The concentration of Cu and Zn in the uppermost layer of the cell provides anecdotal evidence that significant vertical treatment capacity remained at the time of the pilot cell's decommissioning.

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