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Geophysical Tools to Delineate ARD and Sulfate in Groundwater at a Former Sulfuric Acid Plant

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ABSTRACT

During the operation of a former sulfuric acid plant located in Canada, sulfide minerals (e.g. pyrite, chalcopyrite), tailings and sulfuric acid were stockpiled on-site and imparted acidic solutions with high sulfate and metal concentrations to the subsurface. The topography is variable, from bedrock outcrops to 20 meters of overburden as clay, sand and gravel. Bedrock controls surface water and groundwater flows which include surface drainage ditches, marshes, an unconfined aquifer, and flow through fractured bedrock. After plant closure, historic remediation efforts included the removal of stockpiles, tailings and visually contaminated soil to the water table, lime amendment of soil at the water table, and importation of clean fill, which resulted in chemically heterogeneous subsurface conditions across the site. Most primary sulfide materials were removed except for sporadic zones that have the potential to generate acid rock drainage (ARD). Surface water and groundwater monitoring confirms near-neutral pH conditions with elevated concentrations of sulfate and metals at various locations throughout the site. Recent studies to delineate groundwater contamination and areas of active ARD included targeted soil and water sampling at select locations, which confirmed the heterogeneity of subsurface conditions. An electromagnetic geophysical survey was completed to minimize uncertainty and validate the results of previous investigations. It identified two zones of high conductivity, coinciding with high sulfate concentrations in groundwater and in static leaching tests on soil. Static test results confirm that soil collected from underneath the location of a former stockpile was depleted in buffering capacity, likely consumed by the infiltration of acidic drainage into the subsurface during plant operations. The results of the geophysical survey proved to be a cost-effective and efficient method to delineate the source and pathway of high sulfate in groundwater and thus demonstrated usefulness in assessing the environmental impact of high sulfide-containing mine wastes on groundwater quality.

Keywords: ARD, sulfate, conductivity, groundwater, geophysics

INTRODUCTION

The site is located on the north shore of Lake Huron (Aird Bay) in northern Ontario, Canada, near the community of Cutler. The 40 hectare site is the former location of the Cutler Acid Plant, a sulfuric acid production plant that was in operation from approximately 1956 to 1963. Iron sulfide minerals including pyrite and chalcopyrite were roasted to produce sulfuric acid, yielding a purple-red iron oxide/oxyhydroxide waste by-product. Historic facilities and structures on-site included the acid plant, pyrite unloading areas, sulfur stockpiles, acid storage tanks, fuel oil tanks, and a tailings storage facility and tailings pond. Site facilities are shown in FIGURE 1.

Figure 1 Site map showing operational facilities and site features

Plant operations resulted in subsurface contamination including the presence of sulfide minerals and acidic conditions in soil and elevated levels of sulfate and metals (Al, As, Cd, Co, Cr, Cu, Fe, Hg, Pb, Mn, Mo, Ni, Se, U, Zn) in groundwater and surface water . These contaminants were most likely introduced to the subsurface through sulfuric acid spills, leaking from acid storage tanks, and oxidation of sulfide minerals in the former stockpile areas and tailings pond.

In 1969, the acid plant and buildings on-site were demolished and debris was distributed across the site. Since then, the site has undergone several studies and remedial projects to address the presence of demolition debris and waste materials, as well as contamination related to the operation of the acid plant. Remedial efforts consisted of the excavation of building debris and visibly contaminated soils, after which both lime and clean imported fill was added in an effort to mitigate acidic conditions. These remedial efforts were limited to the depth of the fluctuating water table, leading to heterogeneous subsurface conditions observed presently on-site.

Past remediation efforts were not completely effective at removing all of the contamination associated with the former acid plant as localized areas of ARD potential in soil, high sulfate concentrations in groundwater, and metal concentrations in soil and groundwater are still observed.

Various subsurface investigations have been completed in an attempt to delineate areas of contaminated soil in support of environmental site assessments (ESA), risk assessments, and remedial options analysis. Soil samples were recovered from test pits and boreholes to assess ARD and metal leaching potential through various static and kinetic test methods, and surface water and groundwater was also analyzed. Results of the various subsurface investigations confirmed the heterogeneous nature of the soil across the site. Local areas of ARD in the soil were identified, however it appears to be buffered locally as evidenced by neutral pH values in tested groundwater and surface water.

Due to heterogeneous conditions on site, a geophysical survey was conducted in lieu of an extensive drilling program in order to more efficiently delineate areas of subsurface contamination related to ARD and metal leaching, specifically those associated with historical plant operations and tailings storage. An electromagnetic geophysical survey well suited to mapping the apparent conductivity of the ground, including shallow buried metal objects, was completed on portions of the site. This approach has been used successfully at various other active and closed mine sites as documented by Gore & Olyphant (2010) and Schutts & Nicols (1991), Campbell & Fitterman (2000), and Paterson (1997). Areas selected for the geophysical survey were identified based on observed contamination and/or locations of historical operational infrastructure. The geophysical survey successfully identified areas of confirmed high sulfate in groundwater and was instrumental in delineating the probable sources and flow of high-sulfate groundwater on site.

SITE CONDITIONS

The site is located in an environment typical of the Canadian Shield with shallow bedrock, frequent outcrops, and poor drainage resulting in standing water. Undulating bedrock ranges from 16.5 meters below ground surface (mbgs) to surface outcropping. Three notable outcrops are present on site and control groundwater flow, including 1) the east shoreline bedrock outcrop, a large outcrop located at the shore of Aird Bay in the center of the site; 2) the west shoreline bedrock outcrop, a long and narrow outcrop on the west side of the site and on the shore of Aird Bay, and 3) the bedrock outcrop, a long and narrow outcrop in the southeast portion of the site perpendicular to the lake shore.

A large marsh is situated on the west boundary of the site and six streams and/or constructed ditches flow across the site and discharge into Aird Bay. The water table is shallow throughout most of the site; groundwater flows through both an unconfined aquifer and within fractured bedrock. Groundwater generally flows from northeast to southwest and discharges to Aird Bay between the west and east shoreline outcrops, as evidenced by downward vertical hydraulic gradients observed within all multi-level monitoring wells in this area. An area of up-ward groundwater flow (seep) exists between this zone of discharge to the lake and the adjacent marsh.

Overburden ranges from relatively coarse grained sand to a fine grained soil consisting of sand, silty sand, silt, and clay in varying proportions. Within the upper coarse grained layer, fill materials are largely comprised of sand similar in nature to that of native sand. Differentiation between native sand and fill materials is challenging unless obvious markers of fill material, such as an organic layer or anthropogenic debris, are present. Based on anecdotal information, it is understood that fill materials of up to a thickness of two meters (m) have been placed over portions of the site. Field programs carried out to date have not identified any visible signs of lime in the soil.

Previous ESAs document metal concentrations above applicable provincial and federal guidelines in soil, groundwater, and surface water throughout the site (Ag, As, B, Ba, Cd, Co, Cr, Cu, Hg, Pb, Mo, Ni, Sb, Se, Sn, Tl, U, Zn). In soil, these elevated concentrations are clustered within several areas that generally correlate with previously identified and partially remediated contaminated areas and/or with former operational areas of the acid plant. Neutral to alkaline surface water and groundwater report various metal concentrations above guidelines at locations throughout the site; however metal concentrations are generally low and not observed to correlate with high sulfate above background concentrations. In Aird Bay near the east ditch discharge, the pH is neutral to alkaline and few parameters have been detected at concentrations above background concentrations and applicable guidelines.

METHODOLOGY

Subsurface Investigations and Soil Sampling

To date 105 test-pits and 33 boreholes have been completed in areas of previously identified contamination and near historic plant facilities to better delineate these zones. Test pits were excavated using a tracked excavator within and around previously identified areas of contamination as well as distributed in other areas of the site in an attempt to locate other previously unidentified areas of contamination.

Ten of the 33 boreholes were drilled using a hollow stem auger/rotary drill and a monitoring well was installed in each borehole. The remaining 23 boreholes were completed using a Geoprobe track-mounted drill rig and targeted areas of high conductivity identified in the geophysical survey. Of the 23 borehole locations, 11 were selected for the installation of monitoring wells screened within the overburden, two of which were multilevel wells. Boreholes were terminated after reaching refusal or to 1.8 m below the last visual sign of soil contamination. Sampling of overburden in each of the boreholes was carried out by the direct push of a 1.0 m long clear plastic Geoprobe sleeve into the subsurface at continual intervals. Geoprobe sleeves were inspected for any noticeable physical characteristics such as staining, evidence of lime or the presence of odors. Overall, 42 samples were collected for laboratory analysis on solid chemistry including sulfur speciation, acid base accounting (ABA), and soil leachate chemistry using the shake flask extraction (SFE) method.

Monitoring Well Installation and Sampling of Groundwater and Surface Water

Each monitoring well was constructed with threaded polyvinyl chloride (PVC) riser connected to a PVC well screen. The well screens were placed at depths intended to straddle the water table, and intersecting only a single overburden unit per screen where possible. Screen lengths were generally 1.5 m, however some subsurface conditions required a 3 m length.

Sampling of groundwater was conducted immediately following well development. Surface water was collected from identified monitoring locations in 4 streams / ditches. Samples were analyzed for general chemistry and total and dissolved metals; pH was measured in the field at the time of sampling.

Geophysical Survey

A geophysical survey was completed in order to further constrain localized ARD zones identified through the subsurface investigation, as well as areas between these zones that were not previously detected. This method was chosen because of its lower cost and short duration (two field days) compared with an extensive drilling program. The geophysical survey was completed using a Geonics EM31 and EM34-3, both of which are electromagnetic induction devices well suited to mapping apparent conductivity of the ground and shallow buried metal objects. The quadrature component measured by the EM31 system is sensitive to materials that have a low induction number, such as earth materials, or poorly conducting metallic targets. The EM31 quadrature response is calibrated to give a measure of the bulk apparent conductivity of the subsurface for a roughly hemispherical volume of radius 5 to 6 meters, centered at the measurement point. The in-phase component measured by the EM34-3 system is most sensitive to targets that have a high induction number and are good conductors, primarily larger surface and buried metal objects or very conductive groundwater such as brine. As such, the results provided by both the EM31 and EM34-3 are valuable in differentiating between buried metal objects and the apparent conductivity of the subsurface.

RESULTS AND DISCUSSION

Soil Chemistry

The soil chemistry of 81 samples was assessed through various static test methods. FIGURE 2 presents a frequency distribution diagram for pH values. A summary of select test results is provided in TABLE 1.

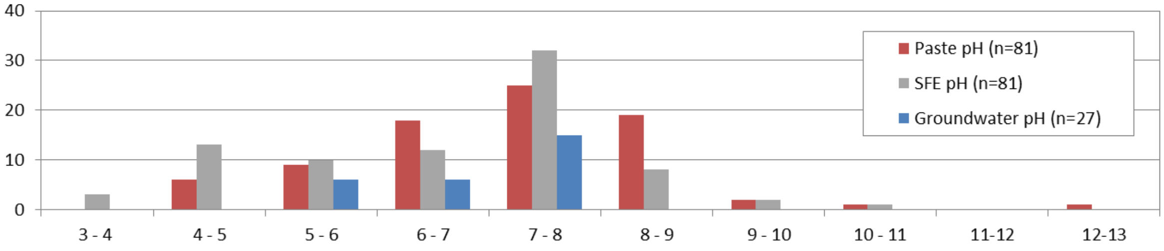

Figure 2 Frequency Distribution for paste pH, SFE pH, and groundwater pH

Table 1 Statistics for select static test results (n= 81 soil samples)

Parameter	Minimum	Maximum	Average
Total sulfur	<0.005%	5.4%	0.19%
Sulfide sulfur	<0.01%	5.3%	0.14%
Sulfate sulfur	<0.01%	1.3%	0.095%
NP	-7.8 t $CaCO_3$/1000t	166 t $CaCO_3$/1000t	13 t $CaCO_3$/1000t
CaNP	0.082 t $CaCO_3$/1000t	104 t $CaCO_3$/1000t	5.5 t $CaCO_3$/1000t
NNP	-164 t $CaCO_3$/1000t	166 t $CaCO_3$/1000t	10 t $CaCO_3$/1000t
NPR	-25	536	31
SFE Conductivity	24 µS/cm	2480 µS/cm	625 µS/cm
SFE Alkalinity	< 2 mg/L as $CaCO_3$	286 mg/L as $CaCO_3$	35 mg/L as $CaCO_3$
SFE SO4	2.1 mg/L	1800 mg/L	315 mg/L

Sulfate is the predominant form of sulfur in the tested soil, as indicated by high concentrations of sulfate compared with sulfide, resulting in low acid potential for most samples. Areas of high sulfide content are sporadically focused around the western part of the site near the former tailings pond, while the samples that dominantly contain sulfate sulfur are distributed throughout the site.

Mineral buffering capacity, defined as the neutralization potential (NP), is variable, with 72% of samples reporting low NP values between -7.8 and 11 tonnes $CaCO_3$/1000 tonnes. The buffering capacity of the samples is predominantly provided by alumino-silicate minerals with lesser carbonate minerals based on the lower calculated carbonate NP (CaNP).

Most tested samples (77%) have no potential to generate acid as indicated by net potential ratio (NPR) values greater than two (MEND, 2009) and neutral to alkaline paste pH values. Potentially acid generating (PAG) samples are sporadically located in the western half of the site around the former tailings pond area and were collected in shallow test pits (up to 3 m deep) above the water table.

Only a small portion of the tested soil samples (15%) were considered to be PAG under laboratory static test conditions. However, circum-neutral pH values in soil leachate and groundwater collected from within these areas suggest that there is sufficient buffering capacity in the system, possibly related to previous lime addition, to neutralize acid that may be generated from localized sulfide mineral oxidation. Therefore, ARD is not considered to be a dominant geochemical process on-site.

Short-term leach testing following the SFE method was used to assess the reactivity of the soil and its propensity to release metals to the receiving environment upon contact with water. Of the tested samples, 95% report circum-neutral SFE pH values. A handful of acidic pH values (3.0 to 4.3) were reported for soil from the eastern part of the site near the former acid storage tanks, but they were not associated with PAG areas and high sulfide content.

High sulfate concentrations in SFE leachate are documented from the following areas: former acid storage tanks, to the east of former process area, north and south of the former tailings ponds and around the former pump house. Samples from these areas also contain little to no buffering capacity (NP < 12 t $CaCO_3$/1000 t), yet report mostly circum-neutral leachate pH values between 4.5 and 8.0, suggesting no acid drainage is currently occurring in these areas. It is postulated that previous sulfuric acid spills near the plant depleted the buffering capacity in the soil, resulting in a high sulfate charge and lower but not acidic pH values in the groundwater.

Groundwater Chemistry

In total 27 groundwater samples were analyzed for alkalinity, sulfate, conductivity, hardness and dissolved metals. A summary of the relevant parameters are presented in TABLE 2. A frequency distribution diagram for pH is presented in FIGURE 2.

Table 2 Select groundwater quality results (n= 27 water samples)

Parameter	Minimum	Maximum	Average
Conductivity	107 μS/cm	6150 μS/cm	1623 μS/cm
Alkalinity	<2 mg/L as $CaCO_3$	506 mg/L as $CaCO_3$	140 mg/L as $CaCO_3$
SO4	5.0 mg/L	5400 mg/L	886 mg/L

No correlation was identified between high sulfate concentrations in groundwater and the PAG conditions observed in soil samples from specific locations. Sulfate groundwater concentrations were measured above the maximum historical background groundwater concentration of 12 mg/L throughout most parts of the site (89% of samples), with average groundwater sulfate concentrations of 886 mg/L over three years of monitoring.

Anomalously high groundwater sulfate concentrations above 500 mg/L occurred in 56% of the samples. This correlated with high groundwater conductivity (>1500 μS/cm) and low alkalinity (<250 mg/L as $CaCO_3$) in the same samples. These trends were identified in the following locations: north of the west shoreline outcrop and south-southwest of the old Pow Wow grounds; east of the existing gravel parking lot; and northeast of the east shoreline bedrock outcrop in the area of the former acid storage tanks and sulfur stockpiles (FIGURE 3).

It is believed that historic plant activities in the northern part of the site introduced sulfate into the subsurface through sulfuric acid spills and leaks from the storage tanks, and/or infiltration from stockpiles where oxidation of pyrite was active.

These areas appear to be hydraulically connected to a zone of observed high groundwater sulfate (>1500 mg/L) in the southwestern portion of the site near the area of groundwater discharge (seep). In this area, the maximum concentration of sulfate in groundwater was observed (5400 mg/L). The high sulfate groundwater is believed to flow through fractured bedrock as evidenced by low sulfate concentrations in overburden groundwater between these two areas and higher concentrations of sulfate in bedrock wells (3300 mg/L) in the northeast area compared with adjacent overburden monitoring wells (470-1400 mg/L).

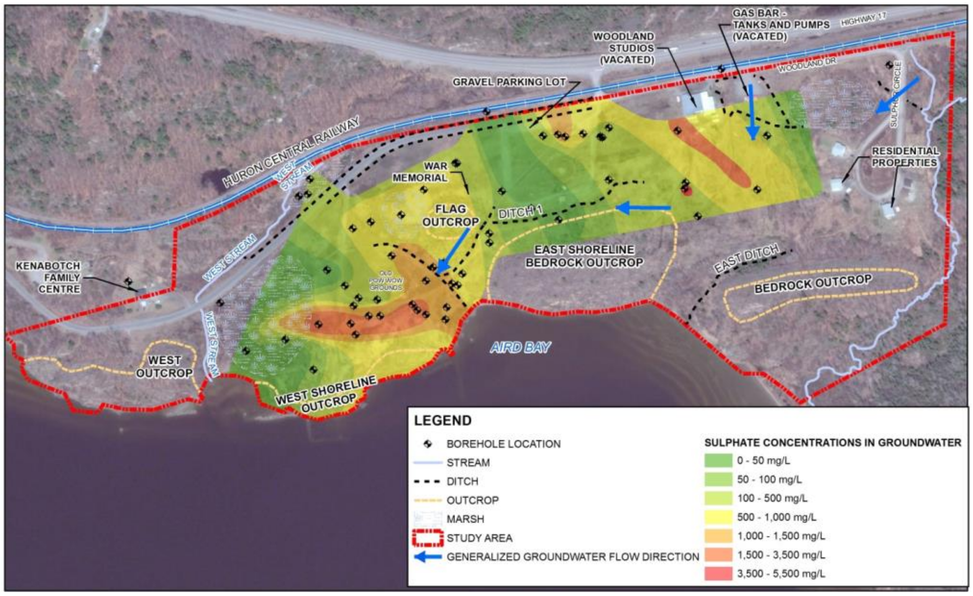

Figure 3 Sulfate concentrations in groundwater (mg/L)

Geophysical Survey

Geophysical survey results indicate that background terrain apparent conductivity values are between 10 and 20 millisiemens per metre (mS/m) in most soils and near 0 to 5 mS/m in the presence of bedrock outcrops or shallow bedrock. Anomalies above these ranges were observed in numerous areas on-site, with conductivity ranges between 75 to 115 mS/m. The results of the geophysical survey are presented in FIGURE 4.

Some of these high conductive areas are interpreted to have buried metal infrastructure from former and/or current site activities based on high in-phase results and documentation of historic remediation activities. The anomalous areas with elevated apparent conductivity readings that were not related to buried metallic objects are believed to be related to the occurrence of elevated sulfate concentrations in the groundwater or soil. These areas of high conductivity were targeted during a subsequent borehole program, with monitoring wells installed in some areas.

Sulfate concentrations measured within the bounds of the geophysical survey demonstrate strong correlation with the measured conductivity (Pearson correlation coefficient r=0.8 for n=15 samples). In the area where there is upward flowing groundwater (seep) in south west portion of the site, sulfate concentrations are greater than 1500 mg/L and up to 5400 mg/L. Conversely, in areas where the in-phase portion of the geophysical survey detected anomalies suggesting buried metallic objects, sulfate groundwater concentrations were in the 0-50 mg/L range (FIGURE 3 and FIGURE 4).

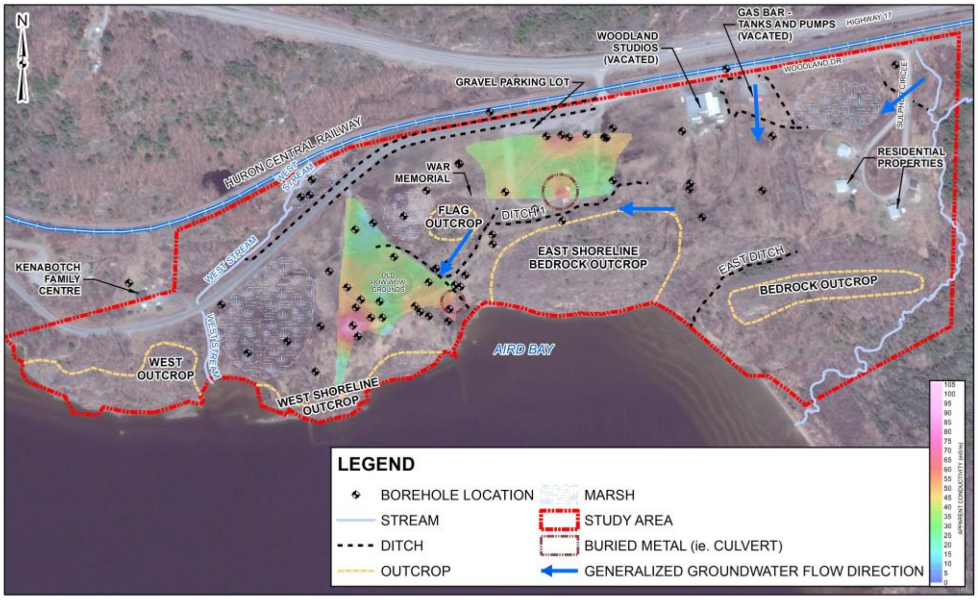

Figure 4 Electromagnetic geophysical survey results (mS/m)

CONCLUSION

During plant operations, sulfide minerals, tailings and sulfuric acid were stockpiled on-site and have historically imparted acidic and metal-loaded solutions to the subsurface through various processes. Site investigations to date identified that, despite remediation efforts, some soil remaining at site has the potential to generate ARD under laboratory conditions. However, sufficient buffering capacity maintains neutral pH conditions in groundwater in these areas.

The electromagnetic geophysical survey did not identify areas of active ARD but detected two conductivity anomalies that were found to correspond with areas of elevated sulfate concentrations in groundwater (500-5400 mg/L). The first anomaly is located in the northeast portion of the site where previous plant activities likely introduced sulfate into the subsurface. The second anomaly, which corresponds with the maximum sulfate concentrations detected across the site, is situated in the southwest portion of the site in the area of upward groundwater flow (seep) and is believed to be hydraulically connected to the first anomaly.

The strong correlation between the electromagnetic geophysical survey and measured sulfate concentrations suggests that geophysics is a useful tool to identify areas of high sulfate concentrations in the shallow subsurface. This tool could be an efficient method to monitor for acidic or neutral pH metal- and/or sulfate-rich waters that can migrate away from stockpiled waste rock and/or tailings storage facilities into the downstream environment.

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NOMENCLATURE

ARD	acid rock drainage
$CaCO_3$	calcium carbonate
CaNP	carbonate neutralization potential
ESA	Environmental site assessment
Kg	kilogram
L	liter
m	meters
mbgs	meters below ground surface
mg	milligram
mg/L	milligrams per litre
mS/m	millisiemens per meter
NP	neutralization potential
NPR	net potential ratio (neutralization potential/acid potential)
PAG	potentially acid generating
SFE	shake flask extraction test
SO_4	sulfate

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