USE OF FLUIDIZED BED SLAG REACTORS FOR PASSIVE TREATMENT OF ACID MINE DRAINAGE

Final Report

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Problem and Research Statement

Coal production has been a major industry in Ohio and because of increasing pressure on petroleum reserves will likely continue into the future. Mining however can have a significant negative impact on water resources, and abandoned underground mines continue to be a serious threat to water quality in southeast Ohio. Ohio coal deposits contain significant quantities of pyrite. As water and oxygen are supplied to these underground pyrite reserves by abandoned mine shafts, chemical and biological reactions oxidize the pyrite forming high concentrations of sulfuric acid and dissolved iron. The resulting low pH also dissolves other metals, typically aluminum being of greatest concern in Ohio. Water released from these mine shafts carry very high acid and metal loads that can kill aquatic life in a stream for miles downstream. For the past twenty years, southeast Ohio has devoted millions of dollars to reducing the impact of this acid mine drainage (AMD). Yet AMD remains a leading cause of surface water pollution in southeast Ohio.

One particularly difficult type of AMD source to treat occurs when a large mine complex empties near an impact point with no space for installation of a large passive treatment system. Active treatment systems are sometimes employed such as alkaline dosing, but the ongoing maintenance costs pose a problem for managing agencies. In the past five years, waste iron slag has emerged as an attractive treatment alternative. When iron ore is melted and purified, slag is the waste product that floats to the top of the melt and is discarded. It is strongly alkaline and inexpensive. When used for AMD treatment, the acidic water is directed through lined pits filled with uniformly sized pieces of slag. However, the elevated pH results in precipitation of metals, primarily iron and aluminum. The metals may clog and armor the slag which over time leads to hydraulic clogging of the slag bed and reductions in alkalinity addition. As a result, slag beds are often used only when a clean water source can be found. Thus, clean water flows through the slag bed, raising the pH to approximately 11 which is then mixed with the AMD. This is a very effective, inexpensive, and treatment option, although, it is only possible at sites with a clean water source, room for installation of the bed, and room for installation of a wetland to collect the metals precipitates before reaching the impact point.

This research tested the effectiveness of a novel treatment configuration. Fluidized bed reactors are extremely efficient, providing significant surface contact time in a very small footprint. Engineered systems like these are seldom considered for AMD treatment because of the energy requirements to fluidize the bed. However, abandoned mine flows often have sufficient pressure to provide enough head for fluidization of the bed. Further, the agitation of the slag particles will allow metal precipitates to flow out of the bed preventing clogging. It is likely that scouring of the slag particles will also prevent armoring and maintain continuous alkalinity addition, until the particles require replacement. In short, this research tests a new treatment technology that if successful will have application to some of our most troublesome AMD sources.

Methodology

The first portion of this experiment was to determine the rate at which different sieved slag fractions fluidized using a fluidized bed reactor. The reactor was composed of a large glass chromatography column 4" inner diameter and 24" length (ACE Glass Incorporated, Vineland, NJ; see Figure 1). Slag fines were supported by a plastic frit supplied with the column. Water flowed through a Materflex adjustable peristaltic pump and a flow equalizer to eliminate pulsing before entering the bottom of the column. pH into and out of the fluidized bed was measured using a WTW Multi 350i pH meter and a Denver Instrument Model 225 pH meter. Influent and effluent samples were periodically collected and analyzed for acidity and alkalinity using standard methods (Standard Methods, 20th Edition, 1998).

Slag sand was obtained from Tube City IMS (Horsham, PA), a company that specializes in slag recovery. Chemical analysis from the company indicated a pH of 12.6 and calcium carbonate equivalent of 612,000 mg/kg for the slag. Slag fines were sieved using #20, #40, and #60 sieves and the fractions were saved. These sieves have mesh sizes of 850 µm, 425 µm, and 250 µm respectively. Mine spoil or gob was collected from a local site that was known to produce significant AMD. A 20-gallon tub was filled with gob and flooded with tap water. After several days, pH and acidity in the water was 2.8 and 170 mg $CaCO_3$/L. In addition, artificial AMD was prepared to simulate measured AMD concentrations measured at a local site. Sulfuric acid was added to 50 L of tap water until pH = 5. 35.1 g of ferrous ammonium sulfate was dissolved and then more sulfuric acid added to drop the pH to 4. Target iron concentration was 100 mg/L

Four sets of tests were performed with this fluidized bed reactor. First, the three different slag sizes were tested at different flow rates to determine flow required for fluidization. Next, effluent pH with clean water running through the fluidized bed was determined. For the third test, AMD generated from the gob pile was delivered through the fluidized bed, and effluent pH and alkalinity and acidity concentrations measured. Finally, artificial AMD was treated with the slag fluidized bed. Influent and effluent concentrations were monitored with pH, alkalinity, acidity, and total dissolved iron. Fresh slag was always used for each test.

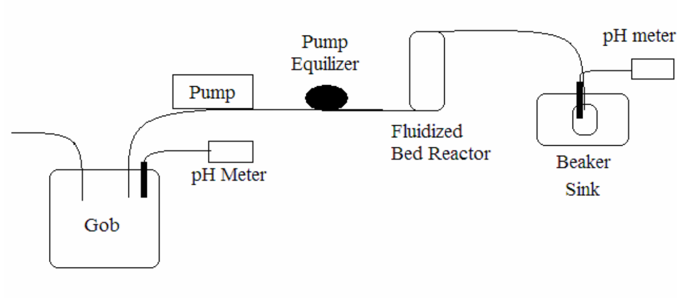

Figure 1: Fluidized Bed Reactor Setup

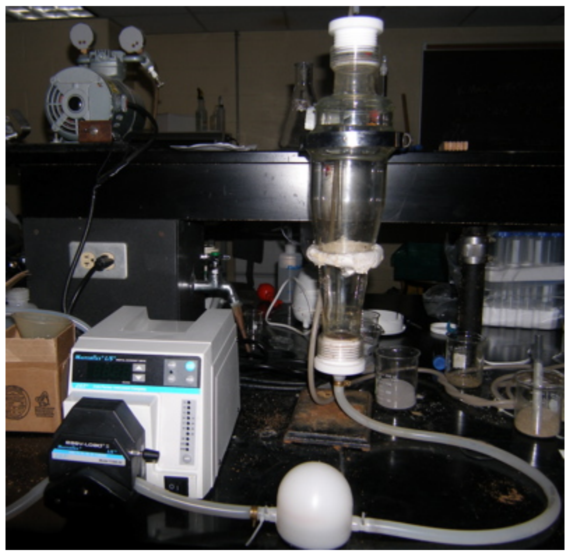

Figure 2: Peristaltic pump and fluidized bed reactor

Principal Findings

Fluidization of Slag

The first part of this project was to determine the flow rate at which different sizes of slag particles fluidize. Originally a glass frit was used, but the glass frit did not allow the fluid to flow at a sufficient rate. It was determined that the plastic frit that was provided with the original glassware produced better results. Below are the tables showing the fluidization tests with the plastic frit of slag particles from #20, #40, and #60 sieves.

Table 1: Fluidization results at different flow rates using #20 slag

Flow Rate (mL/min)	Description for 1" #20 slag layer	Flow Rate (mL/min)	Description for 1.25" #20 slag layer
100	No movement	100	No movement
200	No movement	200	No movement
300	No movement	300	There was some small shaking in a vibrating like motion.

400	No movement	400	There was some small shaking in a vibrating like motion.
500	There was some small shaking in a vibrating like motion.	500	There was some small shaking in a vibrating like motion.
600	There was little movement of small particles on top layer.	600	There was some small shaking in a vibrating like motion.
700	There was little movement of small particles on top layer.	700	There was some small shaking in a vibrating like motion.
800	There was little movement of small particles on top layer.	800	There was faster shaking in a vibrating like motion.
900	One tunnel of movement 3/4in wide.	900	There was some small movement of slag pieces in one 1in section.
1000	Single tunnel flowing faster	1000	There was faster movement of slag pieces in one 1in section.
1100	Single tunnel was about 1in wide and flowing faster. Little to no movement in other areas.	1100	Faster movement in 1.25in section. Little to no movement in other areas.
1200	Single tunnel was now about 1in wide and flowing faster. Little to no movement in other areas.	1200	Faster movement in 1.5in section. Little to no movement in other areas. Section in motion raised 1/16in.
1300	Single tunnel is now about 1in wide and flowing faster. Little to no movement in other areas.	1300	Faster movement in 1.5in section. Little to no movement in other areas. Section in motion raised 1/16in.
1400	Another section was starting to flow about 1.25in wide. Section in motion was raised 1/4in.	1400	Section in motion was raised 1/8in. 1 in of moving perimeter was fluidized.
1500	1/4 of perimeter was fluidized. Little to no movement in other areas.	1500	1.75in of perimeter was in motion. 1.25in fluidized. Little to no movement still in other areas.
1600	1/4 of perimeter was fluidized. Little to no movement in other areas. Tunnel was raised 1/4in.	1600	1.5in fluidized. Section in motion was raised 1/4in.
1700	1/4 of perimeter is fluidized. Little to no movement in other areas. Tunnel was raised a little under 1/2in.	1700	2in of perimeter was in motion. 1.5in fluidized.
1800	About 1.75in of perimeter was fluidized.	1800	1.75in fluidized. Section was in motion raised 5/16in.
1900	2in of perimeter was fluidized.	1900	Faster movement
2000	Section in motion raised 5/8in and flowed faster.	2000	Faster movement
2100	Section in motion was raised 3/4in and flowing faster.	2100	2in of perimeter was fluidized. There was little to no movement in other areas.
>2100	Fluidized section grew a little in height and the speed of flow increased with increasing flow rate. Areas not fluidized had little to no movement.	2200	Fluidized section raised 3/8in.
		2300	2.125in fluidized. Fluidized section raised just under 1/2in.

		2400	Faster motion
		2500	2.125in fluidized. Fluidized section raised just under .5in.
		2600	Fluidized section grew a little in height and the speed of flow increased with increasing flow rate. Areas not fluidized had little to no movement.

Table 1 shows that #20 slag started to have sections fluidize around 1500 mL/min. In trial 1 the maximum amount fluidized was 2 in of the perimeter, this occurred at 1900 mL/min. In trial 2 the maximum amount fluidized was 2.125 in of the perimeter and this happened at 2300 mL/min. Significant fluidization was not achieved with this size slag at any flow rate.

Table 2: Fluidization results at different flow rates using #40 slag

Flow Rate (mL/min)	**Description for 1.25" #40 slag layer**	**Flow Rate (mL/min)**	**Description for 1.5" #40 slag layer**
100	No movement	100	No Movement
200	One small tunnel formed with very slow movement. The slag as a whole was in a wave like vibration.	200	There was some shaking of whole mass
300	Same wavelike vibration, but faster	300	There was some shaking of whole mass
400	Original tunnel grew and was 3/4in wide. Small tunnels formed in bottom half of slag.	400	Faster shaking. There was some movement of particles in 1/4 of perimeter.
500	Original tunnels became wider. Other tunnels formed with slower flow.	500	Faster shaking. There was some movement of particles in 1/4 of perimeter.
600	1/2 of perimeter was in motion. The slag has raised 1/16in.	600	More tunnels were formed toward the top. Slag was raised 1/16in. 1/4 of perimeter had motion
700	Faster motion in perimeter. Instead of tunnels the slag was moving in sections. 2/3 of perimeter had movement	700	1/4 fluidized. There was some movement in 1/2 of perimeter.
800	1/3 of perimeter fluidized. Faster flow in other formed tunnels.	800	There was faster movement in 1/2 of perimeter. Slag has raised 1/8in
900	1/2 of perimeter was fluidized. Slag has raised 1/4in	900	1/3 of perimeter was fluidized. Faster movement in another 1/3 of perimeter. Slag had raised 3/16in.
1000	1/2 of perimeter was fluidized. Slag was raised 1/4in. There was faster movement of slag.	1000	1/3 of perimeter was fluidized. There was faster movement in another 1/3 of perimeter. Slag had raised 1/4in.

1100	2/3 of perimeter fluidized. There was faster movement of slag.	1100	1/2 of perimeter was fluidized. Slag had raised 7/8 in
1200	2/3 of perimeter was fluidized. There was faster movement of slag.	1200	2/3 of perimeter fluidized. Other areas had little to no movement.
1300	There was faster higher flow in fluidized areas.	1300	There was faster movement in fluidized areas.
1400	1/3 of slag had little to no movement. There was fast fluidization in all other areas.	>1300	Movement in fluidized areas just sped up with increasing flow rates. Areas with little to no movement remained that way.
1500	1/3 of slag had little to no movement. Fast fluidization in all other areas.		
>1500	Above 1500 flow of areas already fluidized just increases and the areas with little to no movement did not change.		

Table 2 shows that Sieve #40 started to fluidize around 800 mL/min. In both trials it shows that 2/3 of the perimeter fluidized was the maximum amount of area fluidized. This occurred around 1200 mL/min in both trials.

Table 3: Fluidization results at different flow rates using #60 slag

Flow Rate (mL/min)	**Description for 1" #60 slag layer**
100	Two sections showing shaking motion
200	As a whole slag raised 1/16in. 2in wide was in motion on one side. 1.5 in wide on other side. As a whole showed shaking flow.
300	1/2 of perimeter showed faster shaking motion. Slag as whole raised 1/8in. 2.25in wide tunnels raised.
400	Section in motion flowed faster. Slag as a whole raised .25in. .25in of perimeter was fluidized
500	1in of perimeter fluidized. Other areas moving faster. Other sections little to no movement.
600	About 2in of perimeter fluidized. Slag raised .5in.
700	1/2 of perimeter fluidized. Tunnels forming in sections that previously had no movement.
800	80% of perimeter is fluidized. No movement in 10% of slag.
900	85% fluidized. 10% has little to no movement.
1000	90% fluidized. 10% has little to no movement.
1100	90% fluidized. 10% has little to no movement.
>1100	There were no extreme differences in the movement of the slag after 1100 and fluidization was never reached at the speeds produced.

Table 3 shows that fluidization occurred at an even lower flow rate with the #60 slag, with the bed expanding with flow rates as low as 400 mL/min and near complete fluidization at 800 mL/min. Even at higher flow rates, however, approximately 10% of the bed never fluidized.

The previous set of experiments showed varying degrees of fluidization with different slag grain size and flow rates. Often partial fluidization would occur, that is, only a small portion of the slag layer would show significant movement, while the remainder of the layer stayed fixed.

Consequently there was not a clear demarcation for the beginning of fluidization. Further even at high flow rates, a portion of the bed always remained fixed.

These results indicate that #20 slag was too large to adequately fluidize at flow rates less than 2500 mL/min and would not be suitable for the apparatus in this experiment. We chose #40 slag at a flow rate of 800 mL/min which provided adequate movement of the particles at a flow rate that our experimental set-up could accommodate. For scaling up of the reactor to a field site, however, these results were discouraging. It required significant flow to fluidize only a 1 in thick layer of fine particle slag. The high flow rate reduces the retention time in the reactor and limits the ability of the slag to release alkalinity. Clearly a deeper layer of slag will be required; however it seems not possible to fluidize it. Also, the fine particles will likely be exhausted of alkalinity earlier than the larger slag particles.

Fluidized Bed Treatment of AMD

The first test that was conducted was running the fluidized bed reactor system with tap water and the Sieve #40 slag at a flow rate of 800 mL/min. For this test only the pH exiting the system was recorded every 20 seconds for 3000 seconds, and pH results are shown in Figure 3. Influent pH to the reactor remained near 7.2 for the duration of the experiment. Initially, pH increased over 9 but then decreased to a fairly stable value of 8.1. The initial high pH was likely due to rapidly dissolving slag fines that were quickly exhausted. The stable exit pH of 8.1 was not significantly higher than the inflow. This was likely due to the short retention time as the water flowed through the one inch layer of slag.

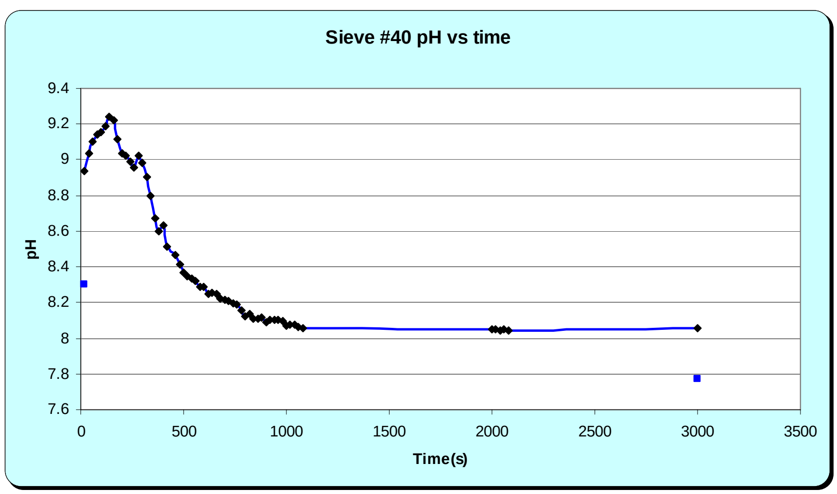

Figure 3: Effluent pH with a 1 in layer of # 40 slag, a flow rate of 800 mL/min, and tap water.

For the next test, AMD generated by the submerged gob was used as influent to the fluidized bed reactor. In order to increase retention time, a 2 in layer of #60 slag was used at a flow rate of 800 mL/min. pH measurements were taken at the entrance and exit every minute for one hour. Samples were taken at 0, 5, 10, 20 and 30 minutes and analyzed for alkalinity and acidity. pH results are shown in Figure 4, and acidity and alkalinity results are shown in Figure 5.

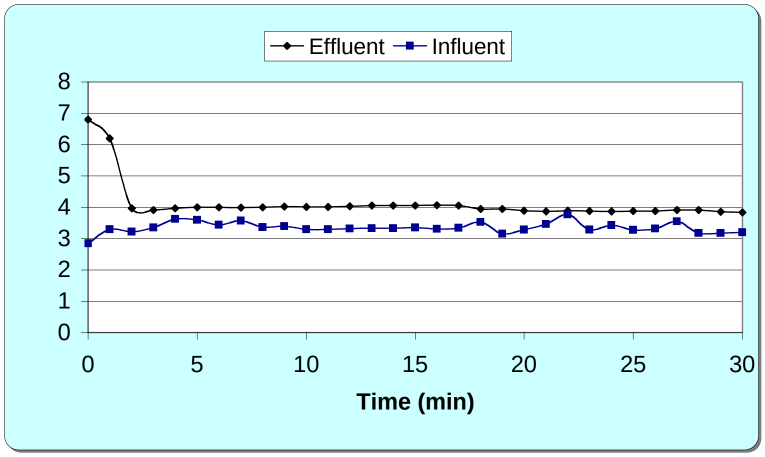

Figure 4: Influent and effluent pH with slag #60, a bed depth of 2 in, a flow rate of 800 mL/min, and acidic influent.

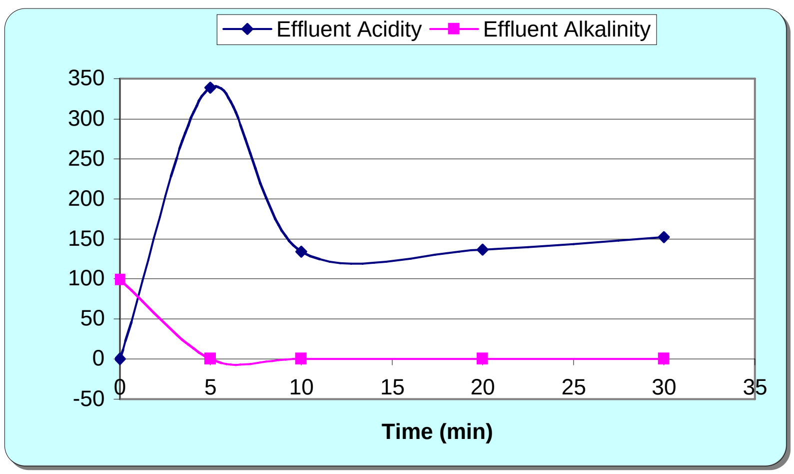

Figure 5: Effluent alkalinity and acidity plotted against the time with slag #60, a bed depth of 2 in, a flow rate of 800 mL/min, and an acidic influent.

Throughout this test the leachate from the gob averaged a pH of 3.4 and remained fairly constant while initial acidity was measured at 230 mg/L as $CaCO_3$. Surprisingly iron concentrations were very low in the leachate and orange hydrolysis precipitates were not observed in the effluent or the fluidized bed reactor. Effluent from the fluidized bed reactor showed very little pH rise, averaging 4.1 over the 30 min test (see Figure 4). Initial pH readings were above 6 but this likely represented initial mixing between clean water in the vessel and the AMD. Alkalinity and acidity results were equally discouraging (see Figure 5). Initial effluent contained 100 mg/L as $CaCO_3$ alkalinity and no acidity, but that quickly reversed with acidity as high as 346 mg/L as $CaCO_3$ being measured in the effluent. Clearly any increase in pH or alkalinity due to the slag was insignificant.

This test was repeated several days later under identical conditions, although the test was run for 60 min. pH results are shown in Figure 6, and acidity and alkalinity results are shown in Figure 7.

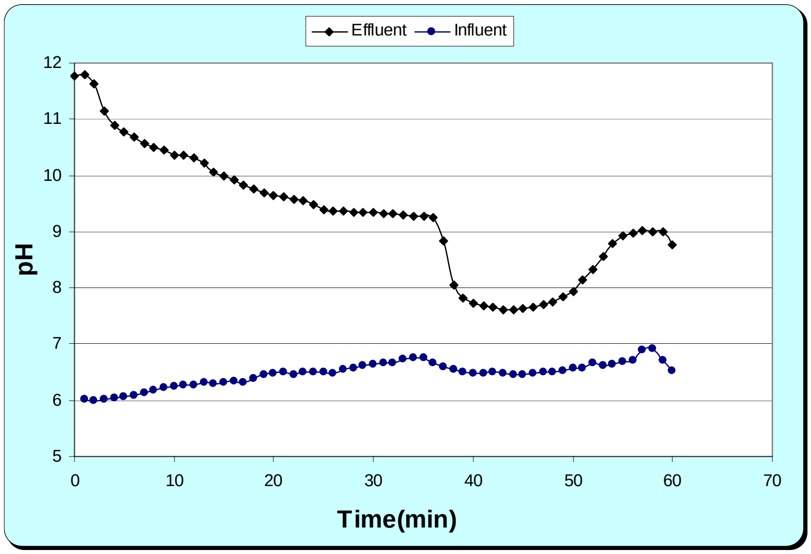

Figure 6: Influent and effluent pH with slag #60, a bed depth of 2 in, a flow rate of 800 mL/min, and acidic influent.

In this test, very high pH values were obtained in the effluent of the fluidized bed reactor, even with acidic input. Effluent pH started at near 12 but decreased gradually to a value of 7.6 after approximately 40 minutes. It did recover somewhat for unknown reasons reaching a pH of 9. The alkalinity and acidity results showed more consistent results. Initially 220 mg $CaCO_3$/L of alkalinity was generated which decreased rapidly to between 100 and 150 mg $CaCO_3$/L. Acidity was zero initially, before acidic water from the gob had reached the effluent. Acidity continually increased reaching a value of 143 mg $CaCO_3$/L by the end of the test, however it may have continued to climb beyond the test to close to the influent acidity of 170 mg $CaCO_3$/L. This residual acidity was likely in the form of hydrolysable metals that were not detected in the alkalinity test. Indeed during the hot peroxide pretreatment for the acidity test, the samples turned orange due to the oxidation and hydrolysis of ferrous iron. According to standard analytical methods the hot peroxide pretreatment step is only performed on the acidity test, not the alkalinity test, thus resulting in the seemingly contradictory result that a sample can have both positive acidity and alkalinity.

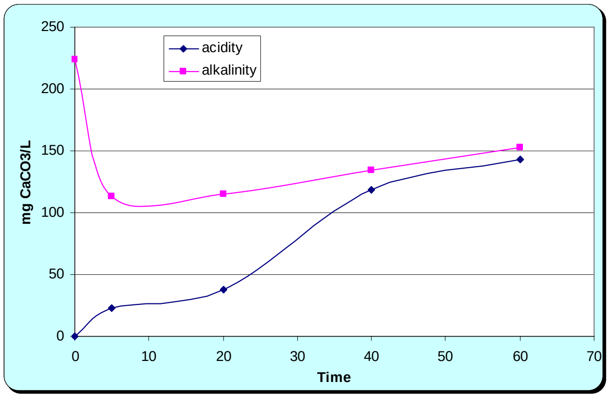

Figure 7: Effluent alkalinity and acidity plotted against the time with slag #60, a bed depth of 2 in, a flow rate of 800 mL/min, and an acidic influent.

Comparing the two tests with gob leachate, the leachate for the second test was much less severe than the first test. pH raised from 3.4 to 6.6 and acidity dropped from 230 mg/L as $CaCO_3$ to 170 mg/L as $CaCO_3$. Further tests confirmed that the gob was no longer producing sufficient acid particularly at a flow rate of 800 mL/min. In addition, the gob leachate never had sufficient iron concentrations to properly simulate AMD. As a result, artificial AMD was prepared for the remaining tests.

For the following test an acidic solution was created using tap water, dissolved ferrous iron, and sulfuric acid as the influent to the fluidized bed reactor. A 1.5 in layer of #40 slag was used at a flow rate of 800 mL/min. pH measurements were taken at the entrance and exit every minute for one hour. Samples were taken at 0, 5, 20, 40 and 60 minutes and analyzed for alkalinity and acidity. pH results are shown in Figure 8, acidity and alkalinity results are shown in Figure 9, and iron results are shown in Figure 10.

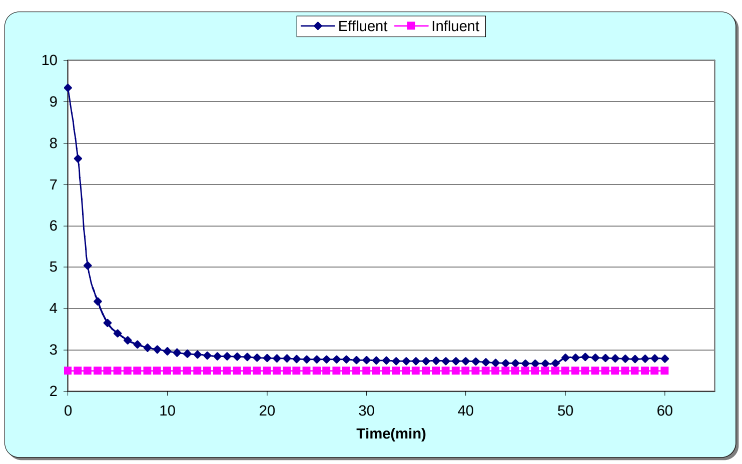

Figure 8: Influent and effluent pH with slag #40, a bed depth of 1.5 in, a flow rate of 800 mL/min, and artificial AMD influent.

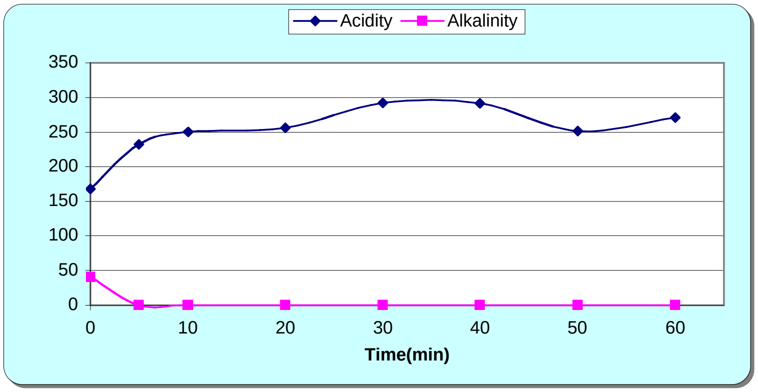

Figure 9: Effluent alkalinity and acidity plotted against the time with slag #40, a bed depth of 1.5 in, a flow rate of 800 mL/min, and artificial AMD influent

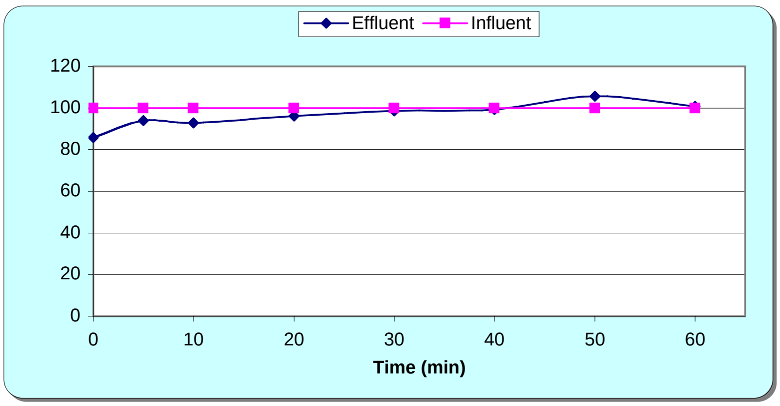

Figure 10: Effluent and influent dissolved iron plotted against the time with slag #40, a bed depth of 1.5 in, a flow rate of 800 mL/min, and artificial AMD influent

Results with the artificial AMD were similar to previous results with gob generated AMD. Influent to the fluidized bed reactor was more typical of AMD with pH of 2.5, acidity of 260 mg/L as $CaCO_3$, and ferrous iron of 100 mg/L. As before, after approximately 10 min, effluent concentrations mirrored influent concentrations for pH, acidity, and iron. Initially, some of the AMD appeared to have been neutralized by the slag, however this may have simply been mixing of the AMD with initially clean water in setting up the fluidized bed reactor.

The same test was repeated under identical conditions with the artificial AMD and results for pH, alkalinity, acidity, and iron are shown in Figures 11, 12, and 13.

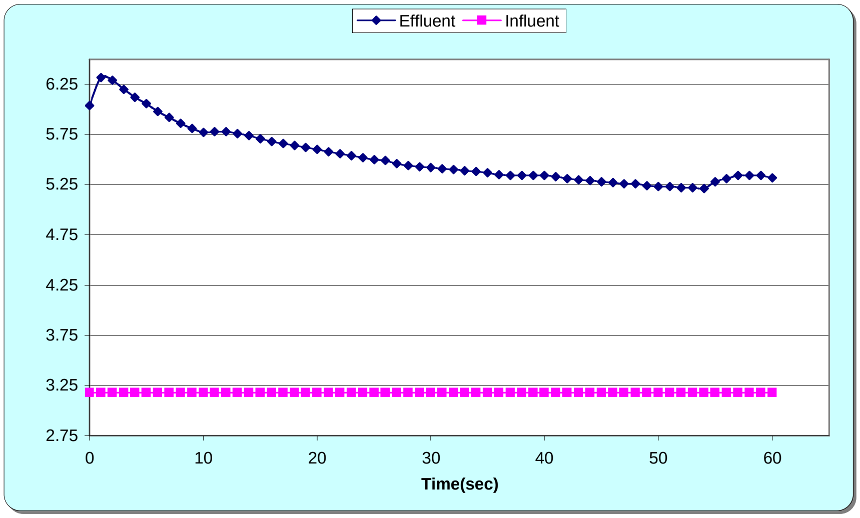

Figure 11: Influent and effluent pH with slag #40, a bed depth of 1.5 in, a flow rate of 800 mL/min, and artificial AMD influent.

In this test, the slag significantly elevated pH values obtained in the effluent of the fluidized bed reactor (see Figure 11). Influent pH averaged 3.1, while effluent pH averaged 5.4. The effluent pH started around 6, but gradually decreased to a value a little less than 5.25 around 55 minutes. It was not clear why this test of the slag with artificial AMD performed significantly better than the previous test. It could be speculated that channeling in the slag impaired results in the first test, though there was no visual evidence for this.

The alkalinity and acidity results shown in Figure 12 were far less encouraging. Initially alkalinity was generated at 132 mg $CaCO_3$/L. This value rapidly decreased to 5.6 and fluctuated slightly reaching a high value of 25 mg $CaCO_3$/L at 30 minutes before arriving at 0 mg $CaCO_3$/L for the remainder of the test. Acidity started out close to zero, but gradually rose to a high value of 176 mg $CaCO_3$/L at 40 minutes where it remained fairly steady. Again, results from this test were superior to the previous test, showing some signs of acidity neutralization and alkalinity generation. However, after the initial 40 min, slag no longer had a significant impact on effluent acidity.

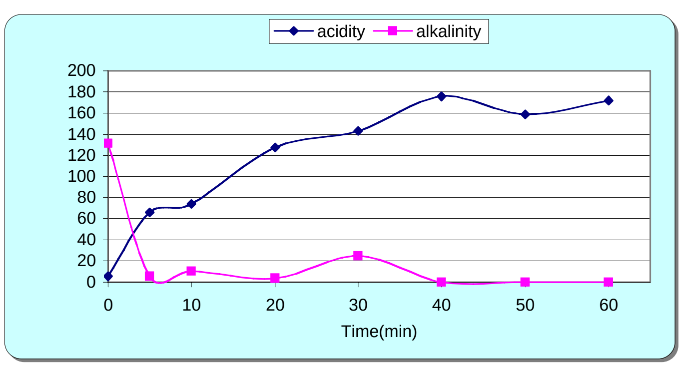

Figure 12: Effluent alkalinity and acidity plotted against the time with slag #40, a bed depth of 1.5 in, a flow rate of 800 mL/min, and artificial AMD influent

Finally, iron concentrations behaved like the acidity, with initial removal of iron but with effluent concentrations approaching influent concentrations by the end of the experiment. Iron was not directly removed by the slag, but ferrous iron oxidation was dependent on pH. As pH increases so does iron oxidation rates. At these pHs ferric iron was relatively insoluble so once oxidized, the resulting ferric iron would rapidly precipitate. In fact, after the 60 min test with artificial AMD the slag was noticeably orange in color from the iron (see Figures 14 and 15). In comparison, no iron floc was observed in the effluent from the reactor. This provided discouraging evidence for a hypothesis of this work. It was expected that fluidized beds would be able to resist clogging because the motion of the slag would release light floc from the bed and grinding of the particles would keep the slag clean and free of armoring. It appeared from this 60 min test that the iron precipitated directly on the surface of the slag rather than forming flocs, and the slag was clearly not protected from this surface precipitation. Most likely after surface precipitation sites were used independent iron floc would form, though this test was to short to confirm. It is still possible that the bed would remain mobile and release the floc, though there was no evidence of that from these experiments. Further it does appear that armoring would be a problem limiting alkalinity generation from the slag, even if the slag remained mobile.

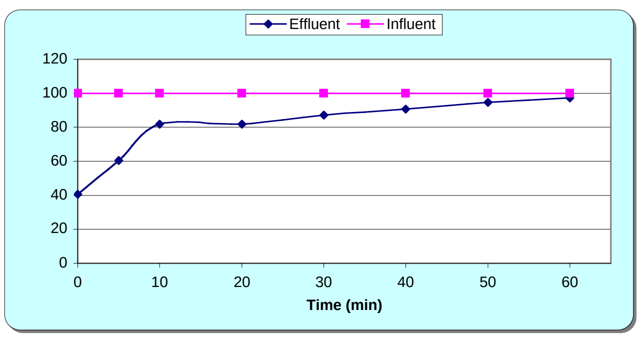

Figure 13: Effluent and influent dissolved iron plotted against the time with slag #40, a bed depth of 1.5 in, a flow rate of 800 mL/min, and artificial AMD influent

Figure 14: Wet #40 slag from the fludized bed reactor after 60 min of 800 mL/min flow with artifical AMD on left compared with fresh #40 slag on the right.

Figure 15: Dry #40 slag from the fludized bed reactor after 60 min of 800 mL/min flow with artifical AMD (left), dry #40 slag from the fludized bed reactor after 60 min of 800 mL/min flow with gob leachate (middle), and fresh #40 slag (right).

Significance

These results indicate that this treatment approach has significant limitations both with regard to hydraulics and chemical transport. First, the slag particles proved difficult to fluidize requiring the use of very small grain size. #20 slag was too large to adequately fluidize, although #40 slag and #60 slag could be adequately fluidized with bed depths of 1-2 inches. For scaling up of the reactor to a field site, these results were discouraging. These particles are extremely fine and would likely increase costs significantly to crush and sieve the slag material to this size window for full-scale implementation. Further, it required significant flow to fluidize only a 1 in thick layer of fine particle slag. The high flow rate reduces the retention time in the reactor and limits the ability of the slag to release alkalinity. Clearly a deeper layer of slag will be required; however it seems not possible to fluidize it. Also, the fine particles will likely be exhausted of alkalinity earlier than the larger slag particles.

The water chemistry results were equally discouraging. With a 1 inch layer of #40 slag, pH of tap water was increased only to around 8.1 from 7.2, not a very significant improvement. Further experiments were conducted with 2 inch layers of #60 slag. When treating AMD generated from gob leachate, pH and acidity was not neutralized except for in the initial few minutes of the test. In a second test better results were achieved, however it was determined that the gob leachate had decreased in severity. Additional experiments with artificial AMD produced similar results, with virtually no change in pH, acidity or iron concentrations after 40 min. Some initial acid neutralization and iron removal was observed initially, but again not to a significant degree. Finally, slag from the fluidized bed reactor treating artificial AMD was coated with ferricoxyhydroxide precipitates which might indicate armoring over the long term. Iron floc was not observed over the 60 min experiment.

From these experiments, it appears that a slag layer small enough to achieve reasonable fluidization was not able to treat AMD significantly, and deeper slag layers face hydraulic limitations preventing fluidization.