Nelson Tunnel Treatment Feasibility Study

ADDENDUM REPORT
Bench Scale Testing of Chemical Precipitation Treatment Effectiveness

Willow Creek Reclamation Committee
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Purpose

The water quality of Willow Creek remains heavily impacted from historic mining in the Creede Mining District. The lower portion of the Creek contains high concentrations of zinc and other heavy metals, and is a major contributor of metals to the Rio Grande. The Nelson Tunnel has been found to be the primary contributor of metal contamination to Willow Creek. The Nelson Tunnel Treatment Feasibility Study, funded by a grant from the EPA, evaluated the feasibility and cost to treat water discharging from the Nelson Tunnel into Willow Creek.

The workplan for the Nelson Tunnel Treatment Feasibility Study included "an evaluation of whether or not a treatment facility will be able to achieve effluent standards". The project study report produced by McLaughlin Rincon recommended use of chemical precipitation to treat Nelson Tunnel water. The study stated that the performance of chemical precipitation systems is well documented, but did not make specific estimates of treatment performance.

Erik Sandvik, PhD, a retired chemist and volunteer with the Willow Creek Reclamation Committee, ran a USGS equilibrium speciation computer program (PHREEQC) given the specific water quality of Nelson Tunnel discharge. The computer program indicated that, given the chemical speciation of Nelson Tunnel water, chemical precipitation treatment could not meet expected effluent standards. This computer program considered equilibrium solubility conditions but did not consider adsorption or co-precipitation processes. Therefore, laboratory was recommended to verify if chemical precipitation methods could really treat Nelson Tunnel water to expected effluent standards. Raw water from Nelson Tunnel was treated with lime and caustic soda on a bench scale to evaluate potential treatment effectiveness. This brief report documents the results of this bench scale testing.

Potential Effluent Standards

The effluent standards that would be required for a Nelson Tunnel treatment system are not currently known. Standards would be developed in relation to a TMDL analysis for the watershed. A TMDL analysis is currently underway but not complete. The standard may be based on table value standards for surface waters. Table value standards are primarily based upon hardness. The hardness of West Willow Creek above the Nelson Tunnel has ranged between 24 and 39 mg/L $CaCO_3$. However, Nelson Tunnel water contains a large amount of calcium that would probably not be removed at probable treatment pH levels. The calcium and magnesium in raw Nelson Tunnel water results in a hardness of over 600 mg/L as calcium carbonate. This hardness is above the maximum hardness for table value standards of 400 mg/L, and a standard based on effluent hardness would result in relatively high standards. The following table shows table value standards based on a range of hardness values.

Table 1. Table Value Standards as a Function of Hardness

Hardness	Cd	Cu	Pb	Zn	Al	Fe*
24	0.8	2.7	0.5	35	750	1000
39	1.1	4.0	0.9	53	750	1000
400	6	29	11	379	750	1000

Note: All concentrations in µg/L (ppb) as dissolved except iron which is as total

Methodology
J.B. Alexander, a retired chemical engineer and volunteer with the Willow Creek Reclamation Committee, performed bench scale testing. Nelson Tunnel water was collected in one gallon jugs. Small amounts of lime or caustic soda (sodium hydroxide) were mixed with Nelson Tunnel water in a beaker and the pH was monitored with a high accuracy electronic pH meter. When a desired pH titration level was reached, a portion of the solution was filtered using sets of paper filters and a 0.45 µm syringe filter. The filtered sample was placed in a 60ml bottle and preserved using nitric acid. Additional lime or caustic soda could then be mixed with remaining solution until a higher pH level was reached. Test samples were analyzed for concentrations of selected dissolved metals at Sangre de Cristo Laboratory in Alamosa Colorado within two weeks of the testing.

Results
Significant amounts of time were needed for pH levels to stabilize due to rates of precipitation reactions, flocculation, and reaction with atmospheric carbon dioxide. It was more difficult to mix and stabilize lime solutions than solutions with caustic soda, but more safety precautions had to be used when working with the caustic soda.

Raw Nelson Tunnel had a pH of about 4.34. Lime was first used to raise raw Nelson Tunnel water to pH 6.0, and samples were collected at subsequent 0.5 pH levels to a pH of 7.5. A later testing with lime raised Nelson Tunnel water to three pH levels between 8.09 and 9.99. Caustic soda was used to raise raw Nelson Tunnel water to four pH levels between pH 8.57 and 9.71, and then to 4 levels between pH 9.71 and 10.63. For one experiment, alum was also added to a pH 9.71 caustic soda sample to investigate if added flocculation from the alum would aid in metal removal. Table 2 details test results, and results are also presented graphically in figures.

Zinc is the primary contaminant of concern in Nelson Tunnel water as concentrations are orders of magnitude higher than table value standards. However, it appears that the removal of cadmium may drive treatment. The bench scale tests indicate that treatment with lime or caustic soda could remove zinc to table value standards (based on the hardness of treatment effluent) at about pH 8.0. However, treatment to about pH 9.4 would be required to remove cadmium to table value standards. This level of treatment would remove zinc to below table value standards based on the hardness of West Willow Creek. The majority of copper was removed below about pH 7.5, but appeared to come back into solution to a limited degree at higher pH levels.

Concentrations of dissolved aluminum and total iron have been observed above the non-hardness fixed standards in Nelson Tunnel water. It is expected that pH adjustment to treat other metals would remove dissolved aluminum and total iron to below effluent standards.

Conclusions and Recommendations
Although computer modeling indicated that traditional chemical precipitation treatment methods would not remove heavy metal contaminants in Nelson Tunnel water to the level of table value standards, bench scale testing indicates that treatment with lime and caustic soda should be able to remove metals to effluent standards. Treatment to pH 8.0 may remove zinc to potential effluent standards, but treatment to pH 9.4 or higher may be needed to remove cadmium to desired levels.

Table 2. Results of Bench Scale Treatment of Nelson Tunnel Water

Num	Date	Description	pH	Al_d µg/L	Cd_d µg/L	Ca mg/L	Cu_d µg/L	Zn_d µg/L	Fe_d µg/L
1	3/22/06	NT Raw	4.34	726.6	62.8	241.5	23.6	58780	
2	3/23/06	NT+Lime, pH 6.0	6.0		63.4	289.6	20.2	53460	
3	3/23/06	NT+Lime, pH 6.5	6.5		200.9	393.9	14.3	54850	
4	3/23/06	NT+Lime, pH 7.0	7.0		45.2	228.5	9.3	53240	
5	3/23/06	NT+Lime, pH 7.5	7.5		32.5	226.3	<1	12430	
15	4/12/06	NT+Lime, pH 8.09 #2	8.09	197.3	30.4	178.2	3.4	149	149
16	4/12/06	NT+Lime, pH 9.01 #2	9.01	232.4	14.4	157.6	1.8	38.2	140
17	4/12/06	NT+Lime, pH 9.99 #2	9.99	458	0.2	125.4	<1	7.2	150
6	3/24/06	NT+NaOH, pH 8.57	8.57		11.7	238.4	<1	220.5	
7	3/24/06	NT+NaOH, pH 9.02	9.02		7.5	242.5	<1	41.3	
8	3/24/06	NT+NaOH, pH 9.39	9.39		6	255.9	<1	27.8	
9	3/24/06	NT+NaOH, pH 9.71	9.71		1.2	217.8	<1	26.6	
10	3/25/06	NT+NaOH, pH 9.71 #2	9.71		0.9	224.9	2.8	26	
11	3/25/06	NT+NaOH, pH 10.01 #2	10.01		0.4	236.4	1.4	23.4	
12	3/25/06	NT+NaOH, pH 10.24 #2	10.24		0.5	170.3	1.5	24.5	
13	3/25/06	NT+NaOH, pH 10.63 #2	10.63		<0.1	186.1	1.9	24.6	
14	3/25/06	NT+NaOH+Alum, pH 9.71	9.71	<3	1.6	47.8	1.7	46.3	

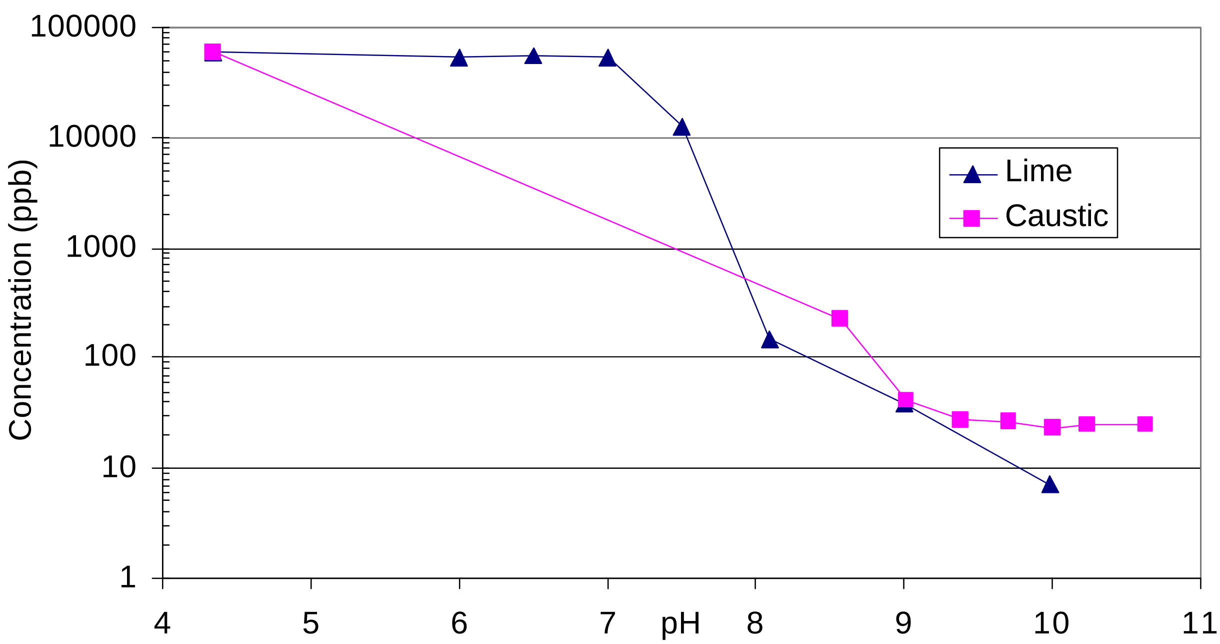

Figure 1. Zinc Concentrations in Nelson Tunnel Water as Function of pH Titration

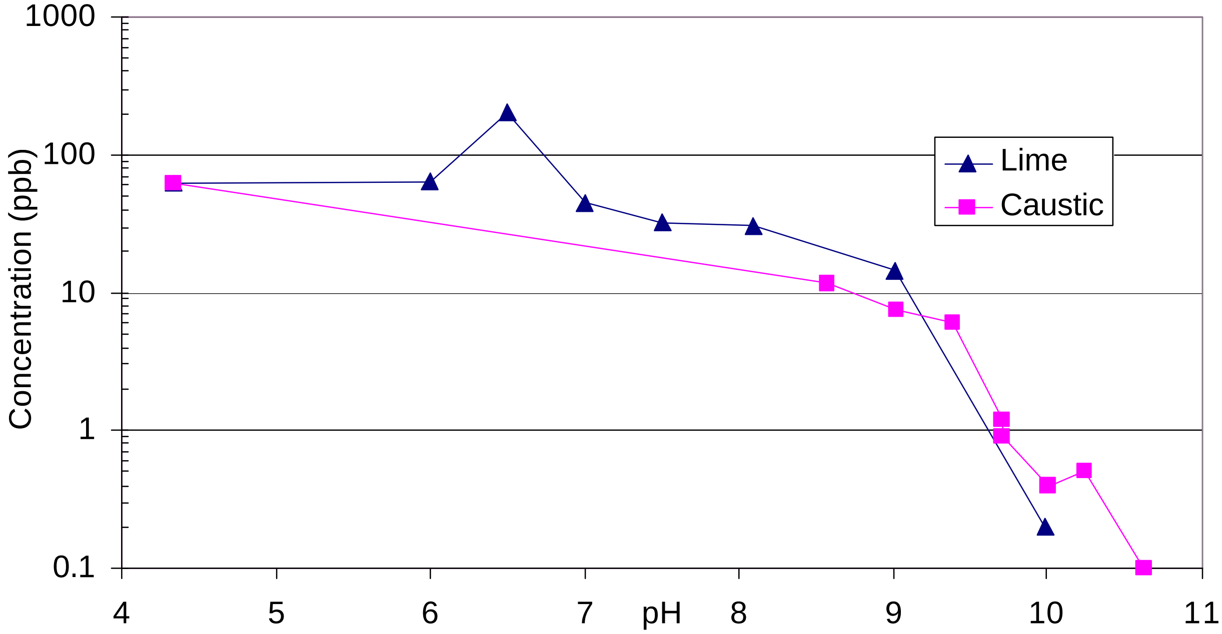

Figure 2. Cadmium Concentrations in Nelson Tunnel Water as Function of pH Titration

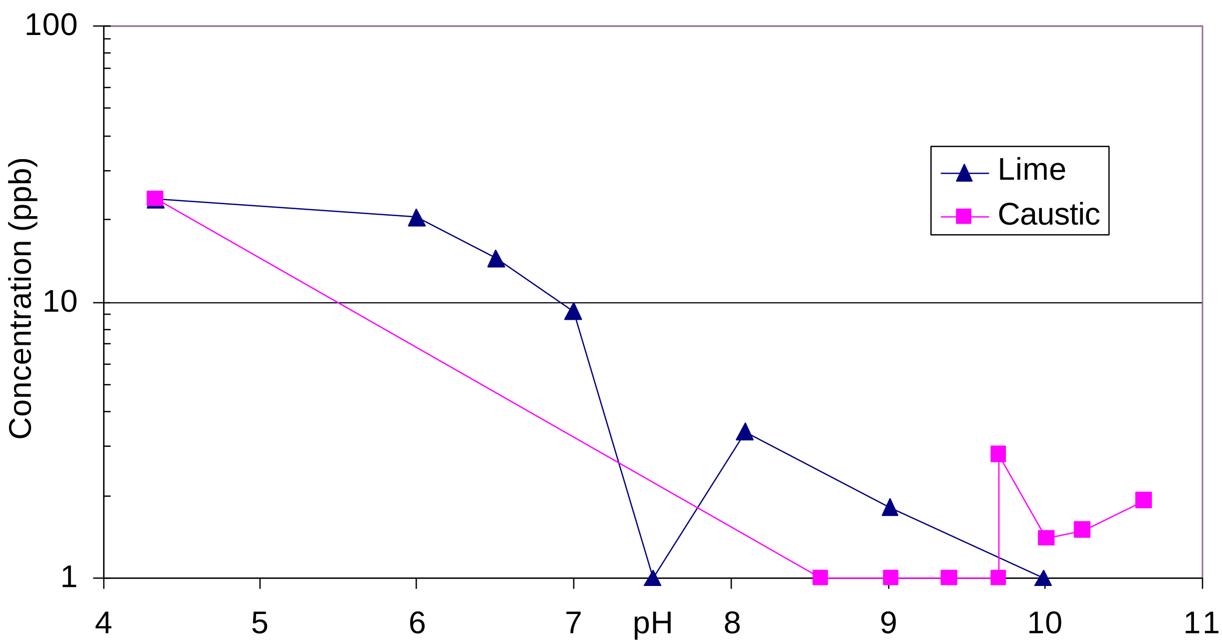

Figure 3. Copper Concentrations in Nelson Tunnel Water as Function of pH Titration