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Sludge Disposal in Mine Workings at Cape Breton Development Corporation

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ABSTRACT

The Cape Breton Development Corporation was a coal mining operation in the province of Nova Scotia, Canada. Coal mining began there in 1673 and final operations were discontinued in 1999. As underground mine workings filled with water following closure, pumping was required to prevent an overflow of acidic metal-laden mine drainage into the Atlantic Ocean. It was determined that lime treatment may be necessary prior to discharging. With iron concentrations in the mine water in the order of 500 mg/L, sludge generation was identified as an important factor. Pilot treatment tests completed jointly by EnvirAubé and CANMET (Natural Resources Canada) generated sludge for use in further testing. Some of this sludge was used to assess the effects of disposal in the underground mine workings. Different rates of sludge addition were simulated and both the solids and liquids were analysed. Results show that some metals can dissolve at lower addition rates but that dissolved iron and aluminium concentrations decrease with sludge addition. As iron is the primary metal of concern, both in the sludge and the mine workings, it was determined that disposing the sludge underground at this site was a viable alternative to surface disposal. This disposal option has since been applied at the site and no detrimental effects have been reported. In this paper, the chemistry of both the mine drainage and the sludge is discussed and the benefits of returning the sludge underground are explained. Possible circumstances why this option may not be viable at other sites are also presented.

INTRODUCTION

This paper presents the result of an evaluation on sludge disposal into abandoned mine workings. The sludge is from lime treatment of acid mine drainage from the 1B System of Cape Breton Development Corporation (CBDC). CBDC exploited coal seams in the province of Nova Scotia, a large peninsula on the Eastern Coast of Canada. The first historical mention of mining here was by the French army in 1673. Exporting mined coal to Boston was reported in 1724. The seams were mined mostly by private companies well into the 20th century. CBDC, a Canadian crown corporation, was formed in 1967 as profitability of the mines was diminishing. An increase in coal prices raised profitability from the mid 1970's into the 1980's until gradual closure was initiated in the 1990's. The last mine ended operation in 1999.

This study was initiated as sludge disposal into the mine workings was considered to be a probable scenario for a treatment plant planned for construction at the time of the investigation. This plant was to be commissioned in 2003 while the tests reported here were completed in December 2002. The current situation for CBDC is discussed further in the paper. The objective of the tests presented here was to determine whether the sludge could negatively impact the mine water and increase the dissolved metal concentrations in this acid mine drainage (AMD). The mine water is expected to improve with time as fresh water is flushed through the mine workings. An increase in metal concentrations due to sludge addition would increase the amount of time required for the mine waters to meet discharge criteria without treatment. Dissolution of the heavy metal component of the sludge would also result in re-treatment of these metals and increased operating costs, due to higher lime consumption.

Sludge Sources

The sludge used for testing was produced by neutralising AMD from the 1B system of the CBDC mine workings. The AMD in this system represents both the feed to the planned treatment system as well as the ultimate site of sludge disposal, if it was to be placed in the mine workings. The AMD had a pH of less than 3 with Fe concentrations in the order of 400 mg/L. Other major components include sulphur (as sulphate), aluminium, calcium, and magnesium. The physico-chemical data of the raw water is shown in tables 1 and 2, along with the results. The sludge was produced by neutralising this AMD using two separate methods as two different treatment systems were under consideration for treatment. One considered treatment system was a high-density sludge plant (HDS) and the other was an in-line neutralisation system with a settling pond for solid-liquid separation. The HDS plant would have included a clarifier, recycle, and aerated reactor for oxidation of ferrous iron to ferric iron. Aeration is a standard practice in these plants as ferric hydroxides are more stable during long-term storage of treatment sludge. The low-density system would not have included aeration and would therefore have produced a ferrous sludge. The designations of the two sludge types are therefore HDS Sludge and Ferrous Sludge.

HDS Sludge

The HDS treatment process is shown in Figure 1. The AMD used to feed the pilot plant was transported from Cape Breton to the CANMET laboratories in Ottawa (Aubé et al., 2002). The AMD was fed to the Lime Reactor where it was neutralised to pH 9.5 with a mixture of lime and recycled sludge from the Lime/Sludge Mix Tank. The overflow from this reactor was fed to a small flocculant tank for contact with an anionic polymer to agglomerate the particles and improve solid/liquid separation in the clarifier. The clarifier overflow was a clear effluent, which met all requirements for discharge. The clarifier underflow sludge is mostly recycled to the Lime/Sludge Mix Tank and partially bled to maintain a constant inventory in the process. During testing, this process produced sludge with more than 25% solids, but the sludge chosen for the disposal tests contained approximately 10% solids.

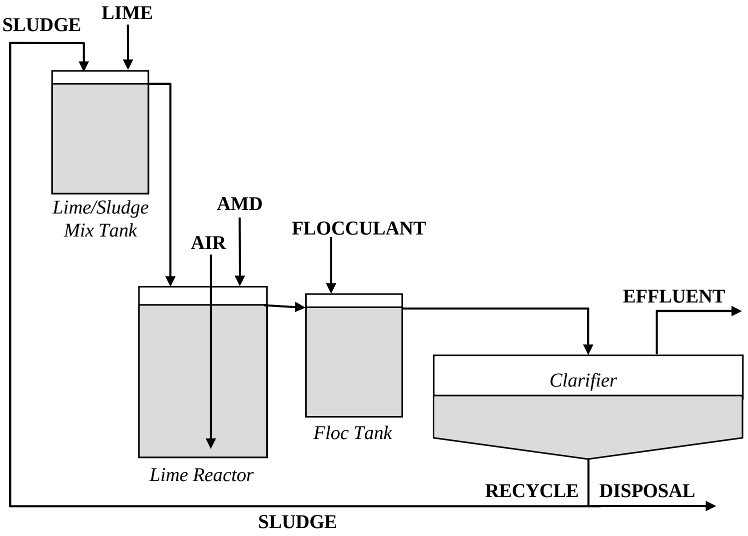

Figure 1: High-Density Sludge Process as Applied on the CBDC AMD (Aubé, 1999a)

Ferrous Sludge

The Ferrous Sludge was produced by taking a large sample of CBDC AMD and neutralising it to pH 9.5 quickly and without aeration. The solids were allowed to settle. The supernatant was then decanted and the sludge kept for the following tests. This represents a typical process of rapid mixing and decanting in a settling pond. To prevent the sludge from oxidizing, this sludge was produced shortly prior to the addition tests.

Test Basis

The methodology is based on the fact that the sludge will descend into the workings and mix with the mine water during this descent. The sludge itself will generally be contacted with a mixture of its' own pore water (essentially treated water) and the mine water, as the pore water will be at least partially entrained with the sludge solids.

These tests simulate only this descent and not the long-term effects of contact with mine waters once settled into the bottom of the shaft or other mine workings. For a detailed evaluation of the long-term effects, extended tests would be required. This would require at least six months to one year and a more elaborate laboratory design than that completed here.

Methodology

The exact solid content of both sludge samples is determined gravimetrically. Twelve volumes of 500 mL of AMD are collected from a large well-mixed sample. All twelve tests are completed on the same day, using the same raw water sample. Before starting the tests, pH, redox, conductivity, and dissolved oxygen content are measured. For each sample:

1. Mix the appropriate volume of sludge to attain the target mass of solids (g of solids) to be added (see results in Table 1).
2. Mix each sample and tumble for 16 hrs.
3. After 15 hours, measure pH, redox, conductivity, DO of slurry and take note.
4. Filter the entire sample using a pre-weighed, pre-dried filter paper (Whatman #3).
5. Send the filtrate for analysis for the following elements: Al, Ca, Cd, Cu, Co, Fe, Na, Ni, Mg, Mn, Pb, S, and Zn.
6. Dry the filter and solids to constant weight and determine the exact mass of suspended solids in the entire volume of slurry
7. When a sufficient mass of solids is collected, scrape the sludge off the filter and send the dried solids for analysis for the same elements as above
8. Simultaneously send a sample of dried, unused sludge solids for analysis (this is the control sludge).

Table 1: Physico-Chemical Results

Sample name	Added Sludge (g)	Added solids (g)	**Added solids (g/L)**	Measured solids (g)	pH	Eh (mv)	Conductivity (ms)	D.O (ppm)
Raw AMD (initial conditions)					**2.79**	**338**	**6.91**	**3.6**
Test 1 Sludge (9.73% solids)								
T1-1 control	0.0	0.0	**0.0**	0.02	2.95	405	6.43	5.0
T1-2	5.2	0.5	**1.0**	0.65	3.93	270	6.12	5.2
T1-3	10.4	1.0	**2.0**	1.42	4.24	229	6.07	5.9
T1-4	20.6	2.0	**4.0**	2.99	4.85	170	6.02	6.3
T1-6 duplicate(T1-4)	20.6	2.0	**4.0**	3.06	4.92	168	5.99	6.4
T1-5	51.6	5.0	**10.0**	7.32	6.70	150	5.93	5.9
Ferrous Sludge (3.52% solids)								
T2-1 control	0.0	0.0	**0.0**	0.00	2.94	401	6.40	5.7
T2-2	14.9	0.5	**1.1**	0.35	4.23	235	5.88	5.6
T2-3	29.4	1.0	**2.1**	0.85	4.43	204	5.89	5.5
T2-4	58.9	2.1	**4.1**	1.74	5.15	141	5.85	5.7
T2-6 duplicate (T2-4)	58.9	2.1	**4.1**	1.70	5.17	134	5.73	5.7
T2-5	147.4	5.2	**10.4**	4.55	6.77	137	5.61	3.4

Results

Detailed results of the tests are given in Tables 1 through 3. The first column in Table 1 shows the weight of wet sludge added, the second shows the calculated weight of solids, and the third (in bold) shows the corresponding concentration of solids added (in g/L). The "Measured Solids" column represents the amount of solids collected on the filter at the end of the tests. The pH, Eh, conductivity, and dissolved oxygen were all measured at the end of the tests. Note that tests T1-6 and T2-6 are shown out of order in the table – this was done because those tests are duplicates of tests T1-4 and T2-4, respectively. This same sequence is shown in tables 2 and 3.

Table 2 shows the analytical results of the water after it was filtered through a 6 µm filter. This water was clear and essentially free of even colloidal particles. Even though some particles may have been smaller than 6 µm, the coagulation of the precipitates on the paper results in essentially 100% capture. The sludge solids chemistry in Table 3 was taken from the dried solids collected on these filters.

Table 2: Chemistry of Filtered Solutions

Sample	**Filtrate Results**												
	Al	Ca	Cd	Co	Cu	Fe	Mg	Mn	Na	Ni	Pb	S	Zn
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Raw AMD	**184.2**	**425.2**	**5.6**	**1.6**	**0.016**	**396**	**552**	**104**	**317**	**3.5**	**8.44**	**1981**	**4.40**
HDS Sludge													
T1-1	180.7	414.3	5.5	1.6	0.023	389	547	102	316	3.5	11.40	1949	4.33
T1-2	177.3	450.5	5.6	1.8	0.015	293	606	116	314	3.7	1.50	1931	4.65
T1-3	117.4	456.6	6.3	2.0	<0.012	293	657	133	313	3.9	0.87	1932	4.87
T1-4	5.7	440.8	6.7	2.0	<0.012	248	744	161	320	3.9	0.46	1818	3.90
T1-6	5.1	452.5	6.2	2.0	<0.012	248	748	165	315	4.0	0.49	1833	3.83
T1-5	<0.29	443.5	1.0	<0.16	<0.012	<0.82	824	163	326	<0.91	0.26	1724	0.03
Ferrous Sludge													
T2-1	181.1	410.0	5.3	1.6	0.018	382	549	102	318	3.5	10.10	1954	4.27
T2-2	157.0	437.5	5.9	1.8	0.018	348	607	119	314	3.9	3.44	1919	4.95
T2-3	59.1	435.7	6.6	2.1	<0.012	379	668	136	312	4.2	1.86	1880	5.40
T2-4	1.7	462.8	7.9	2.0	<0.012	273	720	170	282	4.2	0.49	1812	2.93
T2-6	1.5	449.1	7.6	2.0	<0.012	262	737	167	314	4.2	0.64	1825	2.93
T2-5	<0.29	453.4	1.7	<0.16	<0.012	<0.82	798	154	318	<0.19	0.20	1715	<0.027

Table 3: Chemistry of Sludge Solids

Sample	**Results from solids**												
	Al (%)	Ca (%)	Cd (%)	Co (%)	Cu (%)	Fe (%)	Mg (%)	Mn (%)	Na (%)	Ni (%)	Pb (%)	S (%)	Zn (%)
HDS Sludge	**2.31**	**16.12**	**0.0003**	**0.0197**	**0.0008**	**6.55**	**5.67**	**1.57**	**0.198**	**0.042**	**<0.0029**	**12.7**	**0.051**
T1-1													
T1-2													
T1-3	4.31	12.73	0.0003	0.0059	0.0012	9.46	1.27	0.20	0.066	0.021	<0.0029	13.1	0.025
T1-4	4.92	12.13	0.0002	0.0093	0.0011	7.93	1.59	0.22	0.063	0.027	<0.0029	12.9	0.050
T1-6	4.84	12.61	0.0003	0.0096	0.0011	7.98	1.60	0.22	0.060	0.027	<0.0029	12.9	0.051
T1-5	3.22	13.58	0.0004	0.0284	0.0003	8.56	3.11	0.86	0.065	0.060	0.003	12.4	0.075
Ferrous Sludge	**4.32**	**7.91**	**0.0002**	**0.0331**	**0.0003**	**9.16**	**7.86**	**2.39**	**0.786**	**0.074**	**0.003**	**8.4**	**0.094**
T2-1													
T2-2													
T2-3	11.49	5.57	0.0002	0.0051	0.0019	8.94	0.44	0.05	0.116	0.028	<0.0030	10.4	0.022
T2-4	9.96	5.15	0.0003	0.0220	0.0037	12.92	2.12	0.17	0.138	0.052	0.003	9.1	0.140
T2-6	9.80	5.27	0.0003	0.0214	0.0020	12.93	2.02	0.16	0.139	0.051	0.003	9.5	0.137
T2-5	6.55	6.20	0.0006	0.0544	0.0014	14.53	4.55	1.52	0.172	0.120	0.003	8.4	0.152

The most pertinent results are illustrated in the following figures for a clear understanding of the measured effects. Figure 2 shows the pH effects of sludge addition. The x-axis shows the added mass of sludge as dry solids and the y-axis shows the resulting pH. It is clear that partial dissolution of sludge is occurring for the pH to increase in the manner shown in this figure. As explained further, Mg and Ca compounds appear to be responsible for the pH increase.

Figure 3 shows the analytical results of important elements for the HDS sludge and the Ferrous Sludge, respectively. The x-axis shows the added mass of sludge as dry solids and the y-axis shows the resulting concentration of the four species illustrated: Al, Fe, Mg, and

Ca. Note that, though it isn’t easily differentiated, there are two points at the addition rate of 4 g/L – this shows that the repeatability is excellent.

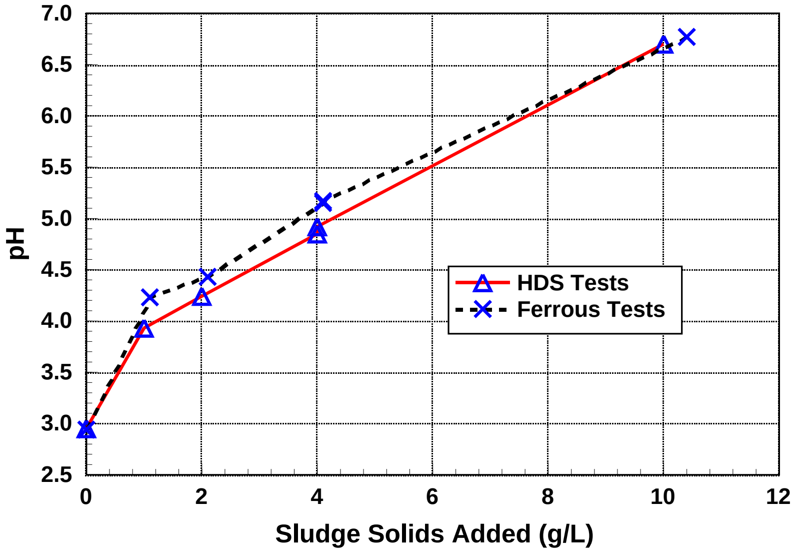

Figure 2: Effects of Sludge Addition on pH

The zero point in Figure 3 is a control test, showing the analysis of a sample of raw water tumbled at the same time as the test samples. The analytical results were very similar for both controls and the original sample of AMD not tumbled. This proves consistency in both the analyses and the test conditions.

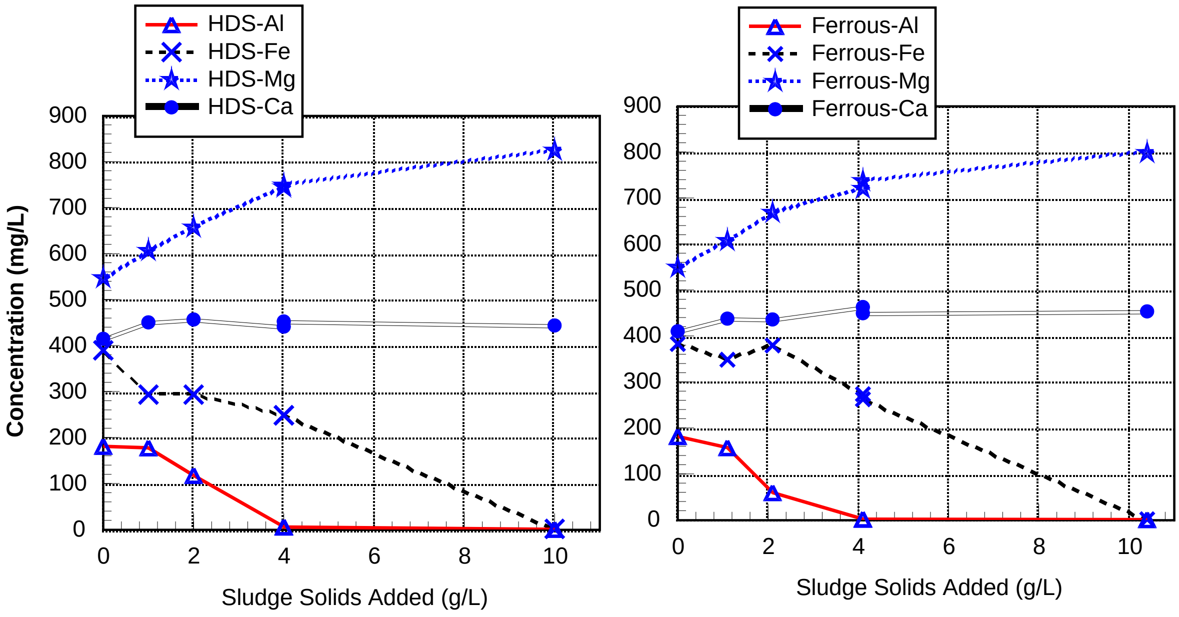

Figure 3: Concentration Trends of Major Cations

Figure 3 shows that the Fe and Al concentrations both decrease as sludge is added. At 2 g/L for the ferrous tests, the decrease of Fe was minimal, but there never was an increase in concentration. When sufficient sludge is added, the concentrations of both these metals decreased to below 1 mg/L. The increase in Mg concentration suggests that the dissolution of a Mg composite from sludge, most likely magnesium hydroxide, is responsible for the pH increase. This compound would have precipitated in treatment due to the high control pH of 9.5. The Ca concentrations do not vary much, suggesting that this element is not active during the test. This suggestion is countered by the sulphur results, as shown in Figure 4.

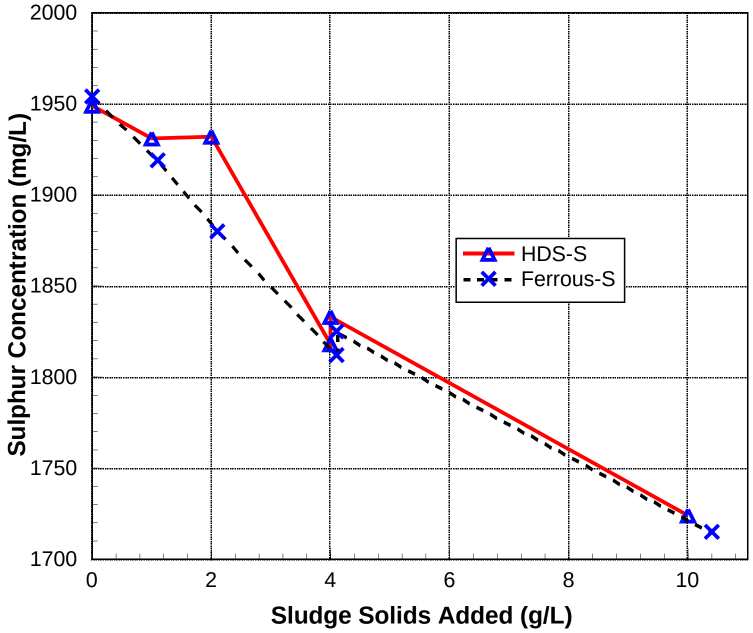

Figure 4: Sulphur Analyses of Filtered Test Waters

Only sulphur was analysed in the samples as it had already been determined that all sulphur was in sulphate form (Aubé et al., 2002). These results therefore show that sulphate was precipitating, suggesting that gypsum was forming during the test. As the Ca concentrations remained relatively stable, this suggests that some Ca, probably in the form of calcium carbonate, was dissolving from the sludge then re-precipitating with sulphate to form gypsum. This is corroborated by a decrease in Ca concentration of the solids (Table 3), as Ca forms a much larger fraction of calcite than of gypsum.

Figure 5 shows that some metal concentrations increase at low sludge addition rates prior to decreasing at higher addition rates. These metals (Cd, Ni, and Zn) are typically mobile at neutral or acid pH. All three of these metals are regulated for liquid discharge in Canada. Note that the concentration increase is not very significant as none of the components exceeded 8 mg/L. The results also show that there is a greater increase in concentration when Ferrous Sludge is added. The maximum attained for each of these components is on average 11% higher when adding Ferrous Sludge as opposed to HDS sludge.

The manganese (Mn) trends are not plotted, but the analyses showed that dissolution continues even into the high sludge ratios (Table 2). Cobalt (Co) concentrations also increase although only marginally. Copper (Cu) and lead (Pb) concentrations decrease in all but the very lowest sludge addition rates.

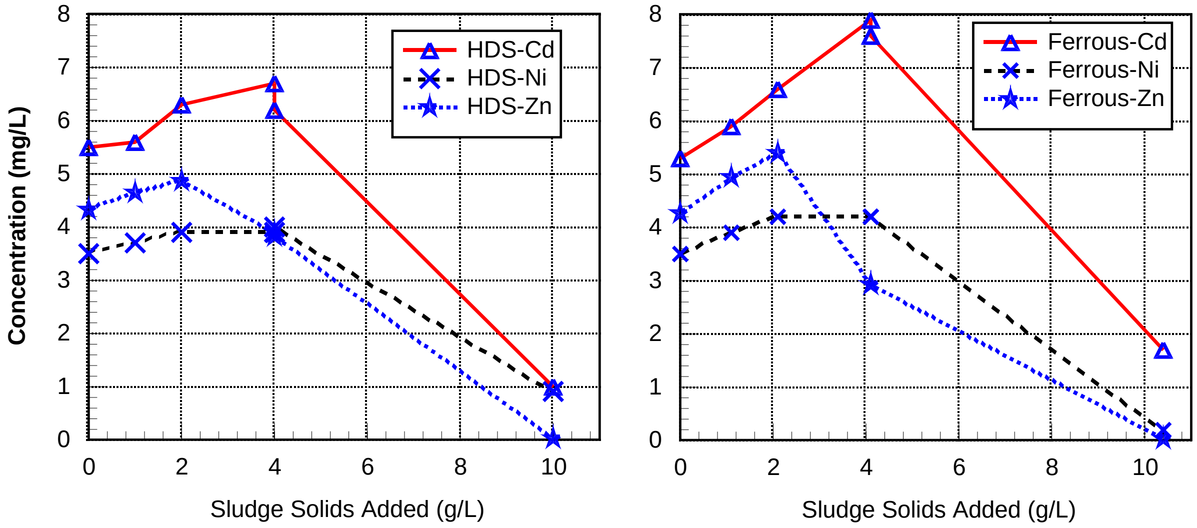

Figure 5: Trends for Minor Heavy Metals

As discussed, solids analyses given in Table 3 show a distinct reduction in Mg content, thus confirming the observations from the liquids. A mineralogical analysis would be required to fully understand the chemical alterations of the sludge solids. As mineralogy is expensive and the solution chemistry is of greater importance, this additional analysis was not recommended.

Conclusions for CBDC

Test results show that an overall mine water improvement is expected when putting sludge back into the mine workings. The main metals being treated, iron and aluminium, decrease at every sludge addition rate. This indication is clear with both sludge types, but only a minor improvement is shown with the Ferrous Sludge at low addition rates.

The results are less positive for heavy metals Cd, Ni, and Zn. There may be a partial dissolution or desorption of these metals as the sludge settles down to the bottom of the mine workings. Tests also show that at high sludge addition rates, all results are very positive. This suggests that the sludge will not dissolve continuously once it is settled to the bottom. This is true even of the more mobile heavy metals. This theory could be tested with more long-term trials that allow the sludge to stay in contact with AMD for months.

Current Situation at CBDC

Given the results of the investigation, CBDC decided to go ahead with underground sludge disposal. The treatment system with a settling pond was constructed and operated for one season in 2003. Sludge was returned to the mine workings and the feed to the plant was regularly monitored. No negative effect was determined and a small improvement in AMD quality was measured during treatment. Treatment is not currently required at the 1B site as the groundwater recharge to the underground workings is intercepted and released as clean water. The treatment plant is being maintained in good order as this fresh water intercept may not be a permanent option. If or when the treatment system is re-started, the sludge will once again be disposed of underground.

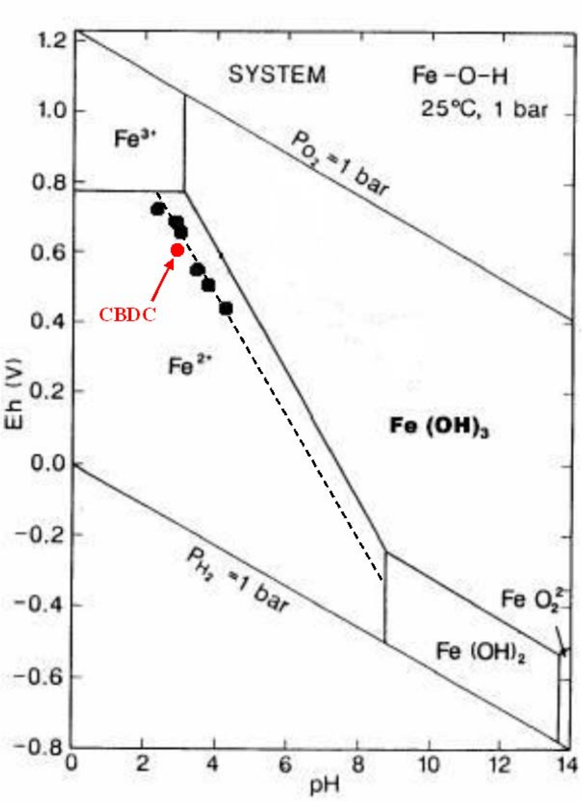

Figure 6: Pourbaix Diagram for Iron (Brookins, 1988)

Mechanisms

The obvious question when looking at these results is “Why does the sludge not dissolve?” This is the generally expected result when contacting metal hydroxides with a solution at a pH of less than 3. The explanation lies in the iron chemistry and the reduction-oxidation potential (redox or Eh).

Figure 6 shows the Pourbaix Diagram for the iron system (Brookins, 1988). The dots added to the diagram represent the conditions measured for AMD from several different sources (Aubé, 1999b). The dashed line represents the approximate equilibrium line for iron concentrations in the order of 100 mg/L (the original diagram was developed for 10^{-6} mol/L or about 0.06 mg/L).

The iron hydroxides do not dissolve simply because the AMD is already at equilibrium with the iron system. In fact, any hydroxides that dissolve would increase the pH and cause precipitation of iron. This is what occurred during the tests as the magnesium and calcium components dissolved, increased pH, and decreased the concentration of iron in the AMD through precipitation of iron hydroxides.

Note that the dot representing the CBDC raw water appears to be in the Fe^{2+} stability field. This is due to the fact that the concentration of iron in the raw is actually 396 mg/L while the diagram was originally developed for a concentration of 0.06 mg/L. As previously mentioned, the dotted line represents the equilibrium line between Fe^{2+} and $Fe(OH)_3$ for an iron concentration of about 100 mg/L. If a third equilibrium line were added for a concentration of 396 mg/L, the CBDC dot would land on this line. This means that the CBDC AMD was actually in equilibrium between ferrous iron and ferric hydroxide prior to addition of sludge, which is why the sludge does not dissolve.

Implications to Other Sites

Test results indicate that a mine water improvement is expected when returning treatment sludge into mine workings at CBDC. Although the actual treatment plant operated for only one year, full-scale results seem to corroborate those found here. This improvement is expected as the CBDC sludge contains mostly gypsum, iron, and aluminium hydroxides, and very low concentrations of mobile heavy metals.

Other sites that contain high fractions of cadmium, nickel, and zinc may not find underground sludge disposal economical. Too much re-dissolution would result in re-treatment and increased lime consumption unless the sludge contains high alkalinity in the form of calcium and magnesium carbonates or hydroxides. On the other hand, sites with high iron, aluminium, and/or copper may find this option attractive. Site-specific testing would need to be completed to evaluate the potential at other operations.

Further Testing

These tests only show the expected result of the short-term sludge contact with the mine water. For a long-term evaluation of sludge behaviour, more intricate trials would need to be designed.

Acknowledgments

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