Getting rid of chemical analysis – Mine water management with indicator parameters

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Abstract

Mine water management within the 1 B Mine Pool of the Sydney, Nova Scotia, Canada coal field is conducted by means of 10 wells. Depending on the infiltration rate between 1 and 10 of those pumps are in operation. Because the pump wells are drilled into different depths, the mineralisation of the pumped mine water differs with a trend to lower mineralisation in the shallower wells. In order to pump only water with low Fe-concentrations the mine water is analysed on a 6-monthly plan. Based on the analytical results the sequence in which the pumps are turned on is determined. The mine operator needed a cheaper but precise method to determine the turn-on-sequence of the pumps. A hydrogeochemical investigation of the mine water in the 10 wells at different flow rates was initiated. Based on statistical investigations, the electrical conductivity and temperature of the mine water were identified as an indicator parameter for the Fe-concentration. In combination with the flow rates of the pumps, the lowest Fe-concentration possible at the discharge pipe is estimated using on-site parameters.

Keywords: chemical analysis; statistics; Nova Scotia; coal mining

Introduction

Mine water management involves measuring of numerous parameters, such as total flow or physico-chemical characteristics of the mine water (Wolkersdorfer 2008, Younger et al. 2002). Some of those parameters can be measured with relatively simple methods, but most of them involve taking water samples on site, filtering, chemical pre-treatment and analysis in a laboratory. Though the analytical industry provides equipment to help with on-line monitoring of a range of parameters, not all of the necessary parameters can reliably be analysed on site. One of the most important parameters in the treatment of mine water, besides the pH or electrical conductivity, is the iron concentration in the water. Depending on the iron concentration, chemicals have to be added or the flow to be modified. Though low blood iron concentrations can be measured with probes (e.g. Fakih et al. 2008), there is currently no reliable technique for measuring high iron concentrations on-line or in-situ.

In the past, we observed that mine water taken at greater depths within a mine pool exhibits a higher mineralisation and, consequently, a higher electrical conductivity (e.g. ERMITE Consortium 2004, Wolkersdorfer 2005). This fact is commonly described as "stratification". Our hypothesis was that mine water from deeper parts of the flooded 1B mine pool, has a higher mineralisation then

shallower mine water and possibly also higher ferric and ferrous iron concentrations. We therefore designed a test to verify this hypothesis.

The 1B mine pool is one of several mine pools in the abandoned Sydney, Nova Scotia, coal field (Shea 2008, 2009, 2010, Wolkersdorfer 2011). Part of that mine pool extends under the Atlantic Ocean, because the coal seams where also mined under the ocean. In the area investigated, the coal seams are part of a geological syncline structure and the syncline axis dips into an Eastern direction. Consequently, on the southern flank of the syncline the flooded coal seams can be found at constantly greater depths while moving northward.

In case of the 1B mine pool, one of the discharge criteria that need to be met is the iron concentration. The water level of the mine pool is kept below the sea level at -5.58 to -5.67 m MHWL (mean high water level) in order to avoid the uncontrolled discharge of polluted mine water into the Atlantic Ocean. This is achieved by means of a pump scheme, currently consisting of about a dozen wells in operation with pumps that reach into the mine pool and keep the water level below the sea level. Depending on the infiltration rate, the number of running pumps needed to keep the water level at its predefined elevation is determined. During dry times only 1 or 2 pumps are running, while during and after storm events or after snowmelt, all the pumps are in operation. In total, the pump rate varies between 7 and 9 m^3/min (Shea 2009).

The water from the running pumps is collected into a discharge pipe which feeds a passive mine water treatment scheme (Wolkersdorfer 2011). This treatment scheme consists of a cascade, a settling pond, an overflow pipe, and an aerobic constructed wetland (Figure 1).

Each of the mine waters in the different wells has a distinct chemical composition with electrical conductivities ranging from 500 to 6100 μS/cm and total iron concentrations between 0.05 and 60 mg/L (2008, 2009 data). Though a general trend can be seen, with water quality deteriorating from the shallower wells to the deeper wells (this is from south to north), the electrical conductivity and the iron concentration can considerably change in the wells during the course of the year. To monitor the development of the iron concentration, the mine water is therefore analysed twice a year.

In order to keep the iron concentration as low as possible, the order in which the pumps are turned on depends on the iron concentration of the mine water in each single well. This means that the pump in the well with the lowest iron concentration is turned on first and the one with the highest iron concentration is the last one to be turned on.

Due to the site-specific characteristics, sampling the mine water in the pump wells takes one to two days and the full water analysis in an accredited lab needs another 2 to 10 days. For the appropriate operation of the mine water treatment scheme, and to keep the iron concentration in the treatment scheme and the point of discharge as low as possible, it would be necessary to have a more regular evaluation of the single chemical compositions in the wells.

This paper describes a method to evaluate a dependency between the iron concentration and parameters that can simply be measured by means of standard on-site parameters. In order to establish a relationship between the chemical parameters and on-site parameters, we conducted a 100 hour pump test, turning on one pump after the other in a 10 hour interval. We analysed all the relevant parameters on site and in two different laboratories. Using statistical investigations we were able to establish a relationship between the iron concentration and the electrical conductivity as well as the temperature of the discharged mine water.

Figure 1 *Sampling locations CPI (Cascade Pond Inflow), CSD (Cascade Settling Pond Discharge), and OSP (Outflow Settling Pond) in the order of the flow direction at the Neville Street Wellfield. Flow through the settling pond is from right to left. Image taken in 2006.*

Methods

We installed eight auto samplers, seven in the first seven wells, and one at the discharge pipe into the settling pond (sampling location CPI). In addition, we manually sampled the mine water at the point of discharge (CPI), at the base of the cascade (CSD) and the outflow of the settling pond (OSP) every six hours during the course of the test. After each 10 hours the next pump in the wells was turned on, starting with the well having the lowest expected iron concentration ending with the highest concentration. At the end, all 10 pumps in all the 10 wells were running. In addition, the flow was measured by means of the bucket-and-stopwatch method during each pump step to verify the in-pipe flow measurement of the mine operator (Figure 2).

On site parameters were measured with a Myron L 6P Ultrameter II (pH, EC, redox, temperature), a HACH LDO (oxygen saturation), a HACH Digital Titrator (base and acid capacity) and a HACH field spectrophotometer (ferric and ferrous iron). In the lab, we verified the field measurements of the acid and base capacity (Metrohm Titrando). Furthermore, we measured Al, Mn, SO_4, NO_3, NO_2, and SiO_2 with a HACH DR 5000. All samples were filtered (0.45 µm cellulose nitrate filter) and acidified (HNO_3) in the field.

An additional sample was taken for chemical analysis in an accredited chemical laboratory. They analysed Sb, As, B, Bi, B, Cr, Co, Pb, Mo, P, Se, Ag, Tl, Sn, Ti, V,

Nitrite and P as well as Ca, Mg, K, Na, S, Al, Ba, Cd, Co, Fe, Li, Mn, Ni, Si, Sr, Zn, Br-, Cl, and SO4.

All data was investigated statistically with the SPSS software package and by means of graphical procedures. Because no full chemical analyses were conducted, chemical-thermodynamic calculations could not be executed. Using the curve fitting software Table Curve 2D, we calculated potential fitting equations for the iron concentration and the statistically most significant correlation parameter, in that case the electrical conductivity.

Results and Discussion

During the course of the test, the electrical conductivity and the mine water temperature at the point of discharge increased at each pump step. This is a result of the pump scheme configuration, where each of the pumps in the series binds into deeper parts of the coal seam syncline. As can be seen from Figure 2, the mine water level was lowered by approximately 0.8 meters and the pump rate increased from ≈ 50 L/s at pump step 1 to ≈ 330 L/s at pump step 10.

Most of the measured chemical water parameters increased during the course of the test (Figure 3).
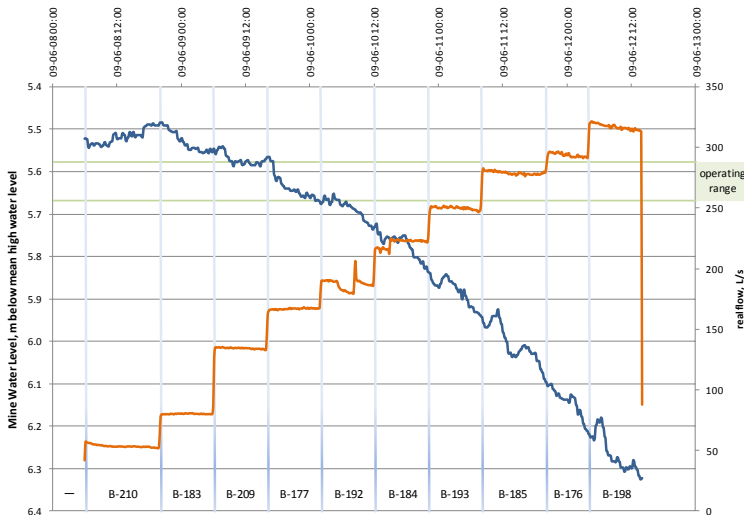

Figure 2 *Discharge readings at the discharge pipe in L/s (orange line), mine water level in m below mean high water level (m MHWL)(blue line) and, shown as vertical light blue lines, duration of each constant pump step. Dates are given in international format (flow data from CBDC and recalibrated to "real flow"). Horizontal green lines indicate the normal operating range of the pump scheme (-5.58...-5.67 m MHWL). Water level fluctuations during operation of pumps B-192 and B-184 are due to maintenance work.*

Because we were mainly interested in the iron concentration, this following discussion shall concentrate on this parameter only. We noticed a nearly linear

correlation between the ferric and ferrous iron concentration and the electrical conductivity (Figure 4). In addition, we also noticed a good correlation between iron and the temperature (not shown here).

As described above, the pumps installed in the 10 wells are pumping water from different depths of the coal seam. One indicator for the fact that deeper water was pumped is the O_2-concentration of the discharge water. The O_2-saturation gradually decreased from approximately 50 % to 35 %. Another indication for deeper water being pumped by the pump scheme is the water temperature, which slightly, but statistically significantly increased from 9 °C to 11 °C. Though several chemical parameters increased during the course of the pump test, the Na and Cl-mass concentrations stayed nearly stable between 120 and 160 mg/L (mean 139 mg/L) for Cl and between 110 and 200 mg/L (mean 150 mg/L) for Na. We can therefore conclude that based on our data, no ocean water is pumped even at the highest pump rate.

Because the electrical conductivity can be seen as a conservative parameter and because of the linear correlation between the iron concentration and the electrical conductivity, this is also the case for the iron concentration in the 1B mine pool. Consequently, the iron concentration and the electrical conductivity at the discharge pipe can be calculated with the general mixing equation (equation 1).

$$Q_d \times \kappa_d = \sum_{p=1}^{10} Q_p \times \kappa_p \qquad \text{(Eq. 1)}$$

With the discharge or pump rate Q and the electrical conductivity κ in wells p = 1...10.
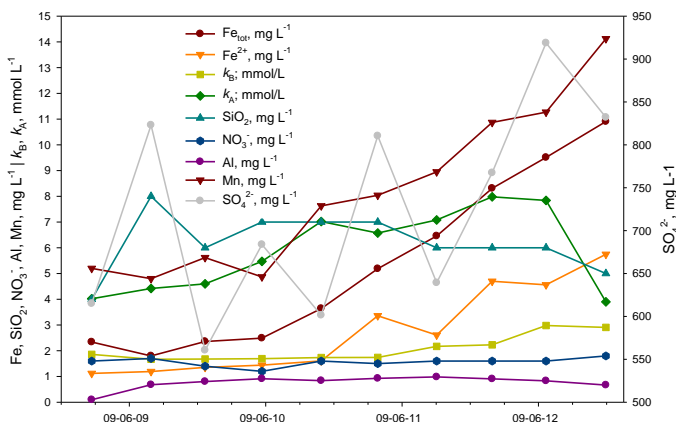

Figure 3 *Time series of the key parameters Fe_{tot}, Fe^{2+}, SiO_2, NO_3^-, Al, Mn, SO_4^{2-}, k_B (base capacity), and k_A (acid capacity). For ease of reading no error bars are shown.*
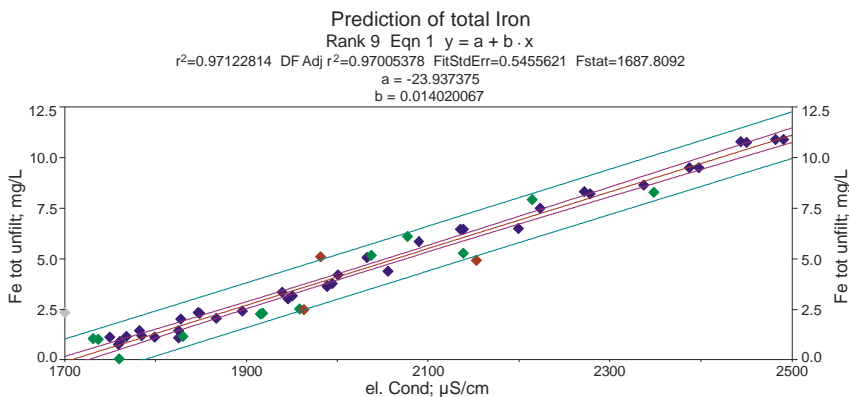
Figure 4 *Correlation of total iron and electrical conductivity (conducted with TableCurve 2D v 5.01.03). y = Fetot, x = electrical conductivity (25 °C). upper lines: 95 % prediction interval, middle lines: 95 % confidence interval, center line: prediction. Colour code for points: red is below 3 times standard deviation, green below 2 times standard deviation and blue within 1 times standard deviation.*

Using a simulation tool such as GoldSim or a fuzzy solver, it is therefore possible to calculate the electrical conductivity or iron concentration by using the known pump rate of each single pump, measuring the flow at the discharge pipe and the iron concentration or electrical conductivity at the discharge pipe. Though the results for the iron concentration might not be very accurate, they can be used to identify which of the wells have which range of electrical conductivity or iron concentration. It is therefore possible, to substitute the regular, cost intensive chemical analysis by a simple measurement of the flow and the electrical conductivity. Because knowing the absolute value of the iron concentration in each single pump well might not always be necessary, our method described here helps to overcome the weakness of the traditional chemical method in this special situation.

This does not imply that chemical analyses are not necessary any more. Yet, in situations similar to the one described above, there might also be a statistically significant correlation between a chemical parameter and one or several on-site parameters that can be measured by means of on-line devices. Chemical analysis would then only be necessary if the indicator parameters change and indicate also a change in the chemical composition (as it is done in drinking water monitoring for example).

Table 1 *Descriptive statistics of all the samples taken at sampling locations CPI, CSD, and OSP. Parameters marked in dark were analysed at Sydney's MAXXAM laboratories. Parameters under the detection limit: Sb, As, B, Bi, B, Cr, Co, Pb, Mo, P, Se, Ag, Tl, Sn, Ti, V, Nitrite and P.*

Parameter	N CPI	Min	Max	Mean	Std. Dev.	N CSD	Min	Max	Mean	Std. Dev.	N OSP	Min	Max	Mean	Std. Dev.
T, °C	20	8,9	10,9	9,7	0,6	20	8,9	10,5	9,6	0,4	20	10,6	15,1	12,2	1,3
pH	20	6,1	6,4	6,2	0,1	20	6,3	6,8	6,6	0,1	20	6,8	7,4	7,1	0,2
el. Cond, µS/cm	20	1.591	2.482	2.021	273	20	1.605	2.491	2.025	276	20	1.731	2.199	1.877	152
Redox, mV	20	267	322	302	14	20	238	296	276	15	20	151	360	270	43
O_2, mg/L	20	4,2	6,4	4,8	0,6	20	8,3	9,9	9,1	0,5	20	9,8	10,3	10,1	0,2
O_2, %	20	37,7	61,4	42,5	5,8	20	73,9	89,1	80,6	4,7	20	90,7	100,1	94,3	2,6
TDS, ppm	20	1.152	1.839	1.482	212	20	1.164	1.856	1.486	216	20	1.251	1.615	1.363	120
Fe tot unfilt, mg/L	20	1,0	10,9	5,1	3,3	20	1,1	10,9	5,0	3,2	20	0,0	6,5	2,3	1,8
Fe^{2+} unfilt, mg/L	20	0,1	5,7	2,7	1,8	20	0,5	5,1	2,5	1,4	20	0,0	2,0	0,8	0,7
k_B, mmol/L	10	1,7	3,0	2,1	0,5										
k_S (k_A), mmol/L	10	3,9	8,0	5,9	1,6										
NO_2, mg/L	10	-	-	-	-										
SiO_2, mg/L	10	4	8	6	1										
SO_4^{2-}, mg/L	10	561	919	725	121										
NO_3^-, mg/L	10	1,2	1,8	1,6	0,2										
Al, mg/L	10	0,1	1,0	0,8	0,3										
Mn, mg/L	10	4,8	14,1	8,1	3,2										
Calcium (Ca), mg/L	10	130	190	163	18										
Magnesium (Mg), mg/L	10	56	99	75	14										
Potassium (K), mg/L	10	16	19	18	1										
Sodium (Na), mg/L	10	110	200	150	28										
Sulphur (S), mg/L	10	180	330	247	51										
Aluminum (Al), µg/L	10	23	950	255	280										
Barium (Ba), µg/L	10	15	19	16	1										
Cadmium (Cd), µg/L	10	0,1	0,3	0,2	0,0										
Cobalt (Co), µg/L	10	11	41	25	10										
Iron (Fe), µg/L	10	670	10.000	3.667	3.088										
Lithium (Li), µg/L	10	50	75	61	8										
Manganese (Mn), µg/L	10	4.500	14.000	8.470	3.355										
Nickel (Ni), µg/L	10	19	60	41	12										
Silicon (Si), µg/L	10	2.700	3.700	3.310	269										
Strontium (Sr), µg/L	10	1.700	2.800	2.190	354										
Zinc (Zn), µg/L	10	26	57	48	9										
Bromide (Br⁻), mg/L	10	0,5	0,9	0,7	0,1										
Chloride (Cl), mg/L	10	120	160	139	13										
Sulphate (SO_4), mg/L	10	640	1.000	823	130										

Conclusions

Our hypothesis, that the iron concentration of mine water can be estimated by means of a simple on-site measurement could be verified. As we showed, the iron concentration in the 1B mine pool can be expressed by a simple linear equation (Figure 4). Though the exact estimation of the iron concentration might no always be possible by measuring the electrical conductivity, it became evident that higher electrical conductivities are an indication for higher total iron concentrations. Therefore, the electrical conductivity can be seen as an indicator parameter for the total iron concentration in the mine water. This means that measuring the electrical conductivity – which is a relatively simple measurement – can be used to determine the order in which the pumps need to be turned on.

Because of the mixing function, it is also possible to calculate the iron concentration in each single well by measuring only the flow and the electrical conductivity as well as the total iron concentration at the discharge pipe.

Acknowledgements

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