

Tracer Test in a Settling Pond: The Passive Mine Water Treatment Plant of the 1 B Mine Pool, Nova Scotia, Canada

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Abstract In order to verify why the design criteria of the Neville Street well field of the 1 B mine pool passive treatment plant were not being met, four mine water tracer tests with uranine (Na-fluorescein) and rhodamine B were conducted in the system's settling pond. Both tracers were injected at the pond's aeration cascade during three separate tracer tests with varying flow conditions (54–158 L s⁻¹). In addition, oxygen saturation and iron concentrations were measured during the first two tests. The aeration cascade works properly; O₂ saturation reaches 81% after less than a second. However, the mean residence time in the settling pond was determined to be only 10–18 h. The plant operator installed five baffle sheets to increase the mean residence time in the settling pond. Tracer tests with uranine after the baffle sheets were installed revealed a new mean residence time of 35 h.

Keywords Cape Breton Island · Tracer test · Mine water · Settling pond · Water treatment · Rhodamine B · Sodium fluorescein · Uranine

Introduction

Tracer tests are a way to study the hydrodynamic characteristics of fluids flowing through open or closed systems (Käß 1998). Closed systems can be porous or fractured media as well as pipes, whereas open systems are channels or ponds. In order to conduct an artificial tracer test, a

gaseous, liquid, or particulate substance is injected into the system to be studied. Tracers that behave similar or equal to the fluid flowing in the system are called conservative; those reacting while in the system are referred to as reactive tracers (Leibundgut et al. 2009). In cases where only the hydrodynamic characteristics of a system are being evaluated, conservative tracers should be used.

Mine water usually consists of numerous compounds that react in one or more of the following ways: oxidizing, reducing, acidic, or alkaline. Therefore, it is essential to test the conservative behaviour of various potential tracers in the corresponding mine water and select the most stable ones (Wolkersdorfer 2008). In the case of the 1B mine water, this test resulted in uranine (Na-fluorescein) and rhodamine B being used for the settling pond tracer tests described hereafter. Kruse et al. (2009) used NaBr instead, but as has been shown by Wachniew et al. (2003), density effects can result in low recovery rates of Br-tracers as the tracer tends to stay in stagnation zones.

Polluted mine water can be treated with either passive or active treatment technologies (Wildeman et al. 1993; Younger et al. 2002). Passive treatment is a collective term for a range of different water treatment options (PIRAMID Consortium 2003), including constructed aerobic wetlands (Hedin et al. 1994; Kleinmann 1990). Passive treatment uses naturally occurring energy sources, such as potential energy or solar energy (PIRAMID Consortium 2003), whereas active treatment involves the use of electricity and chemicals. In most cases, passive treatment is used to treat less polluted mine waters.

The 1B mine pool of the flooded Sydney Coal Mine field contains 76·10⁶ m³ of mine water. Since 2003, the water level in the mine pool is controlled by the Neville Street Wellfield pumps. Between 2005 and 2008, the mean flow from underground was 7–9 m³ min⁻¹, with mean Fe_{tot}

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concentrations of 0.4–5.2 mg L⁻¹ (Shea 2009). In 2008, a passive treatment system was constructed to treat this mine water; it consists of a 2 m high, 4 step aeration cascade, then the water flows into a 11,000 m² and 2.6 m deep settling pond with a capacity of 23,000 m³, and finally into a 13,000 m² reed bed (Figure 1). Wetland construction finished in January 2009, the wetland plants were planted in June 2009, and mine water from the settling pond (Figure 2) first flew through the wetland system in September 2009. Before the construction of the aerobic wetland was finished and at present during high flow conditions, the mine water was, and is, discharged into a natural wetland of a nearby brook (the settling pond discharge, labelled as SPD, and Cadegan's Brook are shown in Figure 1).

Iron precipitates range in size from 1 to 300 µm (Klemm and Degner 2001; Mikkelsen and Keiding 2002); based on the Navier–Stokes equation, the smallest of these particles require a settling time of more than 100 h in a 2.5 m deep settling pond (Iannacone et al. 2009). Yet, actual settling times for a 99% settlement rate of particles are typically much less (Iannacone et al. 2009). Based on experience with mine water treatment systems, the PIRAMID Consortium (2003) recommends a mean residence time of 48 h for settling ponds, and their guidance was followed at the Neville Street passive treatment site (pers. comm. J. Shea).

Between 2009 and 2010, the mean filtered Fe_{tot} concentration at the settling pond inflow was 7.3 mg L⁻¹, with a maximum of 15.0 mg L⁻¹. The pH was 6.2, base

capacity ('acidity') 1.6 mmol L⁻¹, electrical conductivity 2163 µS cm⁻¹, redox potential 376 mV, and the O₂ saturation was 46.9%. At the outflow, the Fe_{tot} values were 3.1 mg L⁻¹ with a maximum of 9.1 mg L⁻¹, the pH was 6.9, the base capacity (acidity) was 0.31 mmol L⁻¹, electrical conductivity was 2,148 µS cm⁻¹, redox potential was 371 mV, and the O₂ saturation was 98.2%. Though the water quality improved after passing through the settling pond, compared to the settling pond's design parameters, the resulting water quality was not satisfactory. The operator of the passive treatment system concluded that the mean residence time of the mine water in the settling pond and the effectiveness of the aeration cascade might not meet the design parameters. Consequently, a tracer test program was initiated using the recommendations in Wolkersdorfer (2008). In May and August 2009, two tracer tests with uranine and rhodamine B were conducted. In addition, the flow over the cascade and the oxygen saturation was measured before and after the cascade as well as the settling pond's outflow.

At the beginning of 2010, five baffle sheets, each reaching 80–90% across and 1.52 m into the pond, were installed in the settling pond (Figure 3) to increase the mean residence time of the mine water in the ponds. In order to evaluate the effectiveness of the baffle sheets, another two tracer tests with uranine were conducted in November 2010.

Although physico-chemical data of the entire passive system was collected and interpreted in conjunction with

Fig. 1 Aerial view of the Neville Street passive treatment system; top is northeast, Cadegan's Brook is flowing from the middle left to the top middle (2010-08-29, Langille Photos, Nova Scotia, for PWGSC and ECBC); OWL outflow wetland, OSP outflow settling pond, SPD settling pond discharge, CPI cascade pond inflow





Fig. 2 View of the Neville Street settling pond with the mine water inflow (CPI) and cascade on the *right* and the outflow (OSP) in the *upper left corner*. Length of the settling pond 150 m, width 60 m (2009-05-12, before the installation of the baffle sheets)



Fig. 3 View of the settling pond with the five baffle sheets installed (2010-06-21)

the tracer test results, this paper will focus only on the results of the tracer tests. Also, although the mean residence time of the mine water in both the settling pond and the constructed wetland are of interest, only the tracers' travel times in the settling pond are discussed herein. Yet, it should be noted that the Fe_{tot} concentrations at the constructed wetland's outflow (OWL) has ranged between <0.1 and 2.5 mg L^{-1} ($n = 30$; $\bar{x} = 0.40 \text{ mg L}^{-1}$; the 14 values below the detection limit were converted to half the detection limit for the calculation) since its commission.

Methods

Na-fluorescein (uranine; CAS 518-47-8; Sigma–Aldrich F6377-500G) and rhodamine B (CAS 81-88-9, Sigma–Aldrich R6626-100G) were injected past the outflow of the discharge pipe of the Neville Street Wellfield pumps (CPI in Fig. 1: inflow of the settling pond). Because impurities in rhodamine B are assumed to be potentially carcinogenic and might be lethal to fish, the dosage was chosen so that the concentration at the points of discharge (SPD and OWL) was significantly below the LD_{50} (50% lethal dose) for fish (314 mg L^{-1} ; Behrens et al. 2001; Field et al. 1995). Concerning the term Na-fluorescein, there seem to be some misunderstandings in the English literature,

because many reports have used the word fluorescein when the author actually used Na-fluorescein (Quinlan 1989). Only the latter is used for water tracer tests, because it has fluorescent characteristics that can be used to analyse even extremely low concentrations in water. Moreover, fluorescein has a very low water solubility ($L = 0.05 \text{ g L}^{-1}$) compared to that of uranine ($L = >600 \text{ g L}^{-1}$; Heumann and Friedlaender 1888; Käß 2004). This might explain why some authors report bad recovery rates for fluorescein and recommend rhodamine WT instead; they likely used the wrong fluorescein. Both substances have the same colour index (C.I. 45,350), which might have caused confusion in the past, but they have different Chemical Abstracts Service (CAS) registration numbers (fluorescein: 2,321-07-5; Na-fluorescein: 518-47-8). In the German literature, Na-fluorescein is called *Uranin*, thus preventing confusion, and rhodamin WT is seldom recommended. To avoid future confusion in water tracer tests, the term fluorescein should be avoided when Na-fluorescein is meant and, as was the case before the Second World War (Google labs 2011), the term uranine should be used instead.

Tracer tests were conducted in May and August 2009, without baffle sheets, and in November 2010, after five baffle sheets had been installed. In all tracer tests, a Dirac-injection (slug or gulp injection) was used with a total injection time of 5–10 min, including washing the canisters

several times with fresh mine water. Uranine and rhodamine B were dissolved in 10 L of tap water (previous tests showed that the fluorescent intensity of uranine decreases unpredictably when diluted in distilled water) and in the lab were thoroughly shaken at least 10 h on an orbital shaker. During the 2009 tracer tests, an auto sampler (SIGMA 900 MAX Portable Sampler) collected 20 min mine water aliquots every hour at the outflow of the settling pond (OSP in Fig. 1). Immediately after the auto sampler bottles were brought to the lab, the tracer was analysed with a spectrofluorimeter (Varian Cary Eclipse Fluorescence spectrophotometer). Every sample was measured 5 times and their arithmetic mean used as the real tracer concentration. Calibration was conducted with known amounts of the tracer using 5–10 dilution steps. In November 2010, two on-line fluorimeters (Geomagnetism Group University of Neuchâtel/Switzerland, GGUN-FL and GGUN-FL20; Flynn et al. 2005; Schnegg and Flynn 2002) were installed at the outflow of the settling pond (OSP in Fig. 1) and the constructed wetland (OWL in Fig. 1). Both instruments were calibrated with a $10 \cdot 10^7$ g mL⁻¹ solution of the tracer according to the fluorimeter manual, and a fluorescence signal was measured every 3 min. Results of the on-line fluorimeters were pH-calibrated using fluorescence measurements with the Varian Cary Eclipse Fluorescence spectrophotometer and 100 µg/L uranine spiked water samples (Table 1).

During all tracer tests, pH, temperature, redox potential, and electrical conductivity were measured with a Myron L Ultrameter II P6. Additionally, during the 2009 tracer tests, the base capacity ($k_{B8.2}$) was analysed with a Hach Digital Titrator using a Hach SensIon pH probe, and oxygen was measured with a Hach LDO[®]101 (luminescent dissolved oxygen) probe attached to a Hach HQ40d. Iron was analysed on site using a Hach DR/890 portable colorimeter or in the lab using a Hach DR/5000 UV-Vis spectrophotometer.

Flow was measured by the operator of the passive treatment scheme using a Greyline ultrasonic AVFM-II flow meter instrument. In addition, the bucket-and-stopwatch method (in 2009 only) was used to verify the Greyline flowmeter results. As has been proven by many researchers (e.g. Baker 2000; Quarini et al. 2007), the bucket-and-stopwatch method gives more accurate results

than a secondary measuring device and is therefore recommended as a calibration method for secondary devices (Minister of Public Works and Government Services 2001). Because of differences between the results of both measurements, only the bucket-and-stopwatch measurements were taken as accurate for the May 2009 tracer tests. After recalibration of the ultrasonic flow meter, flow measurements were taken as accurate within the error ranges of the method during the August 2009 and November 2010 tracer tests.

All tracer test results for this paper were evaluated using the software tool QTRACER2 (Field 2002), which uses the method of moments (Yu et al. 1999). They slightly differ from the results given in Wolkersdorfer (2010), where the cumulative curve method described in Käß (1998) was used instead. For the tracer tests described here, both methods produced similar results, but for more complicated situations, the method of moments is preferred (Leibundgut et al. 2009). Małozewski et al. (2006) used the multi-flow (MFDM) and the single-flow (DM) dispersion models to evaluate their tracer test in a settling pond. Their approach has not been used here, because the mean residence time was the key parameter of interest in the Neville Street treatment scheme tracer study.

Results and Discussion

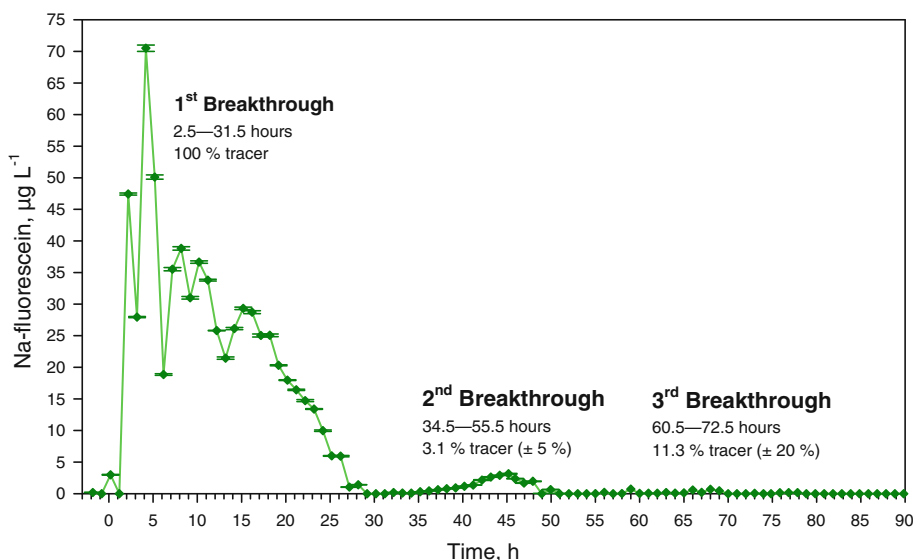
Before Installation of the Baffle Sheets (2009 Tracer Tests)

Recovery rates based on the Greyline ultrasonic flow measurement were 115% in May and 102% in August 2009, while those based on the bucket-and-stopwatch method were $100 \pm 2\%$ (1 standard deviation unit errors are given for all data in this paper). Between the May and the August tracer tests, the ultrasonic flow measurement system was recalibrated and so the August tracer test matched the recovery rate of the bucket-and-stopwatch method. The first tracer arrived 2.5 and 4 h after injecting the tracer in the May (Fig. 4) and August (Fig. 5) tracer tests, respectively. Their mean residence times were 11 ± 7 and 19 ± 6 h, with maximum residence times of 31.5 ± 0.5 and 28.5 ± 1 h. This difference is due to the dissimilar flow

Table 1 Tracer tests conducted in the Neville Street's passive treatment settling pond

Date	Tracer	CAS	Amount (g)	Flow rate (L s ⁻¹)	Sampling and analytical method
May 2009	Uranine	518-47-8	250	102	Auto sampler/spectrofluorimeter
August 2009	Rhodamine B	81-88-9	383	54	Auto sampler/spectrofluorimeter
November 2010 (test 1)	Uranine	518-47-8	250	125	On-line fluorimeter
November 2010 (test 2)	Uranine	518-47-8	250	125	On-line fluorimeter

Fig. 4 Breakthrough curve of the May 2009 tracer test in the Neville Street settling pond (location OSP)



conditions, with a mean flow of $\approx 102 \text{ L s}^{-1}$ in May and $\approx 54 \text{ L s}^{-1}$ in August. Both tracer tests show three peaks (breakthrough 1–3), due to two reasons: the flow condition within the settling pond itself and potential seepage of the discharged mine water in Cadegan’s Brook back into the flooded mine workings. The first breakthrough, between 3 and 32 h, belongs to fast-flowing, near-surface water and slower-flowing water in the deeper parts of the settling pond. Visual inspections clearly showed that the first tracer arrival was related to fast-flowing, near-surface water ($v \approx 0.35 \text{ m min}^{-1}$; all velocities are calculated by using the potential flow path and the corresponding tracer arrival times). In both tracer tests, the first breakthrough summed up to a recovery rate of 100%.

The second and third peaks were less obvious. The time lag between the first tracer arrivals for each breakthrough in both tracer tests was, independent of the flow rate,

$27 \pm 2 \text{ h}$. In addition, second and third peaks showed a low pass filtered curve progression. Consequently, the hypothesis that the second and third peaks result from re-circulated mine water was tested. As described in the introduction, the settling pond discharged into a natural wetland of Cadegan’s Brook (SPD in Fig. 1). From statistical investigations of the mine water chemistry and flow measurements, it appears that a portion of Cadegan’s Brook infiltrates into the mine workings and that the second and third peaks are due to water seeping from Cadegan’s Brook into the mine workings and being returned to the surface by the mine water pumps. Using the peak area under the breakthrough curve of the May tracer test, it can be calculated that $\approx 3 \pm 5\%$ of the treated mine water is infiltrating back into the mine workings.

Oxygen saturation was measured at three locations: before the cascade, at the bottom of the cascade, and at the

Fig. 5 Breakthrough curve of the August 2009 tracer test in the Neville Street settling pond. The three curves belong to the sampling locations at the settling pond (OSP, higher concentrations) and the outflow wetland (OWL, lower concentrations). The curve with the lowest, nearly constant concentration is the background at the inflow of the cascade (CPI)

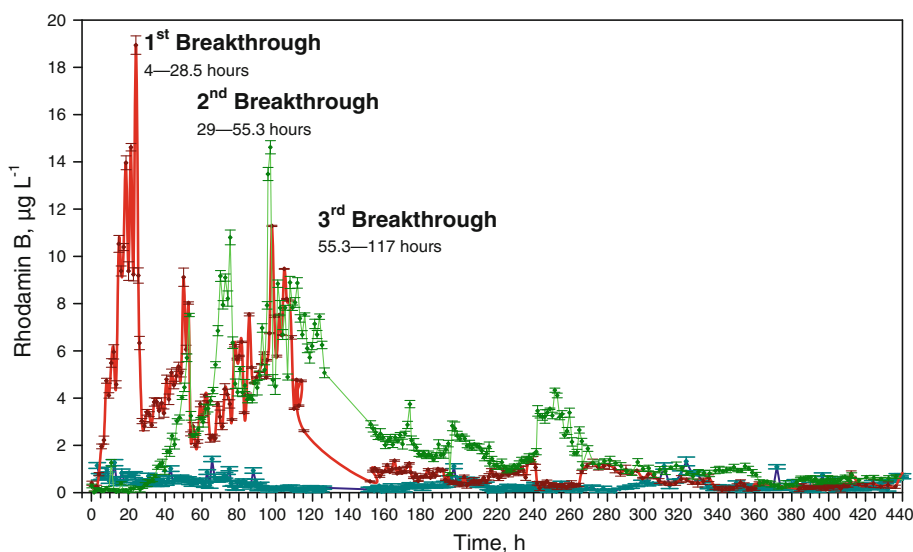
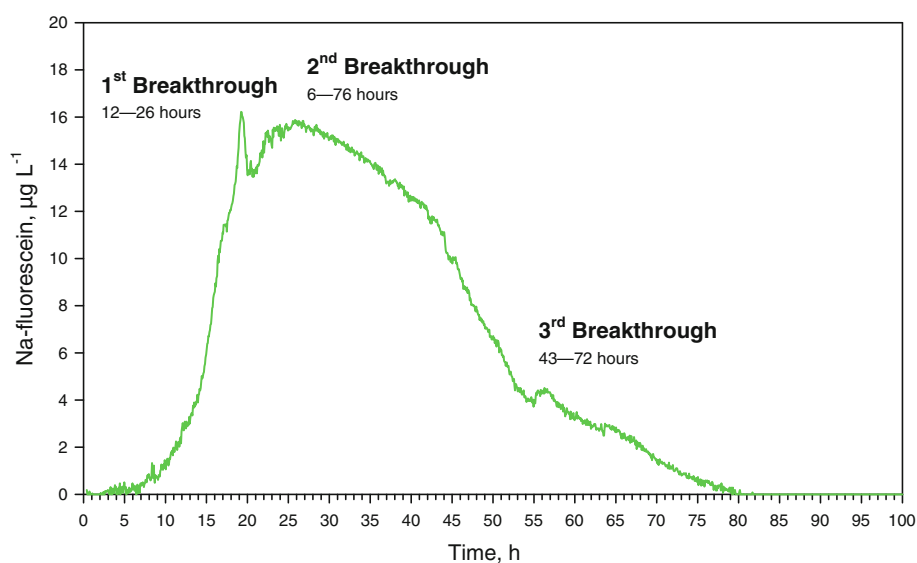


Fig. 6 Breakthrough curve of the November 2010 tracer test in the Neville Street settling pond (location OSP)



outflow of the settling pond. Before the cascade, the saturation was $42.5 \pm 5.5\%$ ($n = 24$). At the bottom, it was $80.9 \pm 4.6\%$ ($n = 23$), and the settling pond outflow was $94.5 \pm 2.5\%$ ($n = 24$). Most of the oxygen in the settling pond was therefore incorporated during the first couple of seconds while the mine water flowed down the cascade, whereas a smaller portion was incorporated by diffusion during detention of the water in the settling pond.

Iron was also measured at those three locations in order to identify the effectiveness of the cascade and the settling pond. Before the cascade, the filtered Fe_{tot} mass concentration was $4.3 \pm 3.3 \text{ mg L}^{-1}$ ($n = 30$). At the bottom, it was $4.1 \pm 3.2 \text{ mg L}^{-1}$ ($n = 27$), and at the settling pond outflow, it was $2.0 \pm 1.7 \text{ mg L}^{-1}$ ($n = 26$). Ferrous iron mass concentrations at the inflow were $2.6 \pm 1.7 \text{ mg L}^{-1}$ ($n = 30$), $2.2 \pm 1.4 \text{ mg L}^{-1}$ ($n = 27$) at the bottom, and $0.7 \pm 0.7 \text{ mg L}^{-1}$ ($n = 26$) at the settling pond's outflow. Statistically, there was no difference before and after the cascade, and the Fe_{tot} concentrations did not meet the design criteria at the settling pond's outflow.

After Installation of the Baffle Sheets (2010 Tracer Tests)

During the November 2010 tracer tests, flow varied between 100 and 158 L s^{-1} due to the influence of weather conditions and the infiltration of rain water into the mine workings. The weighted mean flow was $\approx 125 \text{ L s}^{-1}$, and the recovery rate was 97.8% . As a result of the rainfall, the on-line fluorimeter at the settling pond's outflow (OSP) failed to work during the first of the two tracer tests. In the second tracer test, the first tracer arrived 5.5 h after the injection ($v \approx 9.7 \text{ m min}^{-1}$; Fig. 6) and the mean residence time was $34.8 \pm 13.8 \text{ h}$, with a maximum residence

time of $101.2 \pm 0.05 \text{ h}$. As in the 2009 tracer tests, the breakthrough curve shows three peaks. The first peak appears 18.2 h , the second one 25.7 h , and the third one 55.7 h after the tracer injection. After the tracer was injected, the green colour of the uranine indicated that part of the mine water was flowing under the first baffle sheet. Consequently, the first peak belongs to relatively fast flowing mine water that shortcuts under the baffle sheets ($v \approx 0.15 \text{ m min}^{-1}$), while the second peak belongs to the mine water that flowed through the settling pond guided by the baffle sheets ($v \approx 0.1 \text{ m min}^{-1}$). Based on the breakthrough curve, the time lag between this main peak and the following peak was $30 \pm 1 \text{ h}$. The third peak represents $\approx 3 \pm 1\%$ of the tracer amount related to the main peak. As in the 2009 tracer tests, it is assumed that this is attributed to the part of the treated mine water that re-infiltrates into the mine workings by way of Cadegan's Brook and is pumped back into the settling pond. Based on the existing data, it is currently not possible to precisely locate the potential re-infiltration zone, which is downstream of the passive treatment system.

Conclusions

The aeration cascade of the Neville Street settling ponds functions according to expectations; the mine water is aerated from 43 to 81% oxygen saturation, reaching more than 95% at the settling pond's outflow. Furthermore, the 2009 tracer tests clearly showed that the elevated iron mass concentrations at the settling pond's outflow were due to the low mean residence time (11 – 19 h) of the mine water in the settling pond. This mean residence time was too low to oxidize all of the iron and for the iron oxy-hydroxide

particles to settle in the settling pond. In addition, the tracer tests' results indicate that part of the discharged mine water appears to re-infiltrate into the mine workings. After the baffle sheets were installed at the beginning of 2010, the mean residence time increased to 35 h. Yet, the Fe concentrations at the settling pond's outflow did not significantly improve, because the mean residence time is still below the mean residence of 48 h time required (PIRAMID Consortium 2003). This can also be seen by a visual investigation of the mine water leaving the settling pond, which is still rich in iron sediment. Consequently, as Hilton (1993) stated, more baffle sheets are necessary to increase the mean residence time and improve the mine water quality at the settling pond's outflow (OSP).

The results also show that baffle sheets in a settling pond should be as high as the depth of the settling pond. Otherwise they can't prevent shortcuts which, consequently, lower the residence time of the mine water in the settling pond. In addition, the results prove that uranine and rhodamine B can be used as tracers in settling ponds of Fe-enriched, circumneutral mine water.

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