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Performance of steel slag leach beds in acid mine drainage treatment

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HIGHLIGHTS

• Performance of 12 steel slag leach beds (SLBs) was monitored quarterly for one year.

• SLBs have potential, but current SLB designs limit alkalinity loading performance.

• Plugging of SLBs by calcium carbonate precipitates negatively affects flow rates.

• SLB alkalinity production decreases with time according to a decay model.

Design changes should allow SLBs to meet performance targets.

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ABSTRACT

Steel slag leach beds are a popular choice for acid mine drainage treatment in southeastern Ohio. Large amounts of alkalinity leached from the surface of steel slag, a by-product of steel manufacturing, have been added to acid mine drainage-affected streams to neutralize pH and precipitate metals. Results from steel slag leach beds are promising, but alkalinity production has decreased significantly over time in all beds. To determine the cause of the decrease, the effluent flow and chemical characteristics of twelve steel slag leach beds were monitored over a one year period and compared to historical data. Alkalinity production fell and remained below design expectations for two main reasons. First, declining effluent flow rates led to low alkalinity loadings. Thick layers of precipitates in the effluent piping contributed to low flow rates. Precipitates also formed within the slag itself, further lowering flow rates. Recommendations to limit precipitation, improve flow and alkalinity loading rates, included using a low-alkalinity influent, and minimizing carbon dioxide contact with the alkaline effluent. Declining alkalinity loadings were also caused by an inherent limitation in the amount of readily dissolvable calcium compounds on the surface of the slag particles. Past and present data were used to model the declining alkalinity production capabilities of slag with time. All steel slag leach beds studied except one were initially capable of high alkalinity loadings, but typically lost more than 75% of peak alkalinity production within 50 empty bed volumes. Similar results were obtained in the laboratory with slag columns.

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1. Introduction

Acid mine drainage (AMD) damages many of the natural waterways in Southeastern Ohio and other mining regions worldwide, filling stream beds with its characteristic yellow–orange precipitates, low pH water, and impaired aquatic life. The pyritic oxidation reactions causing AMD have been well-studied [1,2] and will not be discussed here.

Steel slag leach beds (SLBs) are a newer and potentially promising treatment method for AMD-affected waterways. Steel slag, a waste product from steel manufacturing, contains high concentrations of readily dissolvable alkalinity on its surface [3]. The alkalinity is present primarily as $Ca(OH)_2$ and Ca-(Fe)-silicates [4]. Ziemkiewicz [3] concluded that steel slag was capable of sustained production of high concentrations of alkalinity in laboratory and field studies. If alkalinity from steel slag is dissolved into neutral pH waters (Eqs. (1) and (2); [5]), and the resulting alkaline waters are discharged into AMD-affected streams, the pH in the affected streams is raised.

$$CaO_{(s)} + H_2O \rightarrow Ca(OH)_{2(s)} \tag{1}$$

$$\operatorname{Ca}(\operatorname{OH})_{2(\operatorname{aq})} \to \operatorname{Ca}^{2+} + 2\operatorname{OH}^{-}$$

$$\tag{2}$$

Steel and coal industries exist in close proximity in Ohio, and in many other parts of the world (i.e. China, India, Russia, Australia, Canada, Czech Republic, United Kingdom), particularly in locations with Carboniferous bedrock bordering Precambrian sea beds. Combining the discharges from both steel and coal industries to neutralize each other can therefore solve two common global problems with an effective, local solution.





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Steel slag has been used for many years in Ohio as a soil amendment to neutralize acidity [6]. This concept can be extended to using slag for amendments to aqueous systems, such as acid mine drainage affected waterways, to neutralize acidity. Leach beds are a convenient means to add alkalinity to a natural system. The advantages of leach beds lie in the low operations and maintenance costs of the passive, continuous treatment system. Disadvantages include the initial construction costs, the difficulty of maintaining flow without plugging, and the inability to determine what is occurring inside the beds. Plugging can be a serious problem in leach beds and is affected by both design and operation of the beds. Steel slag leach beds have yet to be optimized for alkalinity production and flow capabilities, as they are a relatively new technology.

Several previous studies have investigated the performance of SLBs in Mingo County, West Virginia [3], Preston County, West Virginia [7] and the Raccoon Creek watershed, Ohio [8]. All three publications show similar trends in that alkalinity production decreased over time in slag beds.

In Mingo County [3], a 9-month demonstration of the potential of an SLB for AMD remediation, reductions in acidity from 350 to 50 mg/L were achieved, with a pH increase from 3.8 to over 5 and a decrease in manganese concentration. Loading and flow rates were not reported. The slag used in the study (International Mill Service, Inc., Mingo Junction, OH, <1/8 in slag fines) was also subjected to an EPA Toxicity Characteristic Leaching Procedure (TCLP) test [9].

The TCLP test is designed to simulate the leaching that occurs in a landfill. TCLP utilizes an acetic acid extraction fluid to mobilize metals into a liquid phase, where they can be analyzed by various methods, including types of spectrophotometry or spectroscopy. The slag leachate passed the TCLP limits for all elements (As, Ba, Cd, Cr, Pb, Se, Ag, and Hg). Other metals not included in TCLP standards were also analyzed in the leachate (results in parentheses): Be, Ni, Sb, Tl, V (all below detection limits of 0.005 mg/kg), Zn (0.012 mg/kg), and Cu (0.017 mg/kg).

Testing each batch of slag from each steel producer before constructing an SLB is important because of the range of trace elements that can be present in slags made from different raw materials or different processes [10–12]. These trace elements may pose a problem if significant quantities leach from slag and co-precipitate with calcite, or remain in solution as an aqueous contaminant. Therefore, before using slag products, it is necessary to perform an analysis of the trace metal content of the slag batch, as well as leaching tests to determine which, if any, metals will leach. TCLP testing would ideally be performed along with XANES testing of the leachate of naturally aged slag, since the oxidation state, mobility, and solubility of metals are dependent on the pH of the leachate [12].

Ziemkiewicz [3] also studied the alkalinity production of the slag in column tests. Approximately 110 L of deionized water was poured through 2 in. diameter columns of varying length over a 3 month period. Alkalinity production began high, above 2000 mg CaCO₃/L, and decreased with time to around 900 mg CaCO₃/L for a 24 in. column and to around 200 mg CaCO₃/L for a 12 in. column.

In Preston County, two mixed limestone/slag leach beds in series were monitored for one year. The series produced high levels of alkalinity (around 1500 mg CaCO₃/L) and pH values initially, but by the fourth month of operation was only producing 30 mg CaCO₃/L. Despite the decrease, the slag bed met its performance goals because all of the acidity in the receiving stream was neutralized with the lower level of alkalinity production [7].

The Raccoon Creek slag beds investigated by Kruse [8] were some of the same beds evaluated in our work. Kruse focused on the types of alkalinity produced by the slag beds, and how a shift from mixed hydroxide, bicarbonate and carbonate alkalinity to predominately carbonate alkalinity could signal the failure of the slag beds.

Despite the decreases in alkalinity concentrations over time, steel slag leach beds produce higher concentrations with lower contact times than limestone leach beds. Typical limestone leach bed alkalinity concentrations are around 5 mg/L CaCO₃/L, with maximums around 80 mg/L CaCO₃/L [3], whereas steel slag leach bed alkalinity concentrations are usually above 100 mg/L CaCO₃/L, even after many years of operation, and maximum concentrations can be over 2000 mg/L CaCO₃/L.

The objectives of this paper were to analyze the effectiveness of SLBs in AMD treatment over time, to identify primary factors for optimal performance in SLB design and operation, and to provide recommendations for future SLB design.

2. Materials and methods

2.1. Slag bed design

Twelve steel slag leach beds were constructed in Southeastern Ohio between 2004 and 2009 to treat the AMD in nearby streams. A picture of an operating SLB is shown in Fig. 1, and a drawing of a typical SLB is shown in Fig. 2. All twelve steel slag leach beds were designed similarly, but have several significant differences which may cause operational differences. For all beds, "clean" (low acidity and dissolved metals) influent was piped by gravity flow from a nearby pond. The influent was either deposited on top of the slag bed or into the bottom of one end of the bed into a spreader pipe. After traveling through the bed, the newly alkaline water left the slag bed through underdrain piping in the bottom of the slag bed. Underdrain piping had either slots or round perforations in its walls to allow the alkaline water to enter the discharge piping system. A water layer was maintained over or at the top of the slag itself with a bypass channel or pipe located at the desired elevation above the slag. Effluent flow rates were maintained by either a valve, an Agri Drain (Agri Drain Corporation, Adair, IA), or in one case, an adjustable height discharge pipe. Finally, most SLBs were constructed with <3/8" slag particles, but one had larger slag particles for a bottom layer, and two had smaller (<1/4'') slag particles. SLBs are listed with their significant design features in Table 1.

2.2. Field methods and chemical analysis

Effluent and influent samples were taken for all operating beds every quarter for one year. Shawnee was not operational the first



Fig. 1. East Branch Raccoon Creek Phase I-Site 3 (EBRCI-3) SLB.

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