USE OF STEEL SLAG LEACH BEDS FOR THE TREATMENT OF ACID MINE DRAINAGE: THE McCARTY HIGHWALL PROJECT[1]

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Abstract. Steel slag leach beds were constructed at the abandoned McCarty mine site in Preston County, West Virginia. The leach beds were constructed as slag check dams below limestone-lined settling basins. Acid water was captured in limestone channels and directed into basins to leach through the slag dams and discharge into a tributary of Beaver Creek. Since installation in October 2000, the system has been consistently producing net alkaline, pH 9.0 water. The water is still net alkaline and has stabilized at a neutral pH after the treated water encounters several other acidic seeps downstream. In addition, other than elevated Cr, which exceeds EPA water criteria for freshwater aquatics at the Beaver pond discharge, metals in the system effluent are within acceptable limits.

Additional Key Words: Passive Treatment, AMD Neutralization.

Introduction

Acid Mine Drainage

Acid mine drainage (AMD) forms when sulfide minerals, particularly pyrite and marcasite, have been exposed to oxidizing conditions during mining and other excavation activities, such as highway construction. In the presence of oxygen and water, sulfide minerals oxidize to form sulfate-rich and often metal-laden drainage (Skousen 1995). “Untreated AMD flowing into streams can severely degrade both habitat and water quality, often producing an environment devoid of most aquatic life and unfit for desired uses” (Kimmel 1983). In addition, AMD can be toxic to vegetation and can reduce the potability of water supplies (Earle and Callaghan 1998).

Various active and passive water treatment techniques have been developed during the last several decades to abate or control AMD. Active systems require the systematic and long-term

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[1] Paper was presented at the 2002 National Meeting of the American Society of Mining and Reclamation, Lexington, KY, June 9-13, 2002. Published by ASMR, 3134 Montavesta Rd., Lexington, KY 49592.

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Proceedings America Society of Mining and Reclamation, 2002 pp 527-538
DOI: 10.21000/JASMR02010527
https://doi.org/10.21000/JASMR02010527

addition of various alkaline chemicals, such as ammonia, hydrated lime or caustic soda. These systems are often very effective at neutralizing acidity; however, they are typically very expensive and require long-term commitments of manpower and maintenance. In contrast, passive treatment systems are less expensive and require very little maintenance.

Passive treatment of AMD has largely relied on the dissolution of limestone to increase pH and alkalinity and precipitate metals. However, limestone is susceptible to armoring due to metal precipitation and has limited effectiveness in highly acidic or high flow discharges. A reliable, inexpensive alkaline source is needed for such situations. Laboratory and field studies indicate that highly alkaline steel slag may be a solution to this problem (Ziemkiewicz and Skousen 1998).

Steel Slag

Production of Steel Slag. Modern steelmaking occurs by one of two technologies: the basic oxygen furnace (BOF) or the electric arc furnace (EAF). Although both types of furnaces produce molten steel, the input materials needed for its production vary. The input materials for the BOF are iron ore, scrap iron, oxygen and limestone. These types of furnaces are typically used for high tonnage production of carbon steel. In contrast, EAFs use scrap and electricity to generate carbon steels and low tonnage alloy and specialty steels (USEPA 1995).

The first step in the production of steel in the BOF, is the generation of molten iron in a blast furnace. Iron ore, coke and limestone are added to the top of the blast furnace while preheated air enters through the bottom of the furnace. The hot air ignites the coke and it reacts to form carbon monoxide (CO) (Equation 1). This CO then reduces the iron oxide to elemental iron (Equation 2). At the same time, the limestone descends through the furnace and reacts to form CaO and CO_2 (Equation 3). The CaO formed from this reaction is used to remove silicates from the iron (Equation 4) (Rochow 1977).

These processes are expressed in the following equations:

$$\mathrm{2C + O2 \rightarrow 2CO} \tag{1}$$

$$\mathrm{Fe2O3 + 3CO \rightarrow 2Fe + 3CO2} \tag{2}$$

$$\mathrm{CaCO3 \rightarrow CaO + CO2} \tag{3}$$

$$\mathrm{CaO + SiO2 \rightarrow CaSiO3\ (slag)} \tag{4}$$

The $CaSiO_3$ becomes the slag, as well as any remaining silica (SiO_2), alumina (Al_2O_3), magnesia (MgO) or calcia (CaO). The liquid slag floats to the top of the molten iron where it can be poured off periodically (Ricketts 2001).

Molten iron from the blast furnace, along with flux (ie, limestone or dolomite), alloys and scrap can then be added to the BOF for the production of steel. The BOF uses high-purity oxygen injection to generate heat, melt the scrap and oxidize impurities. Slag is produced from the impurities, which are removed from the scrap by a combination of the fluxes and the injected oxygen.

In EAF steelmaking scrap metal is melted and refined using electric energy generated by graphite electrodes. Scrap, lime and carbon are added to the furnace where an electric arc, produced by the electrodes, penetrates the charge. As the temperature in the furnace increases, the charge begins to melt and oxygen is added for additional heat and to react with impurities in the scrap (Jones 2001). Oxidation of phosphorous, silicon, manganese, carbon and other materials occurs and a slag containing these oxidized products forms on top of the molten metal (USEPA 1995).

<u>Characteristics of Slag</u>. Slag is the fused glassy compound formed by the action of a flux upon the impurities of an ore (US Steel 1964). It is formed during the addition of limestone dolomite or lime to the molten iron ore during the production of steel. These calcium compounds react with aluminum, silica, phosphorous and other impurities in the ore to form slag. The slag floats to the top of the melt and is poured off into piles for disposal, where it cools rapidly. What results is much stronger steel product and a pile of glass-like, calcium alumino-silicate oxides, more commonly called slag.

Since slag is formed at such high temperatures, most compounds with lower boiling points have been driven off. Any residuals of these compounds, such as sulfur, selenium, carbon, cadmium, lead, copper and mercury, are typically encased within the slag's glassy matrix. Since the chemical bases of slag consists mostly of lime, magnesia and other basic compounds, leaching of this material results in the liberation of high concentrations of alkalinity to the dissolving fluid. However, the lime in slag, unlike ordinary agricultural lime, is in loose chemical combination with silica, iron and manganese and does not "burn" nor revert to carbonates (US Steel 1964). This is an extremely important property, since it means slag can be left outside, exposed to the atmosphere, and still achieve high levels of alkalinity upon dissolution.

Blast furnace slag is composed primarily of Si, Al, lime and magnesia (where dolomite is used as a flux). These compounds comprise nearly 95% of the total slag. In addition, the slag also contains small amounts of Mn, Fe and alkali oxides, sulfur compounds and iron (1-2%). The basicity of the slag, a function of the CaO/ SiO_2 ratio, is approximately 1.

Oxidized forms of Si, Mn and P make up the largest portion of BOF slag. It also contains various amounts of Ca silicates and Al, Fe, Ca and Mg oxides. BOF slag has a higher CaO/SiO_2 ratio than blast furnace slag (2.5-4.0) and contains as much as 7% free lime. Compared to blast furnace slag it is much more chemically variable and contains higher percentages of iron.

The composition of EAF slag is highly dependent upon the specific grades of steel scrap, iron-bearing materials and fluxes added to the furnace. In general, they have lower basicities than BOF slags and higher concentrations of FeO and P_2O_5 (AISI 2001). Table 1 shows the characteristics of all three steelmaking slags.

Table 1. Amount Generated, Iron and Basicity Characteristics of the Three Types of Steelmaking Slag. *Millions of tons of slag produced in 1997 and the % Fe and Ca:SiO2 ratio of each slag. (Source: American Iron and Steel Institute.)*

	Blast Furnace	Basic Oxygen Furnace	Electric Arc Furnace
millions of tons/ year produced	11.7	6.2	4
% Iron	<2%	20-25%	20-25%
Ca/SiO2	1	2.5-4.0	varies

Uses of Slag. In 1997 approximately 22 million tons of iron and steelmaking slag were produced in the United States (AISI 2001). Of this amount, 11.7 million tons were blast furnace slag, 6.2 million tons were BOF slag and 4.0 million tons were EAF slag.

Slag is considered a waste product but it has various uses outside of the metal industry. It is used extensively in construction as a component of concretes, pavements and roofing granules (US Steel 1964). In addition, steel slags have a high neutralization potential (Table 2) and can be used to add alkalinity to acid-producing materials.

Table 2. Neutralization potential (NP) (g CaCO3 equivalent/ Kg of slag) of various basic steelmaking slags. NP determined using the Sobek (1978) method.

Slag Identification	NP	%
Weirton c-fines	770	77%
Mingo c-fines	665	66%
Mingo Cool Springs	628	63%
Waylite	421	42%
Fairfield	469	47%

Due to its coarse particle size and low basicity, nearly 100% of all blast furnace slag produced in the US is reused in commercial applications. The most common uses of blast furnace slag are railroad ballast, slope protection, anti-skid material, roofing granules, mineral wool, soil conditioner, embankments and fills.

BOF slag is most often used as road aggregate, Portland cement, anti-skid material and landfill covers. The use of BOF slag in construction can be limited due to its high concentrations of free lime. The soluble lime can hydrate and cause expansion and disintegration of roadbeds and embankments. However, the free lime concentration can be beneficial in agricultural and mining applications, where it can be used to neutralize acid producing materials.

Currently, EAF slag has limited uses inside or outside of the steel plant. Typically, only 50% of the iron contained within the slag can be recovered and recycled back into steel production. In addition, shipping costs of these low value materials is too great to permit their sale for commercial applications. Therefore, most of this slag is sent to landfills for disposal. The use of slag in mine reclamation and AMD treatment provides another potential use for this high alkaline material.

The McCarty Field Demonstration Site

Background

The abandoned McCarty surface mine is located about 5 km southeast of Bruceton Mills in Preston County, WV. Pre-law (Surface Mine Reclamation and Control Act of 1977) contour mining of the Bakerstown and Freeport coal seams have altered both the surface topography and water quality of this region. Prior to construction, the site consisted of a small pit lake, less than 1 acre in size, a highwall and numerous vegetated spoil piles or varying sizes. Water in the pit lake was net alkaline. However, seeps originating within the spoil material down-slope of the pit lake were acidic, with a pH between 3.7 and 3.9, average acidities of 26 mg/L, and average concentrations of iron, aluminum and manganese of 0.6 mg/L, 3.6 mg/L, and 3.3 mg/L, respectively. Prior to construction, water seeping out along an old spoil pile flowed into a channel and mixed with a second spoil seep approximately 150 m (500 ft) downstream. These two seeps formed a small acid stream that flowed south, encountering several other small AMD seeps before flowing into Beaver Creek.

System Design and Construction

Due to the acidity of the on-site AMD sources and the presence of additional acid sources downstream, limestone treatment was not selected. Instead an innovative neutralization system, using high alkaline steel slag was designed. Earlier laboratory studies of steel slag neutralization of AMD indicated the suitability of slag for this type of treatment. In addition, economics demanded that the system be inexpensive and last for at least 10 years without maintenance.

In October 2000, a series of open limestone channels (OLCs) and steel slag leach beds were installed downstream of seeps 1 and 2. Figure 1 shows the placement of the OLCs and leach beds and the amounts of limestone and slag used in each. All four OLCs were constructed of a limestone sand liner and 15-20 cm of limestone rocks. The leach beds consisted of a settling basin and steel slag check dam.

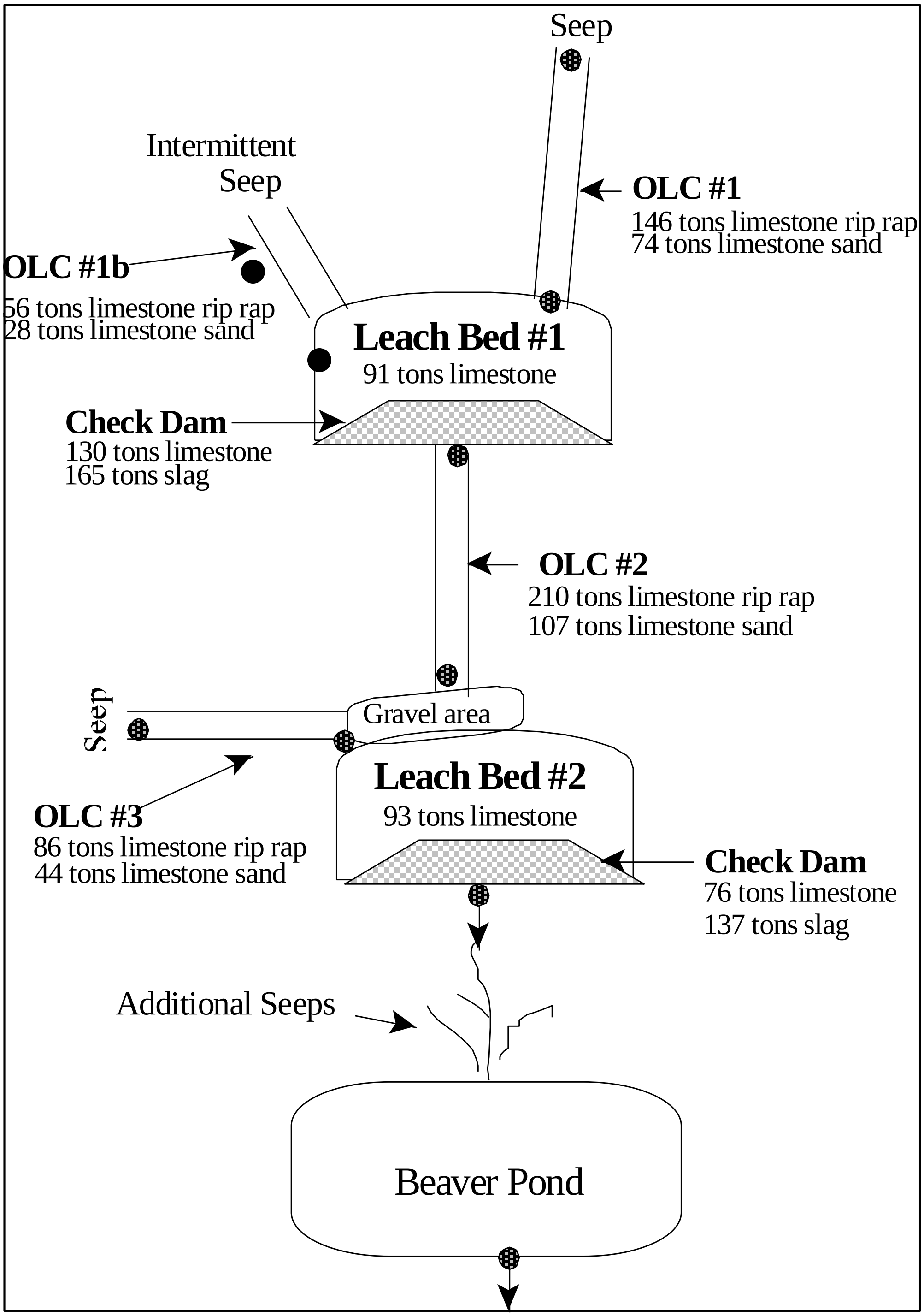

Figure 1. Diagram of McCarty Highwall AMD Treatment System. *Acidic seep water enters the leach beds through three open limestone channels. Treated water exiting the system from leach bed #2 encounters additional acid seeps downstream of the site.*

Both check dams were formed from approximately 136,000 kg (150 tons) of Weirton c-fines steel slag (NP=77%) and rip-rapped along the back with 15-20 cm limestone rocks. A 61 m (200 ft) OLC (#1) was constructed from the upper spoil seep to the edge of the first settling basin. A secondary OLC (#1b) was constructed to the left of OLC #1 to carry AMD from an intermittent spoil seep to the first basin. Water leaches from the basin through the center of a steel slag check dam and enters a 91 m (300 ft) OLC (#2). Water from OLC #2 flows into a limestone gravel area along the edge of the second settlement basin. Additional AMD flows through a 30 m (100 ft) OLC (#3) into a gravel area at the edge of the second settling basin. Water enters into settling basin #2 from OLCs #2 and #3 and exits the system through a second steel slag check dam. This water then flows south into Beaver Creek, picking up several additional acid seeps along the way.

Results and Discussion

Water samples were collected throughout the system and downstream of the second leach bed seven times within the first year following construction. Water samples were taken at the influent and effluent of each treatment unit within the system in order to evaluate the effect of each treatment. These sample stations are shown on Figure 1 as black dots.

Samples were analyzed for pH, acidity, alkalinity, sulfate, Ca, Mg, Fe, Al, Mn, Sb, As, Ba, Be, Cd, Cr, Pb, Hg, Se, Ag, Cu, Ni, Tl, V and Zn (dissolved metals). Pre-treatment water at this site (sample stations Top OLC #1, Top OLC 1b and Top OLC #3) contained various concentrations of all metals, except Hg, Tl and V. Increased release of metals from the slag or from the resolubilization of precipitated metals as a result of slag addition, was determined by the concentration of metals in the effluent that were higher than could be attributed to the raw water.

Initial samples collected from the slag leach beds contained extremely high concentrations of alkalinity (1479-1513 mg/L of $CaCO_3$ equivalent) and high pH values (11.6). However, by the fourth month, alkalinity had fallen to about 30 mg/L (pH 9.0) and has stabilized between 20-30 mg/L. Alkalinity from the downstream beaver pond has remained constant throughout the treatment period, despite a large generation of alkalinity from the slag beds during the first three months of treatment and a spike of alkalinity from the beds during September (Figure 2).

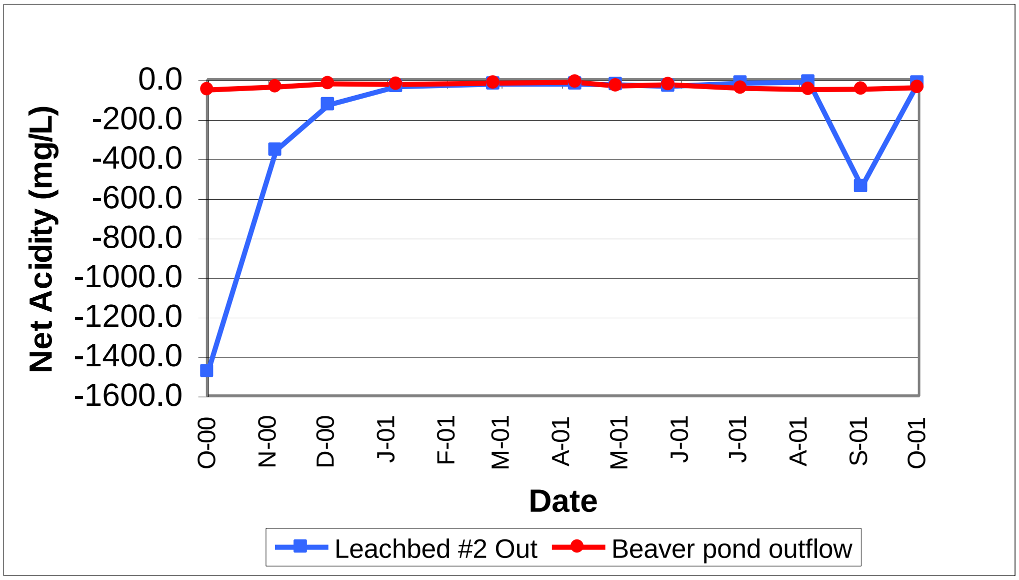

Figure 2. Net Acidicty Concentrations for System Discharge and Downstream of McCarty Highwall. *Discharge occurs at the downstream toe of the second slag leach bed and the beaver pond is located approximately 1/2 downstream of the treatment system.*

Table 3 shows the average pH, net acidity and metal concentrations of samples taken throughout the treatment system during the first year of treatment. Of the 18 metals analyzed, 15 were present at some time in the system discharge water (Leach Bed #2). Mercury, selenium and thallium were undetected in the discharge. In addition, arsenic, beryllium, cadmium and silver were detected in only one sampling event and therefore have very low yearly averages. Sb, Ba, Cr Cu, Tl and V were higher in treated waters than in the influent, however, only Cr concentrations exceeded the US National Water Quality Criteria for freshwater aquatics (USEPA 1999).

In the past steel slag leach beds have only been used to increase the alkalinity of upstream fresh waters to indirectly treat downstream acid sources. There was some concern regarding the leachability of metals within the slag matrix under acidic conditions. After extensive laboratory testing on various steel slags, it was determined that slag could be a safe, highly effective, alternative to standard alkaline sources. The first year of water quality monitoring at McCarty Highwall supports these laboratory findings. The limestone and steel slag system is treating all of the acidity in the AMD and has caused no increase in metal concentrations, other than Cr, in

Table 3. Average Water Quality at the McCarty Highwall Project. *Monthly water quality monitoring for the first year of treatment Top OLC #1, Top OLC 1b and Top OLC #3 are raw AMD sampled at the seep locations. OLC #1 and OLC 1b flow into Bed #1 and OLC #3 and OLC #2 flow into Bed #2. Metal concentrations in bold face exceed influent metal concentrations. Also included in the table are the National Water Quality Criteria for freshwater aquatics. Only Cr exceeded these limits in the downstream Beaver pond discharge. Concentrations are in mg/L.*

	National Water Quality Criteria for freshwater aquatics	Top OLC#1	Top OLC 1b	Slag Bed #1 Out	Bottom OLC #2	Top OLC #3	Slag Bed #2 Out	Beaver Pond Discharge
pH	NS	4.4	5.1	8.0	9.3	4.1	9.5	7.7
acidity	NS	29.7	37.4	3.0	7.5	32.2	0.6	0.0
alkalinity	NS	1.4	25.5	171.4	48.5	0.2	226.4	35.6
net acidity	NS	28.3	11.8	-168.4	-41.0	32.0	-225.8	-35.6
Magnesium	NS	50.1	28.6	30.2	25.7	30.2	19.1	19.4
Calcium	NS	85.9	78.1	276.5	258.1	68.4	284.7	64.3
Iron	NS	0.3	37.7	0.3	0.5	0.2	0.5	0.4
Aluminum	NS	2.5	0.6	1.3	1.1	1.9	0.7	0.4
Manganese	NS	3.9	5.3	4.7	1.9	2.5	0.9	0.3
Sulfate	NS	403.8	212.8	349.5	337.5	270.1	329.4	173.9
Antimony	NS	0.002	0.002	**0.003**	0.002	0.001	**0.003**	**0.004**
Arsenic	0.340	0.001	0.001	0.000	0.000	0.000	0.000	0.000
Barium	NS	0.060	0.052	**0.064**	0.049	0.033	0.033	0.046
Beryllium	NS	0.001	0.001	0.000	0.000	0.000	0.000	BDL
Cadmium	0.004	0.000	0.000	0.000	0.000	0.001	0.000	0.001
Chromium	0.016	0.000	0.001	**0.004**	**0.004**	0.000	**0.005**	**0.019**
Lead	0.065	0.001	0.002	0.001	0.001	0.002	0.001	0.001
Mercury	0.014	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Selenium	NS	0.002	BDL	0.001	BDL	0.001	BDL	0.000
Silver	0.03	0.004	0.002	0.002	0.000	0.004	0.000	0.000
Copper	0.013	0.001	0.001	0.001	**0.002**	0.003	0.002	0.000
Nickel	0.47	0.131	0.036	0.085	0.082	0.154	0.036	0.021
Thallium	NS	BDL	BDL	**0.003**	BDL	BDL	BDL	BDL
Vanadium	NS	BDL	BDL	**0.003**	0.001	BDL	0.001	BDL
Zinc	0.12	0.258	0.026	0.181	0.150	0.178	0.063	0.017

NS= No Standard

BDL= Below Detection Limit

the receiving stream. Monitoring will continue at this site to determine the long-term performance of the slag and to identify potential metal leaching from the slag.

Acknowledgements

Funding for the McCarty Highwall AMD treatment system was provided by the Friends of the Cheat through funds allocated by the United States Office of Surface Mining.

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