

The Use of Steel Slag in Acid Mine Drainage Treatment and Control

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Introduction

Slag is defined as the solid material resulting from the interaction of flux and impurities in the smelting and refining of metals. The solid product generally forms a silicate glass-like material, which is primarily nonmetallic. In the power industry, boiler slag is the residue from coal burning which sticks to the walls and pipes of the boiler. This slag is removed from the boiler and pipes through routine maintenance and is a valuable product in the construction industry (sometimes called "black beauty"). Boiler slag should not be confused with bottom ash or fly ash, which are by-products of coal burning, and both are continuously generated and removed during coal combustion. In the base metal industry, slags result from the smelting of various ores of copper, zinc, lead, etc. These metal ore slags can have high concentrations of heavy metals imbedded in the glassy matrix or residing on the solid's surface.

In making steel, iron ore or scrap metal are melted in combination with limestone, dolomite or lime. Pure iron is soft, bends easily under loads and has only limited uses. Adding small amounts of carbon, nickel, manganese and other elements convert the iron into various alloys of steel. There are hundreds of grades of steel, ranging from basic carbon steel to high grade stainless steel, with each having unique properties. In this paper, only the slags from the steel making process are discussed.

Steel making begins by reducing metal oxides (removing oxygen) in the melt to pure iron metal, while scavenging ions such as aluminum, silicon and phosphorus. The latter three elements cause problems in steel making because they cause the steel to become weak, brittle or otherwise difficult to roll into sheets in a predictable way. These elements make it nearly impossible to make anything useful out of iron. Even though iron is much more readily available as a resource, these element impurities caused enough problems with making tools

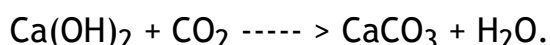
from iron that man began making tools from copper (Bronze Age) after stone tools became obsolete (Stone Age). Fortunately, our ancestors discovered that iron's imperfections could be controlled by adding limestone or dolomite. These calcium compounds complex with aluminum, silicon and phosphorus to form slag. Slag floats to the top of the melt, is poured off and placed in piles for disposal. Slag starts its life at about 2,700 degrees F and cools almost immediately. The slag cools so quickly, in fact, that very few crystals form. Rather, the slag solidifies as an amorphous, glass-like solid ranging from fine sand particles to large blocks, both of which can be extremely hard.

Enormous slag dumps or piles can be found anyplace where steel was made over the past 150 years. Many of these slag piles (containing both nonmetallic slag and wasted steel products) are being processed for use as aggregate in road construction, rail ballast and structural fill. Processing involves crushing and grading the slag. Much of the metallic fraction (the discarded steel products in the pile) is removed with large magnets and sold as steel scrap. All of the resulting nonmetallic grades have applications in construction. The finest fraction (- 1/8 in.) is the one of particular interest for acid mine drainage (AMD) treatment. This product is referred to as slag fines. Some slag fines are further refined using the proprietary Recmix process. This process involves further grinding and a hydraulic separation process. The fine grinding and flotation further remove metals, which are imbedded in the glassy matrix.

Previous work at the National Mine Land Reclamation Center has centered on other low cost alkalinity sources like kiln dust and fluidized bed combustion (FBC) ash. Both are effective for AMD control and both are heavily utilized by the industry. In an effort to provide the coal industry with the broadest choice of alkaline materials, we are constantly looking for other low-cost alkaline products which may be available in large supply and located within short haul distances to our mining districts. We have worked with slag fines produced by International Mill Service, Inc. (IMS) and Recmix, a product of Recmix of PA, Inc., and have found both to show positive results for AMD control. The products are very different and have different applications.

Properties of Steel Slag

Steel slags are calcium alumino-silicate oxides. Since they form at the melting point of iron (>2,700 degrees F), most compounds with lower boiling points have been driven off. These compounds contain elements like sulfur, selenium, carbon, cadmium, lead, copper, and mercury. Most of the residuals are encased within a glassy matrix. Fortunately, the matrix is soluble and releases calcium and manganese oxides, which can drive the pH of the dissolving fluid to 10 or 11. Since slag is a coarse glass, it will maintain high permeability ($\sim 4.5 \times 10^{-2}$ cm/sec) regardless of how much water has passed through it. The permeability of this material can be reduced if it is compacted or ground up into smaller particles. Recmix, on the other hand is a much finer material and barely lets any water pass through (permeability is $\sim 1.0 \times 10^{-6}$ cm/sec). Unlike lime, steel slags do not absorb CO_2 from the air and convert back to relatively insoluble limestone according to the reaction:



This is an extremely important property, since it means slag can be left outside, exposed to the atmosphere for years, and still achieve high levels of alkalinity upon dissolution.

The neutralization potential (NP) of steel slags range from 45 to 78% (Table 1). Most of the residuals are in the form of aluminosilicates and iron oxides. Table 2 summarizes the chemical compositions of Recmix and a slag from IMS in Mingo Junction, Ohio.

Table 1. Neutralization potential of various steel slags.

Steel Slag Type	Neutralization Potential	
	(%)	Tons/1000 tons
C fines; Mingo Jct., OH	78	780
C fines; Weirton, WV	77	770
Slag fines ½ X 0; Weirton, WV	76	760
Fallen slag; Cartech; Reading, PA	71	710
Fallen slag; Lukens; Coatesville, PA	70	700
Recmix; Washington, PA	69	690
Slag fines - 1/8 in.; Mingo Jct., OH	66	660
EAF; Waylite; Johnstown, PA	59	590
Slag fines - 1/8 in., Hecate; Ashland, KY	59	590
Slag fines - 1/8 in., USX; Fairfield, AL	53	530

Table 2. Total elemental compositions of Recmix and Mingo Junction slag fines.

Element	Recmix (mg/kg)	Mingo Jct. Slag Fines (mg/kg)
Al	21,625	29,200
As	6	<3
Ba	130	34
Be	<3	<3
Cd	5	67
C	N/A	4,300
Ca	297,320	501,000
Cr	1,988	1,227
Cu	30	75
Fe	8,327	284,000
Pb	14	84
Mg	57,162	98,000
Mn	9,252	70,000
Hg	0.05	<1
Mo	87	36
Ni	157	12
P	74	8,260
K	325	<100
Sb	N/A	<3
Se	5	<3
Si	142,196	85,000
Ag	5	<3
Na	299	N/A
S	1,805	1,492
Ti	3,285	6,000
Tl	N/A	<3
Zn	61	80

N/A = Not available

Slag Leaching and Analysis

Column leaching studies were performed with various thicknesses of - 1/8 inch IMS slag from Mingo Junction, OR Two-inch diameter columns were filled with slag to thicknesses ranging from 4 to 24 inches. Four times each day, 0.5 L of deionized water was poured through these columns for five days (giving 20 teachings per week). Leachings were not performed on weekends. This leaching procedure occurred over a period of three months. After pouring the water into the columns, leachate was collected and a water sample was taken from the collected leachate. Leachate samples were analyzed for pH, electrical conductivity, alkalinity concentration, and metals. Alkalinities are given as mg/L CaCO₃ equivalent.

Water pH of leachate was 11.7 and alkalinity averaged 1,450 mg/L (Table 3). Figure 1 summarizes the alkalinity concentration of the leachate samples over time with 12- and 24-inch thick slag columns. The results can be related to the leaching procedure (constant leaching for 5 days, followed by a 2 day wait). The highest levels of alkalinity were found on the Monday leachate samples (the peaks on the graphs) because the slag had time to dissolve and accumulate alkaline products during the weekend when leaching was suspended. The 12-inch-thick layer of slag produced initial alkalinities of 2,000 mg/L, and these alkalinity concentrations gradually declined as more water was flushed through the system. At the lowest points (toward the end of the week after constant leaching), alkalinities of about 100 mg/L were found. The 24-inch-thick layer of slag produced similarly high initial alkalinity concentrations and the decline in alkalinity over time was much slower. Even after 100 L of water had flowed through the 24-inch-thick slag column, the alkalinity was still in the 1,750 mg/L range.

Alkalinity in the leachate declined over time due to the dissolution of the finer slag particles, leaving only larger particles in the column for reaction. Larger particles provide less surface area, which in turn give less reaction time and alkalinity production. As mentioned, concentrations of about 100 mg/L were reached, which showed no tendency to decrease further.

In comparison, crushed limestone leached in a similar way yielded alkalinities near 5 mg/L. In order to reach its maximum alkalinity of 80 mg/L (under open conditions), water had to be in contact with the limestone for about 12 hours.

In general, steel slag yielded more alkalinity than equal weights of limestone (from 500 to 2,000 mg/L compared to 60 to 80 mg/L). Hydrated lime or quicklime will yield similar alkalinities as steel slag for a short period, but these lime products expand when wet, seal off allowing little permeability, and gradually turn into limestone. In order to be effective in a leaching application, lime products need periodic agitation.

Measurements on the time it took for the water to flow through the columns gave permeability values of 4.5×10^{-2} cm/sec. These permeability values were maintained throughout the teachings, and they are similar to the permeability values of large sand-sized particles and fine gravel. Alkalinity concentrations stayed near 2,000 mg/L for extended periods depending on the thickness of the slag layer.

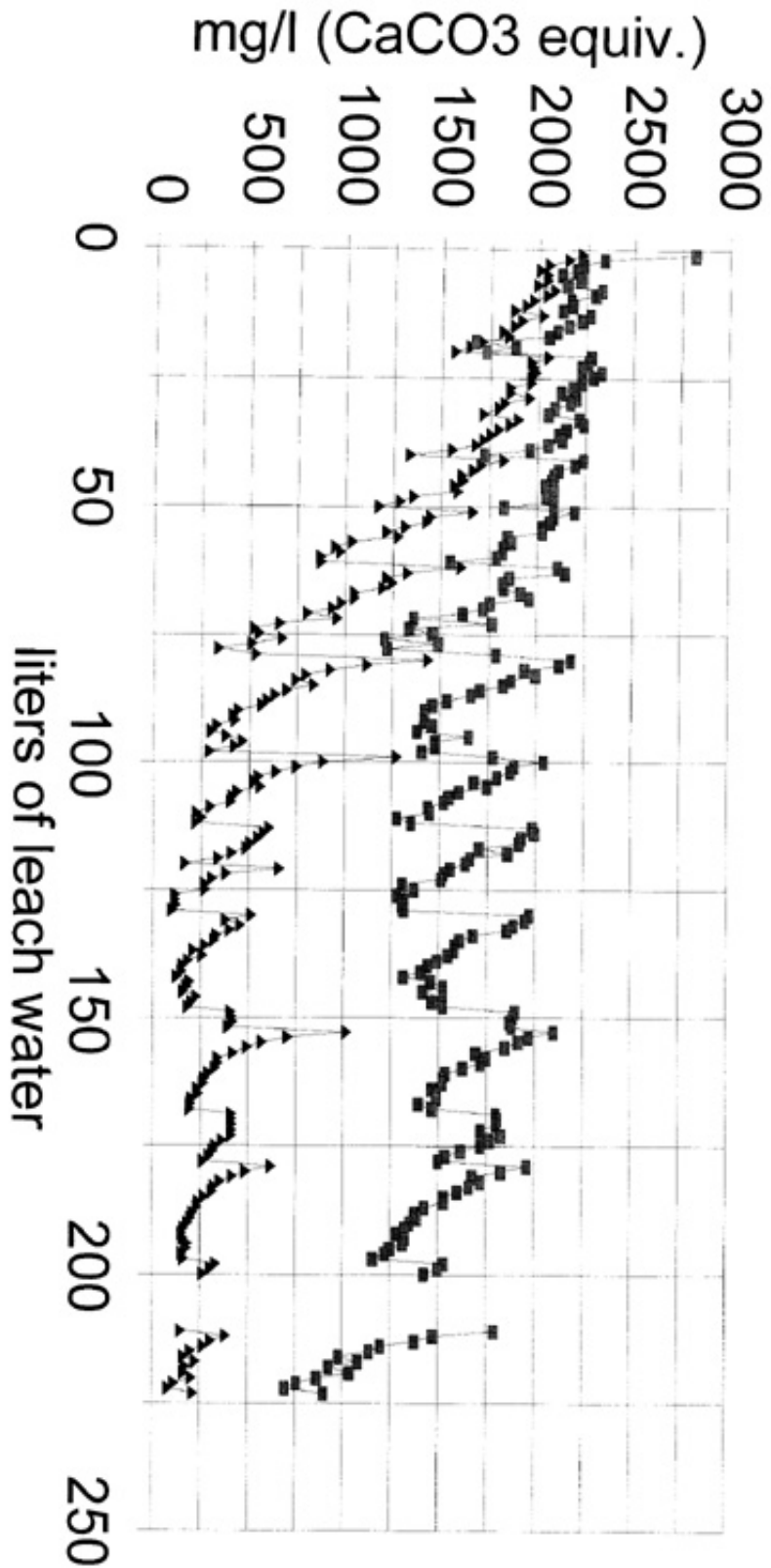
Heavy Metals in Steel Slag

Since most steel slags contain heavy metals, extensive leaching tests were performed with slags. It is important to remember that all steel slags are not the same; they vary in composition, quality, and fineness. Nonetheless, similar steel-making processes (like basic steel vs. specialty or stainless steels) should produce slags that are comparable. In general, basic steel slags like Mingo Junction have lower concentrations of metals than specialty steel slags that often add other metals for specific purposes. Recmix has even lower concentrations of metal than basic steel slags.

Table 3. Metal concentrations of leachate after Mingo Junction steel slag was leached with deionized water compared to USEPA TCLP and drinking water standards.

Mingo Junction Slag - 1/8 in.		TCLP		EPA Drinking Water	
		Limit	Pass	Limit	Pass
pH	11.7				
Cond.	4780 uS/m				
alkalinity	1450 mg/L				
As	<0.05 mg/L	5 mg/L	yes	50 ug/L	yes
Se	0.05 mg/L	1 mg/L	yes	50 ug/L	yes
Ba	0.02 mg/L	100 mg/L	yes	2000 ug/L	yes
Cd	<0.001 mg/L	1 mg/L	yes	5 ug/L	yes
Cr	0.03 mg/L	5 mg/L	yes	100 ug/L	yes
Cu	0.058 mg/L				
Pb	0.1 mg/L	5 mg/L	yes	15 ug/L	yes
Ni	0.041 mg/L	70 mg/L	yes	10 ug/L	no
Zn	<0.002 mg/L	1 mg/L	yes	6 ug/L	yes
V	<0.05 mg/L				
Tl	<0.05 mg/L	7 mg/L	yes	2 ug/L	?
Be	0.0013 mg/L	0.007 mg/L	yes	4 ug/L	yes
Ti	<0.05 mg/L				
Sb	0.08 mg/L				
Mo	0.008 mg/L				
Ag	<0.005 mg/L	5 mg/L	yes		
Hg	<0.0003 mg/L	0.2 mg/L	yes		
SO ₄	1.6 mg/L			2 ug/L	yes

Figure 1. Alkalinity from steel slag columns in two thicknesses.



Deionized water was passed through a 2-inch diameter by 24-inch long column of Mingo Junction steel slag fines. The leachate metal concentrations were compared to metal standards for the U.S. Environmental Protection Agency's Toxicity Characteristic Leaching Procedure (TCLP) and to EPA's drinking water standards. The results indicate that the slag did

not release any element in quantities higher than TCLP limits (Table 3). As for drinking water standards, other than high pH and alkalinity, only Ni was above the EPA drinking water standard. The Ni concentration in leachate was 41 ug/L versus the drinking water standard of 10 ug/L (Table 3).

The same slag was subjected to a TCLP test, which included extracting metals from the slag with a weak acetic acid leaching solution while being shaken for 18 hours (standard EPA procedures). All of the metals listed under leachate parameters in TCLP were below the maximum allowable limits (Table 4), and most of the metals were below detection using an analytical instrument commonly used for measuring metals in solution (ICP-AES).

Given the amount of alkalinity in steel slag, few metals were expected to be mobilized unless the leaching medium became extremely acid or continued leaching eventually exhausted the alkalinity in the slag material. To check the release of metals in an acid situation, an acid-producing coal refuse was amended with 2% and 4% slag for neutralization (these rates represent only one quarter to one half the amount of neutralizing material needed to neutralize the acid that is produced from the refuse). The two slags used in this study, J&L and CarTech, were from specialty steel mills. As expected, most of the columns leached acidic water. Nonetheless, the leachate concentrations were, in nearly every case, less than that from the untreated refuse (Table 5). Nickel and manganese, two important elements, both increased in leachates from refuse treated with slag compared to leachate from untreated refuse.

Field Applications Using Steel Slags

Leach Beds

The alkaline load achievable from a leach bed of steel slag is determined by the amount of fresh water available to drive the leaching process. It is important to note that slag fines in leach beds will plug up if exposed to AMD or sediment. Metals will precipitate within the slag material and cause it to stop transmitting water. Leach beds containing slag fines should be used only in conjunction with fresh (metal free) water. Slag beds can be constructed to catch runoff without a sediment load or to use direct rainfall. The effluent from the leach beds can be allowed to infiltrate directly into a spoil or refuse pile to achieve in-situ AMD treatment, or the effluent can be combined with an AMD source to treat downstream of the spoil. Either application has potential for very low maintenance AMD treatment in either active mining or AML programs. Figure 2 shows how a leach bed might be designed.

Table 6 indicates expected performance and volume requirements in both limestone and steel slag leach beds for a specific flow of water. The alkaline leach bed (with a steady flow of fresh water) can provide up to 1,800 lbs per day of alkalinity compared to 95 lbs per day with open limestone leach beds (open limestone) and 235 lbs per day with an anoxic limestone leach bed (closed limestone).

Table 4. Metal concentrations in leachates following TCLP testing on Mingo Junction slag fines.

Element	Concentration (mg/kg)	Detection limit (mg/kg)	Maximum allowable (mg/kg)
As	BDL	<0.005	5.0
Ba	BDL	<0.005	100.0
Be	BDL	<0.005	NL
Cd	BDL	<0.005	1.0
Cr total	0.047	<0.010	5.0
Cu	0.017	<0.005	NL
Pb	0.006	<0.005	5.0
Hg	BDL	<0.001	0.2
Ni	BDL	<0.005	NL
Sb	BDL	<0.005	NL
Se	BDL	<0.005	1.0
Ag	BDL	<0.005	5.0
Tl	BDL	<0.005	NL
V	BDL	<0.005	NL
Zn	0.012	<0.002	NL

BDL = Below Detection Limit NL = Not Listed in TCLP (40 CFR 261.7/1/91)

Table 5. Leachate quality resulting from the addition of 2% and 4% slag from two sources (J&L and CarTech). The results are from the fifth leach cycle in an accelerated leaching procedure.

Analyte	Units	Control No Slag	Refuse + 2% J&L Slag	Refuse + 4% J&L Slag	Refuse + 2% CarTech Slag	Refuse + 4% CarTech Slag
pH		2.6	4	5.3	3.5	7.3
acidity	(mg/L)	1155	157	24	139	9
alkalinity	(mg/L)	0	0	7	0	25
SO ₄	(mg/L)	2080	1551	1424	1650	1413
As	(mg/L)	34	18	31	32	40
Se	(mg/L)	1	5	15	3	30
Ba	(mg/L)	639	21	31	773	28
Ag	(mg/L)	2	11	3	2	2
Cr	(mg/L)	41	5	5	36	3
Ni	(mg/L)	507	1000	283	713	57
Cd	(mg/L)	23	38	6	18	3
Pb	(mg/L)	25	9	13	3	20
Mn	(mg/L)	8	36	22	17	3
Fe	(mg/L)	207	162		216	0
Al	(mg/L)	10	1		6	1

Figure 2.
Leach Bed

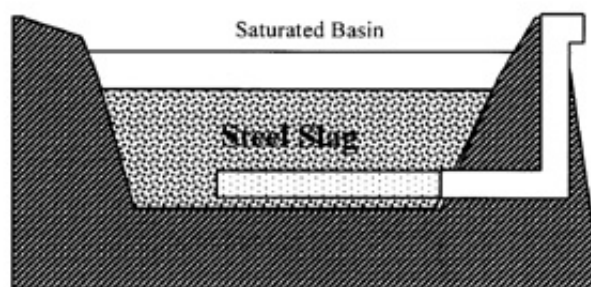


Table 6. Expected performance from leach beds constructed with limestone versus steel slag. Two types of leach beds are presented: those with a steady flow of fresh water (alkaline leach bed) and those driven by precipitation only (dry leach bed).

ALKALINE LEACH BED							
	FLOW gpm	SIDE LENGTH ft.	DEPTH ft.	MATERIAL REQUIRED tons	FINAL ALK mg/L	LIFE years	ALKALINE LOAD lbs/day
LIMESTONE OPEN	100	135	4	6,160	79	200+	95
CLOSED	100	120	4	4,900	196	100+	235
STEEL SLAG OPEN	100	118	4	3,009	1,500	5	1,800

DRY LEACH BED							
	AREA acres	DEPTH ft.	FLOW gpm	MATERIAL REQUIRED tons	COST	FINAL ALK mg/L	ALKALINE LOAD lbs/day
LIMESTONE	5	1	9.13	16,000	\$240,000	20	2.2
STEEL SLAG	5	1	9.13	11,760	\$176,400	800	87.6

Direct Water Treatment

Water treatment using slag was also tested. This involved placing slag directly in a stream of AMD as a replacement for lime in an Aquafix doser. A site at Lenox, WV was selected, and the acid mine drainage to be treated had high manganese (56 mg/L) and moderate iron (10 mg/L) concentrations. This approach had mixed results. Slag fines were too coarse to dissolve quickly and very high application rates were needed for adequate treatment to achieve

effluent limits.

On the other hand, Recmix, due to its smaller particle size, worked well as a treatment chemical. It removed manganese at a pH of 8.7 at about twice the application rate of CaO. Iron was also removed. Table 7 shows the performance of Recmix compared to CaO in the Lenox water treatment trial.

In addition to monitoring for Fe, Mn and Al in the water, we analyzed for TCLP metals in the initial AMD and also in the water 300 feet downstream of the Aquafix machine applying Recmix. The results indicate that all of the TCLP metals dropped after treatment with Recmix. The only surprising result was the tendency for Al to remain around 7 mg/L in the treated water. At a pH of 8.7, Al is certainly not expected to be dissolved in the water. The water sample was taken at the inlet to the settling pond and we expect that the Al would precipitate given time. This is something that we will continue to monitor.

Field Considerations

Until more is understood about the leachability of various slags in acid environments, we do not recommend that steel slags be placed in areas that may become acid. If slag is to be used as an alkaline amendment, we recommend that enough slag is added so that the spoil or refuse cannot turn acid. Both Recmix and slag fines have been used successfully as alkaline amendments to spoils. We recommend that slags be considered as surface amendments to soils, as amendments to slightly acidic spoil and refuse (where the slag will overwhelm the small potential for acid production), and as an alkaline material in freshwater leaching beds.

Acid mine drainage treatment with Recmix appears promising as long as treatment is maintained. Given the solubility of slag's alkalinity, this might be a promising application. Slags generally do not feed well through an Aquafix unless dried to <3% moisture. For proper dosage, a lime hopper with a shaker is required for adequate flow of the slag. Another promising alternative is to directly apply slag into AMD in a ditch upstream of a settling pond, much like limestone sand applications.

Cost

In most locations in the Appalachian coalfields, slag can be obtained very inexpensively. Transportation is the major cost component.

Conclusion

Steel slag appears to have a number of applications for AMD control and treatment. In addition to the uses identified so far, future work will evaluate its use as a capping material and as an alkaline amendment. Several field studies were initiated in the summer of 1997 and their progress will be reported in future Task Force meetings.

Table 7. Water quality of untreated AMD at Lenox, WV and the quality after treatment with CaO and Recmix. Both chemical and slag were applied by an Aquafix machine. Treated water was sampled at 30 and 300 feet from where the Aquafix machine was located.

	Calcium Oxide Treatment			Recmix Treatment		
	Upstream Aquafix Lenox B	30' Downstream CaO Aquafix Lenox 2	300' Downstream CaO Aquafix Pond Inlet	30' Downstream Recmix Aquafix Lenox 2	300' Downstream Recmix Aquafix Pond Inlet	
pH	4.3	4.9	4.7	8.1	8.7	
alk	0	2	1	25	555	
acd	270	141	171	61	0	
Al	31	8	19	6	7	
Fe	10	5	6	0	0	
Mn	56	55	50	21	0	
Cond.	2190	2120	2120	2180	2150	
Sb	.6				.4	
As	.7				.5	
Ba	BDL				BDL	
Be	BDL				BDL	
Cd	.1				BDL	
Cr	.1				BDL	
Pb	.4				.3	
Ni	1.2				BDL	
Se	.8				.6	
Ag	BDL				BDL	
Tl	1.3				.9	
Hg	BDL				BDL	

BDL = Below Detection Limit