SEDIMENT POND REMOVAL OF PRECIPITATES FROM NEUTRALIZED ACID ROCK DRAINAGE

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ABSTRACT

Water containing neutralized acid rock drainage flows from the Carlton Tunnel, an 11-kilometer long tunnel that drains the regional ground water table that includes the Cripple Creek Mining District, located the Rocky Mountains of Colorado, USA. Settling ponds are used to remove chemical sediment that forms in the approximately 88 liters/second of water that flows from the tunnel, so that the discharge water can meet Total Suspended Sediment (TSS) water quality limits. The precipitate is made up of micron-sized particles, and is extremely difficult to remove from the water by conventional sedimentation ponds. The behavior of these particles has been evaluated using physical, chemical, and optical testing of the sediment, together with physical and chemical testing of the water conveying it. The results are used to develop an advanced design for sedimentation of colloid-sized particles. The pond system has been redesigned using this method and removes sediment to below the required permit limits.

1. INTRODUCTION

The Carlton Tunnel was constructed in 1941 to drain the regional groundwater regime in an area that includes the Cripple Creek mining district, in Colorado, USA. The tunnel is approximately 11 kilometers long, and flow currently averages approximately 88 liters per second.

The tunnel has lowered the regional water table in the mining district to a depth of approximately 1,000 meters below ground surface. This has exposed sulfide minerals to the atmosphere, allowing oxidation of the sulfides and the formation of acid rock drainage (ARD). The products of the oxidation are neutralized by abundant carbonate in the rockmass. The water that exits the tunnel from the mining district therefore contains neutralized acid rock drainage (NARD), and is saturated in calcium carbonate and calcium sulfate.

At the portal of the tunnel the water contains significant sediment load. To remove sediment from the discharge to concentrations that are required under permit the water is passed through sedimentation ponds.

The sedimentation capability of the pond system was required to be improved as a result of regulatory order. To guide the design, a study of the formation, physical characteristics, and behavior of the sediment was conducted. The results of this study were used to re-design the ponds, which have operated within permit limits since implementation.

2. FORMATION OF PARTICULATES

The sediment that is present in the Carlton Tunnel water is a chemical precipitate. It forms from the NARD when the partial pressure of carbon dioxide is reduced from close to 100% in the mining district to levels approaching atmospheric (~350 ppmV or 0.035%) after discharge. The nature, grainsize, and concentration of the particulates in the Carlton Tunnel water have been evaluated with the following results.

Particulate Composition

The chemical composition of the particulate was determined by collection of the particulate, digestion by EPA Method 3050, and analysis of the digestate using EPA Method 6010B (ICP) and EPA Method 6020 (ICP-MS). The results are presented in Table 1 for a sample of sediment taken close to the tunnel portal (“Portal”), and a second sample taken close to the discharge point of the sediment pond system (“Ponds”).

Table 1. Chemical Analysis of Carlton Tunnel Sediment

Analyte	Unit	Portal	Ponds
Carbonate (ABA)	%	33.6	50.8
Calcium, total (3050)	%	25.2	38.9
Iron, total (3050)	%	11.6	2.1
Aluminum, total (3050)	%	2.2	0.4
Sulfate (ABA)	%	1.8	1.0
Manganese, total (3050)	%	1.2	0.4
Silica, total (3050)	%	0.5	0.7
Zinc, total (3050)	%	0.013	0.008

Notes: "ABA" = EPA Method 600/2-78-054 1.3
"3050" = EPA Method 3050 extraction

Based on laboratory evaluation (XRD), and chemical analysis, the approximate mineralogy of the sediments (ignoring attached water) is shown in Table 2.

Table 2. Approximate Mineralogy of Carlton Tunnel Sediment

ANALYTE	UNIT	Portal	Ponds
Calcite ($CaCO_3$)	%	61	96
Hematite ($Fe(OH)_3$)	%	22	4
Anhydrite ($CaSO_4$)	%	3	1
Alumina (Al_2O_3)	%	4	1
Manganite ($MnO(OH)$)	%	2	1
Quartz (SiO_2)	%	1	1

Notable in this evaluation is that there is almost no quartzitic material in the sediments, indicating that the particles are not transported sand, silt, or clay. The particulates all appear to be chemical precipitates, derived from the NARD water that is discharging from the Carlton Tunnel.

Water Composition

To evaluate the feasibility of the formation of chemical precipitates from the discharging water, the discharge water was analyzed, with the analysis results for water discharging from the tunnel portal and from the original sediment pond system presented in Table 3.

Table 3. Carlton Tunnel Discharge Water Quality

Species	Unit	Portal	Discharge
pH	s.u.	6.68	7.23
Temperature	°C	22.9	21.9
DO	mg/L	6.0	7.4
TDS	mg/L	2147	2154
TSS	mg/L	28	13
Acidity	mg/L *	28	19
Alkalinity	mg/L *	280	276
Ca	mg/L	465	471
Mg	mg/L	43	44
Na	mg/L	94	87
SO4	mg/L	1190	1188
HCO3	mg/L	347	343
CO3	mg/L	6.0	5.5
Cl	mg/L	24	24

Species	Unit	Portal	Discharge
Ag	mg/L	0.001	0.001
Al	mg/L	0.48	0.33
As	mg/L	<0.005	<0.005
Cd	mg/L	0.003	0.003
Cr	mg/L	0.002	0.002
Cu	mg/L	0.005	0.005
Fe	mg/L	0.37	0.24
Hg	mg/L	<0.0002	<0.0002
K	mg/L	5.2	5.0
Mn	mg/L	2.2	2.0
Ni	mg/L	0.006	0.006
Pb	mg/L	<0.001	<0.001
Se	mg/L	0.005	0.005
Zn	mg/L	0.39	0.38

* as $CaCO_3$

The behavior of this water after it emerges from the Carlton Tunnel is expected to be dominated by carbon dioxide, which is created when the ARD is neutralized in the mining district rock[1]. To evaluate this behavior, the water was speciated using PHREEQC (Parkhurst and Appelo, 1999) for a range of partial pressures of carbon dioxide. The partial pressure of $CO_2(g)$ was adjusted until the computed pH of the solution matched the measured pH, producing the saturation index for calcite (calcium carbonate). The results are presented in Table 4.

Table 4. Saturation Index of $CaCO_3$ in Carlton Tunnel water

Location	**pH (s.u.)**	**CO_2 Partial Pressure (atm)**	**Saturation Index ($CaCO_3$)**	**Comment**
Carlton Tunnel Discharge	6.682	0.051	-0.002	At equilibrium
Sediment Pond Outlet	7.226	0.014	0.545	Significantly supersaturated

The saturation index for calcite in the water leaving the tunnel is approximately zero, indicating that the water is saturated with calcium carbonate at that temperature and pH. The computed partial pressure of $CO_2(g)$ required to maintain that equilibrium is approximately 5%, which would appear to be reasonable for atmospheric conditions in the eleven-kilometer tunnel.

By the time the water has traversed the five settling ponds that existed at the time of the measurements, the measured pH had risen from 6.7 to 7.2, and the computed partial pressure of $CO_2(g)$ required to maintain that pH had dropped to 1.4%. The partial pressure of $CO_2(g)$ in the atmosphere is approximately 0.035%, so it is clear that exposure of the water to the atmosphere is causing out-gassing of carbon dioxide to approach the atmospheric concentration.

As a result of this outgassing, calcite moves from saturated at the portal to significantly supersaturated at the sediment pond outlet. Thus precipitation of calcite would be expected as the water traverses the pond system and carbon dioxide is lost.

Particulate Generation

Accordingly, there are two suspended particulate sources that are the sediment ponds are removing:

1. Particles that precipitate as the water is flowing down the Carlton Tunnel, and which emerge at the portal.
2. Particles that precipitate in the ponds themselves, due to outgassing of carbon dioxide and the concomitant increase in pH causing super-saturation of calcite.

Sediment ponds must remove sediment from both these sources to be effective.

3. SEDIMENT CHARACTERIZATION

To allow design of the pond system to remove the particulates to meet the required TSS concentrations at discharge, the particulates were sampled and characterized for grainsize and mass distribution.

Grainsize

The grainsize of the influent and effluent water was tested by filtering 100 liters of influent and effluent water through a 0.45 micron glass filter. The filter papers and the captured sediment were sent for optical grainsize analysis by Tri-State Testing Laboratories, of Hamilton, Ohio. Examples of the images of influent and effluent sediment are presented in Figure 1.

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[1] During the extensive underground gold mining of the Cripple Creek mining district in the last century, carbon dioxide generated from neutralization of ARD was a major safety risk for miners, resulting in a number of fatalities due to asphyxiation.

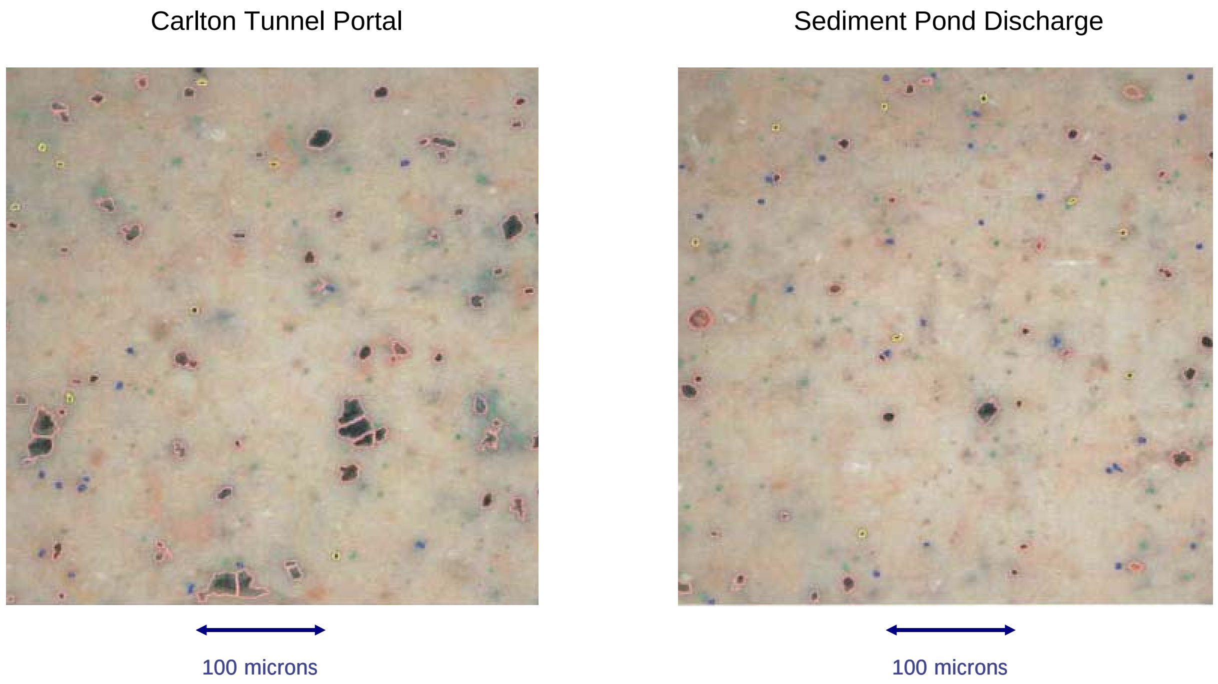

Figure 1. Optical micrographs of sediment samples

The dimensions of each of the grains on the magnified digital image were measured using PAX-it™ Image Analysis software. Visual grainsize discrimination was achieved down to a minimum dimension of 1 micron; smaller grainsize distributions were determined by extrapolation. The distributions of the effective diameters of the grains are shown in the upper traces of Figure 2. The particles display the following characteristics:

1. The sediment particles are approximately spherical.
2. The sediments are very fine; more than 50% of the \particles is less than 3 microns in diameter.
3. The particulates at the portal are slightly coarser than at the pond discharge.

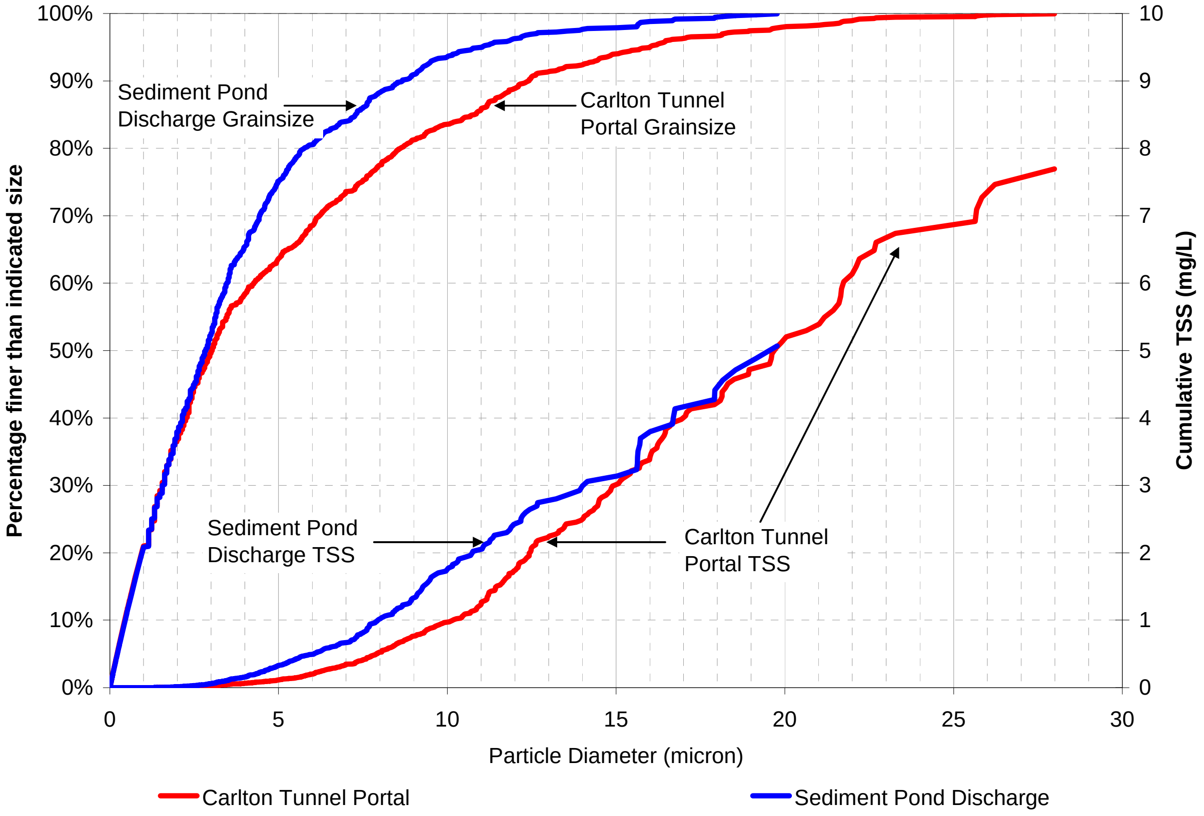

Figure 2. Sediment Particle Grainsize and Mass Distribution

Mass

The particulate mass distribution has been computed assuming spherical particles, and a uniform density. The results are presented in Figure 2 (lower curves), and indicate the following:

1. Most of the mass is contained in the coarsest particles: 50% of the mass is contained in the coarsest 5% of the particles, and 99% of the mass is contained in the coarser half of the particles.
2. The mass distributions are similar for the input and the output, except that input particles coarser than 20 microns have been removed by sedimentation by the time the water discharges.
3. The mass that has been removed between the Carlton Tunnel Portal and the Sediment Pond Discharge is primarily the result of the sedimentation of the coarser particles that were in the Portal discharge.

In summary, the sediment micrographs support the two-part sediment genesis model: sediment being imported from the Carlton Tunnel flow, with additional sediment being generated by precipitation in the ponds due to carbon dioxide outgassing.

Particle Density

The density of the particles that precipitate is critical to the rate at which they settle, and hence to the effectiveness of the sedimentation ponds in removing them from the flowing water. In the event that the particles are solid (i.e. zero porosity) calcite, the density of the particles would be 2.710 tonne/m^3. However, it is likely that the calcite particles form as a lattice, with high porosity and low relative density.

The support for this observation is derived from sampling of calcium carbonate crystal growth on the base of the ponds. Almost the entire sediment mass in the ponds was found to be made up of an openwork calcium carbonate lattice. Specimens of the lattice were recovered (Figure 3), and were found to have an effective porosity of 94%, and a dry density of 0.102 tonne/m^3.

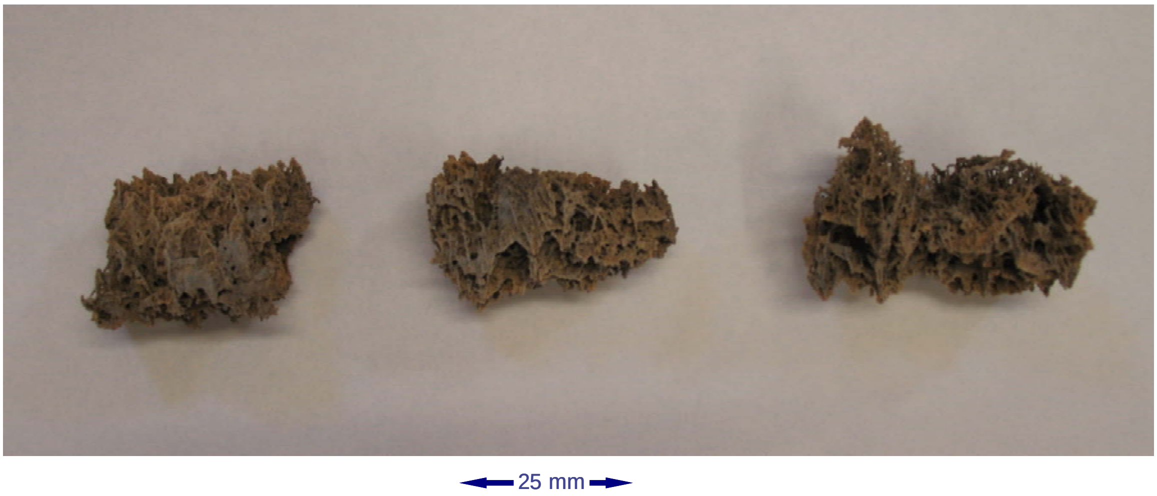

Figure 3. Calcite Lattice Growth in Carlton Tunnel Sediment Ponds

4. SEDIMENTATION BEHAVIOR

Model

The behavior of the sedimentation ponds in removing the fine calcium carbonate precipitates has been modeled, using the observed behavior of the ponds prior to modification as the calibration point. A model of one-dimensional sedimentation was created, which used the following algorithm:

1. The (978) particles that were measured in the Carlton Tunnel Portal were used as the initial particle set.
2. The particles were introduced to the pond system at randomly determined depths in the pond, simulating the actual situation.
3. The particles were allowed to grow in size, based on precipitation of calcite at a selected constant rate per unit area of the particle per unit time.
4. The particles were allowed to settle in the pond system over time, based on Stokes' Law (Streeter, 1962):

$$V = \frac{2gr^2}{9\mu}\left(\rho_1 - \rho_2\right)$$

where: V = settling velocity [LT^{-1}]
r = equivalent radius of sphere [L]
g = acceleration due to gravity [LT^{-2}]
ρ_1 = density of particle [ML^{-3}]
ρ_2 = density of fluid [ML^{-3}]
μ = viscosity of medium [$ML^{-1}T^{-1}$]

5. When any particle reached the base of the pond, it was removed, and replaced with an infinitesimal seed particle introduced at a random depth in the pond.
6. The concentration of TSS in the pond was computed at each time step by dividing the total mass of the particles in the pond by the volume of water in which they were suspended.

Calibration

The model was calibrated against the observed conditions during the testing of the TSS in the input and output during the testing period when the sediment testing was performed (June 17, 2007). The calibration points were:

Table 5. Calibration Targets for Carlton Tunnel Sediment Pond Model

Parameter	Units	Inlet	Outlet
Flow Rate	m3/day	8,722	8,722
Volume of Ponds	m3	0	3,170
Pond Depth	m	1.5	1.5
Retention Time	day	0	0.36
TSS Concentration	mg/L	7.7	5.1

The results of the calibration were as follows:

1. Particle growth rate is slow: The best calibration was achieved for a calcite deposition rate of 1 micron/day (1.1×10^{-11} $m^3/m^2/sec$). The model would not calibrate with a growth rate greater than 5 microns per day (6×10^{-11} $m^3/m^2/sec$).
2. Particle effective density is low, and porosity is high: the best calibration available was for a porosity of 92.5% and a dry particle density of 0.128 tonne/m^3, very similar to the porosity and density observed in the sediment lattice forming in the ponds.

Behavior

The behavior of the sediment ponds was determined using the calibrated model, by evaluating the reduction in TSS achieved by the ponds as a function of pond retention time and pond depth. The results are presented in Figure 4. The results indicate that control of chemical sediment is strongly a function of the retention time and the pond depth. The results presented in Figure 4 are expected to be generally applicable to all NARD discharges that are saturated with respect to calcite.

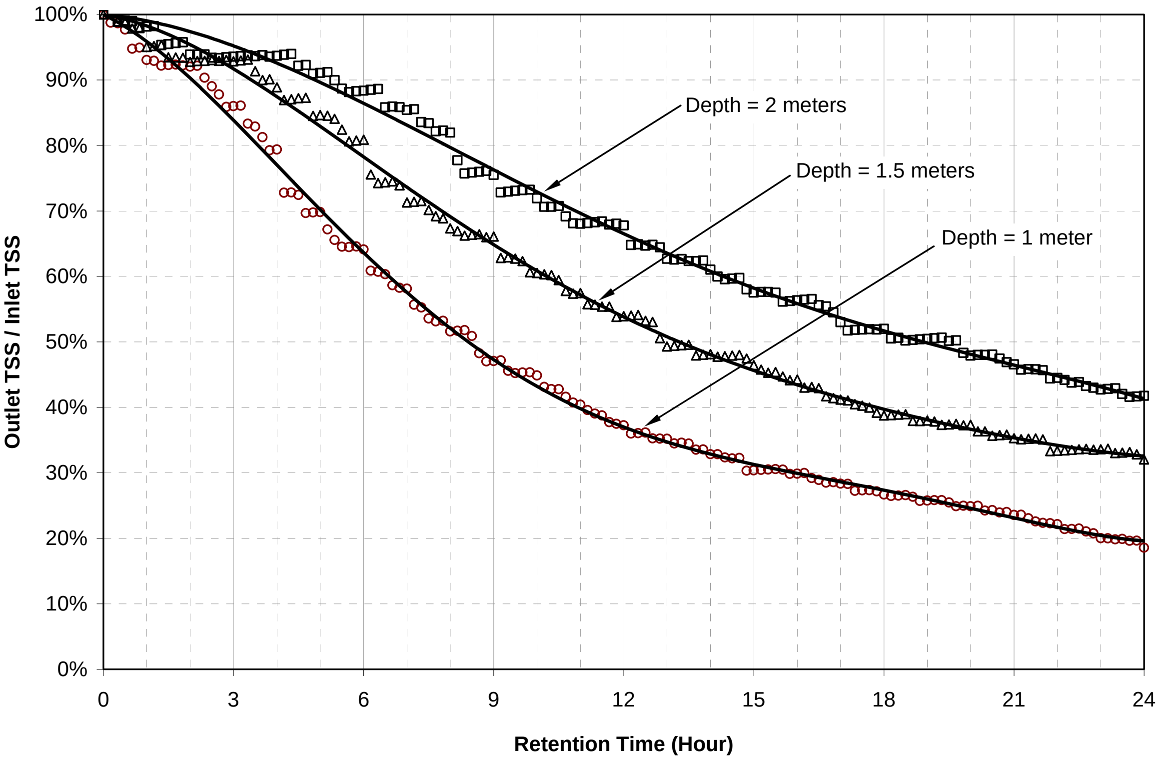

Figure 4. Relative TSS Concentration for NARD Sedimentation Ponds

5. APPLICATION

Pond Modification

Based on this evaluation, the sediment pond system at the Carlton Tunnel portal has been expanded by the addition of a sixth shallow pond, sediment cleaned out, and baffles modified to minimize flow velocity and turbulence. The specifications of the pond system before and after the modification are presented in Table 6.

Table 6. Carlton Tunnel Sediment Pond Expansion Specifications

Parameter	Units	Inlet Water	Prior Pond System	Expanded Pond System
Flow rate through ponds	m3/day	8,722	8,722	8,722
Volume of Ponds	m3	0	3,170	5,721
Retention time	hour	0	8.6	15.8
Test Concentration	mg/L	7.7	5.1	3.3*
Output TSS / Input TSS	ratio	100%	66%	43%*

* Anticipated Performance

Performance

The Carlton Tunnel Sedimentation pond system was upgraded in January of 2008, and has operated continuously since. The performance of the pond system is summarized for the period before and after the modification in Table 7.

Table 7. TSS Performance of Carlton Tunnel Sediment Ponds

Location	Average TSS (mg/L)	Peak TSS (mg/L)	TSS Load (tonne/yr)
Carlton Tunnel Portal	12.0	330	63
Pre-Modification Discharge	10.4	52	17
Post-Modification Discharge	<10	11	<16

The ponds have reduced the TSS concentration at discharge to below detection (10 mg/L) on all but one occasion since the modification; the exception was a reported detection of 11 mg/L in the high flow spring period of 2009.

6. CONCLUSIONS

The conclusions of the Carlton Tunnel Sediment Pond study are:

1. Control of very fine chemically precipitated suspended solids in NARD discharge in the Cripple Creek Mining District has been achieved using sedimentation ponds.
2. Sediment pond performance has been explained and quantified using detailed observation of sediment, flow, solid-phase chemistry, mineralogy, liquid phase chemistry, and sedimentation theory.
3. The sedimentation rate of chemical precipitates of calcite is approximately a factor of 20 lower than would be expected if the particles were solid calcite; they are in fact made up of a very sparse crystalline lattice, with high flow resistance and low terminal velocity in water.
4. Control of sediment precipitated from flows containing NARD is strongly dependent on long retention times and shallow ponds with limited turbulence.
5. The design approach to sediments generated from NARD has been demonstrated by the successful expansion and modification of the Carlton Tunnel Sediment Pond system.

7. REFERENCES

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