A Novel Treatment for Acid Mine Drainage Utilizing Reclaimed Limestone Residual (RLR).

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Principal Author(s):	Horace. K. Moo-Young, Ph.D. and Charles. E. Ochola, Ph.D.
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Submitting Organization:	Lehigh University.
Address:	13 East Packer Avenue, Fritz Lab, Bethlehem, PA, 18018.
Phone Number:	610-758-4412
Fax Number:	610-758-6405

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ABSTRACT

The viability of utilizing Reclaimed Limestone Residual (RLR) to remediate Acid Mine Drainage (AMD) was investigated. Physical and chemical characterization of RLR showed that it is composed of various minerals that contain significant quantities of limestone or calcium bearing compounds that can be exploited for acid neutralization. Acid Neutralization Potential (ANP) test results showed that RLR has a neutralization potential of approximately 83% as calcium carbonate ($CaCO_3$). Neutralization tests with most of the heavy metals associated with AMD showed removal efficiencies of over 99%. An unexpected benefit of utilizing RLR was the removal of hexavalent chromium Cr (VI) from the aqueous phase. Due to an elevation in pH by RLR most AMD heavy

metals are removed from solution by precipitation as their metal hydroxides. Cr (VI) however is not removed by pH elevation and therefore subsequent ongoing tests to elucidate the mechanism responsible for this reaction were conducted.

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Introduction

Reclaimed Limestone Residual (RLR) is a co-product of the steel making process, and is developed during the refining of crude iron products to steel. It has been shown to have redox capabilities that facilitate reduction, and also has significant acid neutralizing potential. The objective of the research was to determine the feasibility of utilizing (RLR) as a treatment media for Acid Mine Drainage (AMD), whereby RLR could be placed either as a geochemical filter, or in a drain or channel along which AMD flows, and this document reports the findings from the research that was conducted.

Demonstrating the Geo-chemical Feasibility

To demonstrate the feasibility of utilizing RLR to remediate Acid Mine Drainage (AMD), the acid neutralization potential of RLR was determined and subsequent neutralization tests utilizing synthetic AMD groundwater were also conducted.

Acid Neutralization Potential (ANP) Results

The results of the neutralization tests by the four different methods are shown in Table 1. From these results it is determined that this particular RLR has an average neutralization potential of approximately 83% as calcium carbonate ($CaCO_3$). A comparison of the determined neutralization potential of this particular RLR with other similar material is shown in Table 2.

Table 1. ANP of RLR from The Waylite Corporation in Bethlehem PA.

Digestion Method	Neutralization Potential	
	%	Tons $CaCO_3$/1000 Tons RLR
Sobek	81.6	816
Boil	84.1	841
H_2O_2	84.4	844
Sobper	80.5	805

Table 2. ANP of Various Steel Slags.

Steel Slag Type	Neutralization Potential	
	%	Tons $CaCO_3$/1000 Tons Steel Slag
RLR: Waylite, Bethlehem PA	83	827
Slag fines: Weirton, WV	76	760
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, USX, Fairfield, AL	53	530

Neutralization Testing Results

Testing to determine the dissolved heavy metal removing capability of RLR from AMD were conducted by utilizing neutralization tests between RLR and synthetic AMD comprised of various concentrations of heavy metals at different pH values. The results from these tests are summarized in Table 3, and show that for the most part RLR was effective in removing over 99% of the dissolved metals from solution. Of interest to note is the removal of hexavalent chromium Cr (VI) since the commonly employed technique of precipitation does not remove it from solution. Based on these finding additional tests were conducted to identify the mechanism responsible for this added benefit of RLR, and are discussed later on.

Table 3. Heavy Metal Neutralization Test Results.

Metal	Initial Concentration Range (mg/L)	Final Concentration Range (mg/L)	Initial pH range	Final pH range	Removal Efficiency (%)
Fe	0.5-200	0.001-0.009	2.7-4.8	10.3-11.3	99.50-99.99
Zn	0.5-200	0.000-0.250	3.0-7.0	10.6-11.3	99.86-100.00
Al	0.5-200	0.002-0.087	2.1-5.9	10.0-11.3	83.80-99.99
Cu	0.5-200	0.010-0.060	2.1-6.1	10.7-11.4	96.00-99.99
Pb	0.5-200	0.001-0.003	3. 2-7.0	10.9-11.5	99.50-99.99
Cr (VI)	0.5-100	0.010-29.98	1.4-7.0	10.8-11.4	70.02-96.00

RLR Analysis.

Testing was conducted on RLR to determine both its physical and chemical properties. Water content, specific gravity, organic content, sieve analysis, and hydrometer analysis, were conducted according ASTM procedures. For a chemical characterization of RLR samples were finely ground and sieved to create a proper sample for both energy dispersive X-ray spectroscopy (EDX) and X-ray Diffraction (XRD). EDX is a micro analytical technique that is based on the characteristic X-ray peaks that are generated when the high-energy beam of the scanning electron microscope (SEM) interacts with the specimen. Each element yields a characteristic spectral fingerprint that may be used to identify the presence of that element within the sample. The relative intensities of the spectral peaks were used to determine the relative concentrations of each element in the specimen. XRD is an analytical technique that is used to study the atomic and molecular structure of substances by directing X-rays at them and causing a slight spreading of the waves (diffraction of the rays) around the atoms. By using measurements of the position and intensity of the diffracted waves, it was possible to calculate the shape and size of the atoms in the samples and subsequently determine what compounds RLR is composed of.

Physical Characterization Results

The RLR used in this study has the consistency of coarse-grained sand, and Figure 1 is an image of what a 5 gram sample looks like. The results of the major physical properties tested showed that RLR has a water content of 0.01 %, an organic content of 1.5%, a porosity of 30%, and a specific gravity G_s of 3.46. Grain size analysis of the material from which RLR is obtained showed that it was well graded, and the results of the analysis are shown in Table 4 and Figure 2.

Figure 1. RLR (approximately 5 grams)

Table 4. Grain Size Distribution Results

Sieve No.	Mass retained (g)	Percent finer (%)	Opening (mm)
4	0	100.00	4.75
10	18800	19.56	2
40	3505.95	4.53	0.425
60	437.08	2.66	0.25
80	176.14	1.91	0.18
100	68.6	1.61	0.15
200	190.04	0.80	0.075
pan	186.62	0	0

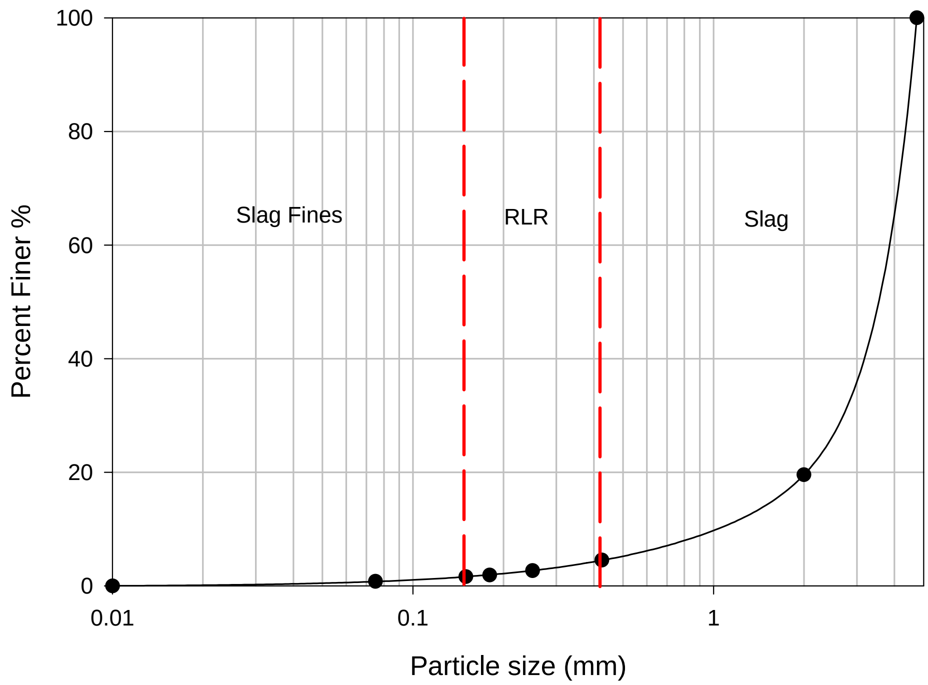

Figure 2. Particle size distribution curve.

Chemical Characterization Results

The EDX analyses of RLR are shown in Table 5 by weight percents, and are averages of analyses from three areas of the SEM preparations. Results of the X-ray diffraction showed that RLR is approximately 92% crystalline and is composed of several compounds including Magnesium oxide, Calcium silicates, Calcium magnesium silicates, Manganese aluminum oxide, Iron silicate, Manganese, Calcium aluminum oxide, and Manganese oxide but not exclusive to these compounds. Table 6 lists these compounds in approximate order of abundance in the XRD pattern:

Table 5. Elemental Composition of RLR

Element	Mg	Al	Si	S	K	Ca	Ti	Mn	Fe
Wt %	6.2	3.9	17.9	0.7	nd	58.6	nd	2.0	11.3

Table 6. Compound Comprising RLR Listed in Order of Abundance.

Compound	MgO	Ca_2SiO_4	$Ca_5MgSi_3O_{12}$	MnAlO	Fe_2SiO_4	Mn	$Ca_2Al_2O_4$	MnO
Order	1	2	3	4	5	6	7	8

***Interesting Findings and Observations*.**

Due to an elevation in pH by RLR the metals in Table 3 with the exception of Cr (VI) were removed from solution by precipitation as their metal hydroxides. The results from these tests also showed a removal of Cr (VI) from solution. Reactions between RLR and Cr (VI) were subsequently investigated by employing various batch and column testing techniques. The averaged results of these preliminary tests are shown in Figure 3 which shows the percentage of chromium reduced vs. the initial Cr (VI) concentration. For the lower concentration of 0.5 mg/l the reduction of Cr (VI) was almost 100% in both the 10-gram and 20-gram samples. As the concentration increased the reduction was less for both the 10 and 20-gram samples [2]. Research on this aspect of the study is ongoing and has resulted in the publication of a journal article. (Ochola, C. E., and Moo-Young, H. K., (2004). Establishing and Elucidating Reduction as the Removal Mechanism of Cr (VI) by Reclaimed Limestone Residual RLR (Modified Steel Slag). *Environmental Science & Technology*. **38** (22): 6161-6165)

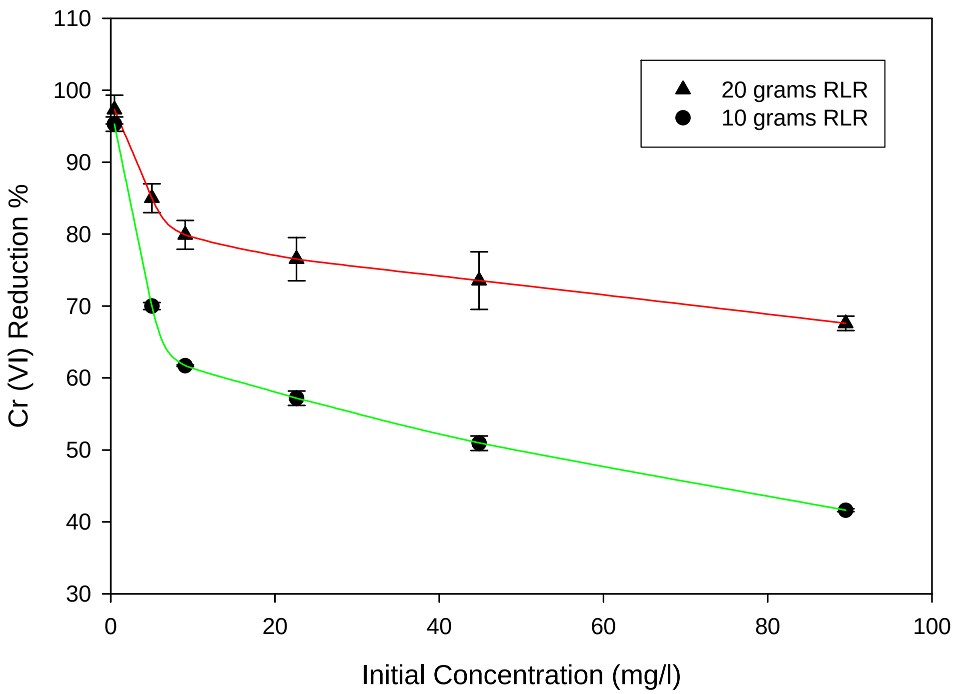

Figure 3. Cr (VI) reduction vs. initial concentration. Averaged data replicates shown with error bars; where no error bars are seen, they are smaller than the size of the data symbol [2].

Recommendations.

To fully exploit the potential of RLR as an AMD treatment media, a rigorous investigation of the structure-reactivity relationship at the molecular level that facilitates these reactions is required before any modifications to its structure for added performance are considered. A two step objective is thus recommended.

In the first step an examination the microscale interactions that enable RLR to remove heavy metals such as chromium by other mechanisms beside those associated with precipitation reactions of other metals is required. Spectroscopic techniques to identify what new compounds are formed should be employed to enable a determination of how the structure of RLR has been changed after these interactions if at all, and what particular constituents of RLR are primarily responsible for the interactions/mechanisms of interest.

After identification of these mechanisms we will in the second step attempt to synthesize nano-RLR to contain only those characteristics relevant to the removal of heavy metals, and if necessary the addition of other components that may enhance the efficiency of nano-RLR by acting as catalysts similar to the interaction of bimetallic compounds. In previous proposals, reviewers have been critical on the utilization of a steel slag by-product due to the environmental concerns over the trace elements (chromium, copper, zinc) in steel slag. Thus, to assuage this concern, the PI's aims to utilize the knowledge gained in step one of this study to synthesize nano-RLR without trace elements.