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Characterisation of hydraulic and hydrogeochemical processes in a Reducing and Alkalinity-Producing System (RAPS) treating mine drainage, South Wales, UK.

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Abstract

A series of tracer tests has been carried out in the compost and limestone Tan-y-Garn Reducing and Alkalinity-Producing System (RAPS), designed to treat iron-rich net acidic mine water (mean pH 6.18, Fe = 47 mg L\textsuperscript{-1}, alkalinity 1.70 meq L\textsuperscript{-1} and mineral acidity 1.82 meq L\textsuperscript{-1}) in South Wales, UK. Conservative tracer breakthrough time in the RAPS basal effluent is approximately inversely related to throughflow rate. Repeat tracer tests indicate a long term decrease in hydraulic conductivity, but not in total porosity.

A specific sodium chloride tracer test from June 2008 is reported, when 15 kg salt was added to a raw mine water inflow rate of 0.87 L s\textsuperscript{-1}. Electrical conductivity and major ion chemistry were monitored for a 170 hour period. Sodium exhibited a retardation of 1.15 to 1.2 in the RAPS medium relative to chloride, due to cation exchange. Simple 1-D advection-diffusion analytical modelling succeeded in simulating the early portion of tracer breakthrough in the RAPS effluent. More complex analytical modelling, accounting for (i) mixing and dilution effects in the supernatant water input signature and (ii) matrix diffusion effects, was found to be required to adequately simulate the later-stage tail of the breakthrough curve in the RAPS effluent.
Keywords
Tracer test, alkalinity, mine water, artificial wetland, matrix diffusion, ion exchange
1. Introduction

1.1 What is a Reducing and Alkalinity-Producing System (RAPS)?

It is common and cost-effective to treat iron-rich mine waters (Banks and Banks, 2001; PIRAMID Consortium, 2003; Sapsford and Watson, 2011) by passive, aerobic methods, such as aerobic sedimentation basins or wetlands. These function by the oxidation of ferrous to ferric iron, followed by the hydrolysis and precipitation of ferric iron from the water. This net process can be described by equation (1):

$$4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ + 10\text{H}_2\text{O} = 4\text{Fe}^{3+} + 12\text{H}_2\text{O} = 4\text{Fe(OH)}_3 + 12\text{H}^+$$ (1)

The overall oxidation and hydrolysis reaction is thus acid-producing (2 moles of protons released for every mole of ferrous iron oxidised and precipitated). However, the hydrolysis and precipitation reaction is strongly pH-dependent: if the pH becomes too low, the hydroxide precipitate will not form. Thus, it is important that sufficient alkalinity is available in the water to absorb the protons produced and to buffer the pH at a reasonably high level (Hedin et al., 1994a; Younger et al., 2002). Alkalinity can be added actively, by dosing the influent mine water with hydroxide or carbonate. However, it can also be released passively by allowing the mine water to flow through limestone drains before entering the aerobic treatment lagoons or wetlands (PIRAMID Consortium, 2003). The limestone slowly dissolves, releasing bicarbonate alkalinity to the water. If the water contains oxygen, however, ferric hydroxide may precipitate out in the limestone drains, “armouring” the limestone clasts and inhibiting further dissolution (Hedin et al., 1994b; Cravotta and Trahan, 1999; Watzlaf et al., 2000a; Bernier et al., 2001). Thus, it is important to strip oxygen from the water before it enters the limestone drain, ensuring that iron remains in its ferrous form (Equation 2). This is most effectively done by a layer with a high organic content and thus a high oxygen demand - for example, a compost layer (represented by CH$_2$O in equation (2)).
4Fe^{2+} + O_2 + CH_2O + CaCO_3 = Ca^{++} + 2HCO_3^- + 4Fe^{2+} \quad (2)

Such a Reducing and Alkalinity-Producing System, or RAPS (Kepler and McCleary, 1994; Watzlaf et al., 2000b; Younger et al., 2002; Amos and Younger, 2003; PIRAMID Consortium, 2003; Fabian et al., 2005) can thus be used as a pre-treatment step in the passive aerobic treatment of acidic/ferruginous mine drainage water. It comprises either:

(i) a layer of compost (or other organic waste) over a porous limestone (or other carbonate lithology) drain, or
(ii) a mixed porous medium comprising compost and limestone clasts, or
(iii) a composite structure containing layers of limestone fragments and compost

If the RAPS becomes excessively reducing, bacterially mediated sulphate reduction can also occur, which can lead to generation of hydrogen sulphide gas and/or to precipitation of metals (Me in Equation 3) as solid sulphide phases within the RAPS:

SO_4^{2-} + 2CH_2O + 2CaCO_3 + Me^{++} = MeS + 4HCO_3^- + 2Ca^{++} \quad (3)

On exiting a RAPS, the mine water will typically:

(i) pass through a re-aeration system, such as an aeration cascade, before entering
(ii) a system of aerobic treatment lagoons and/or wetlands, where the iron content of the water is removed by the reactions in equations (1).

RAPS have typically been applied to iron-rich, net-acidic coal mine waters.
1.2 The Tan-y-Garn site

Tan-y-Garn was a small drift colliery at Garnswllt, Ammanford, Carmarthenshire, South Wales, UK (51.7696°N 3.9849°W; OSGB36 Grid reference SN 6313 0973). The mine complex underlies a total area of less than 0.3 km$^2$ and worked the “Ynysarwed” coal seam from 1876 to 1990. The “Ynysarwed seam” is often taken to be synonymous with what is currently referred to as the Rhondda No. 2 seam (Strahan et al., 1907), although the naming of seams has historically been somewhat arbitrary and problematic to tally with current accepted nomenclature. In the specific case of Tan-y-Garn, it seems more likely that the seam worked was the stratigraphically slightly higher Rhondda No. 1 (or Duke) seam (see the published geological map by BGS, 1977 and the report by SRK, 1994). Both the Rhondda No. 1 and No. 2 seams lie in the Rhondda Beds member of the Lower Pennant Measures of the Westphalian Upper Coal Measures. The seams are associated with a relatively thick sandstone unit with subordinate silts and shales. The worked seam was recorded as 2ft 11 inches (89 cm) thick at “Old Garn Swllt” colliery by Strahan et al. (1907). The local dip of strata is between 10° and 17° S to SW according to BGS (1977).

Following abandonment in around 1990, the Tan-y-Garn workings flooded, and overflowed via a mine entrance as a polluting ferruginous discharge to the south side of the local stream, the Afon Cathan. The workings of Tan-y-Garn are estimated to underlie an area of c. 0.12 km$^2$ and are located south of the mine water discharge point on the south side of the River Cathan. They thus lie below the discharge level, reaching down to elevations of -30 m below sea level and are presumed to be flooded. The mine was connected to the adjacent Garnswllt colliery (SRK, 1994) to the west of the discharge point. The Garnswllt workings, of very limited areal extent (0.017 km$^2$), being largely above the discharge level, are assumed to be unflooded.

The discharging mine water at the site has a typical flow rate of 2 L s$^{-1}$ (equating to around 451 mm of annual recharge, distributed over a worked
area of c. 140,000 m$^2$, for a location with an estimated annual average precipitation of 1265 mm), although this can vary significantly with rainfall from 0.5 to 5 L s$^{-1}$.

Table 1. Physico-chemical properties of mine water at Tan-y-Garn (arithmetic means cited). Changes through the RAPS are shown as percentages of the raw (input) average concentration, with the exception of figures marked *, which are in the cited units. Parameters showing a significant decrease through the RAPS are shaded. Modified after Watson et al. (2009).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Raw mine water Mean</th>
<th>St.dev.</th>
<th>N</th>
<th>RAPS outflow Mean</th>
<th>St.dev.</th>
<th>N</th>
<th>Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow</td>
<td>L/s</td>
<td>2.05</td>
<td>1.38</td>
<td>81</td>
<td>1.89</td>
<td>1.22</td>
<td>81</td>
<td>+0.79*</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>11.05</td>
<td>1.10</td>
<td>59</td>
<td>11.84</td>
<td>2.87</td>
<td>59</td>
<td>+207%</td>
</tr>
<tr>
<td>Total organic carbon</td>
<td>mg/L as C</td>
<td>0.94</td>
<td>0.38</td>
<td>51</td>
<td>2.89</td>
<td>2.46</td>
<td>55</td>
<td>+83%</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>6.18</td>
<td>0.22</td>
<td>60</td>
<td>7.01</td>
<td>0.22</td>
<td>57</td>
<td>+0.83</td>
</tr>
<tr>
<td>Dissolved Oxygen</td>
<td>mg/L</td>
<td>1.29</td>
<td>0.60</td>
<td>53</td>
<td>2.10</td>
<td>1.18</td>
<td>53</td>
<td>+63%</td>
</tr>
<tr>
<td>Electrical Conductivity</td>
<td>µS/cm</td>
<td>673.1</td>
<td>32.7</td>
<td>59</td>
<td>841.4</td>
<td>62.9</td>
<td>57</td>
<td>+25%</td>
</tr>
<tr>
<td>Eh</td>
<td>mV</td>
<td>-13.3</td>
<td>28.6</td>
<td>55</td>
<td>-92.3</td>
<td>43.3</td>
<td>54</td>
<td>-79%</td>
</tr>
<tr>
<td>Field alkalinity</td>
<td>meq/L</td>
<td>1.70</td>
<td>0.30</td>
<td>60</td>
<td>4.58</td>
<td>0.51</td>
<td>59</td>
<td>+169%</td>
</tr>
<tr>
<td>Sulphate</td>
<td>mg/L as SO$_4$</td>
<td>254.2</td>
<td>13.1</td>
<td>60</td>
<td>227.8</td>
<td>33.0</td>
<td>61</td>
<td>-10%</td>
</tr>
<tr>
<td>Chloride</td>
<td>mg/L</td>
<td>12.5</td>
<td>1.4</td>
<td>61</td>
<td>12.2</td>
<td>1.9</td>
<td>57</td>
<td>-2%</td>
</tr>
<tr>
<td>Calcium</td>
<td>mg/L</td>
<td>42.9</td>
<td>2.2</td>
<td>61</td>
<td>121.8</td>
<td>14.2</td>
<td>59</td>
<td>+184%</td>
</tr>
<tr>
<td>Magnesium</td>
<td>mg/L</td>
<td>29.1</td>
<td>1.6</td>
<td>60</td>
<td>29.2</td>
<td>2.4</td>
<td>59</td>
<td>0%</td>
</tr>
<tr>
<td>Sodium</td>
<td>mg/L</td>
<td>10.3</td>
<td>1.1</td>
<td>60</td>
<td>11.1</td>
<td>2.7</td>
<td>59</td>
<td>+9%</td>
</tr>
<tr>
<td>Potassium</td>
<td>mg/L</td>
<td>6.4</td>
<td>1.8</td>
<td>61</td>
<td>6.6</td>
<td>1.2</td>
<td>59</td>
<td>+3%</td>
</tr>
<tr>
<td>Manganese</td>
<td>mg/L</td>
<td>3.64</td>
<td>3.36</td>
<td>61</td>
<td>2.90</td>
<td>0.90</td>
<td>57</td>
<td>-20%</td>
</tr>
<tr>
<td>Aluminium</td>
<td>mg/L</td>
<td>0.13</td>
<td>0.09</td>
<td>59</td>
<td>0.03</td>
<td>0.06</td>
<td>43</td>
<td>-77%</td>
</tr>
<tr>
<td>Ferrous Iron</td>
<td>mg/L</td>
<td>46.23</td>
<td>2.60</td>
<td>60</td>
<td>7.07</td>
<td>4.14</td>
<td>57</td>
<td>-85%</td>
</tr>
<tr>
<td>Total Iron</td>
<td>mg/L</td>
<td>46.60</td>
<td>3.91</td>
<td>60</td>
<td>7.14</td>
<td>3.85</td>
<td>58</td>
<td>-85%</td>
</tr>
<tr>
<td>Iron Loading</td>
<td>kg/day</td>
<td>8.27</td>
<td>0.47</td>
<td>42</td>
<td>1.16</td>
<td>1.05</td>
<td>42</td>
<td>-86%</td>
</tr>
</tbody>
</table>

Shortly after the mine flooded and overflowed, SRK (1994) recorded iron concentrations of around 72 mg L$^{-1}$, pH of 5.7 and sulphate of 480 mg L$^{-1}$. Since then the quality has improved somewhat (Table 1), presumably as accumulated products of pyrite oxidation have been flushed out of the mine.

The Welsh coals generally have a “moderately low” sulphur content of 1 to 1.5%, according to Spears et al. (1999), citing data by Wandless (1959). The fact that the Pennant series coals are of more continental facies, as opposed
to the deeper Middle Coal Measures seams, which are more commonly associated with marine bands, also suggests that their sulphur content might be expected to be modest (Lee, 1995). Greenwell and Elsden (1907) cite a sulphur content of 0.94% for the Pennant series Little Vein coal at Ammanford colliery and 0.74% sulphur for the Rhondda No. 3 coal in Glamorgan. Davies (1921) cites around 1.3% sulphur for the Rhondda No. 2 seam, also in Glamorgan.

![Diagram of Tan-y-Garn mine water treatment system showing logger locations L1-L3 and B1. Tracer injection at L1. Based on maps in Atkins (2006). Inset shows cross-section of RAPS structure. HDPE = high density polyethylene.](image)

The chemistry of the raw untreated mine water shows relatively little variation, despite rainfall-related flow variations, and is summarised in Table 1 (after Watson et al., 2009). The mine water has a pH of around 6.2 and is chemically reducing. It contains, on average 46.6 mg L⁻¹ iron, of which the overwhelming majority (46.2 mg L⁻¹ = 1.65 meq L⁻¹) is ferrous. The total alkalinity is on average 1.70 meq L⁻¹. On the basis of the mean values in Table 1, the total mineral acidity (non-CO₂) is calculated (Hedin et al., 1994a; PIRAMID Consortium, 2003; McAllan et al., 2009) as 1.82 meq L⁻¹. This suggested a mildly net acidic mine water that would benefit from alkalinity
addition, e.g. via a RAPS, prior to treatment by aerobic oxidation and precipitation of iron (Coal Authority, 2014). Such a RAPS was thus constructed at Tan-y-Garn (Figure 1): it commenced operation in January 2006 (Atkins, 2006; Geroni, 2011; Geroni et al., 2011) and comprises:

- Up to 30 cm of standing water. The mine water drains out of the mine tunnel into the RAPS, and ponds as supernatant water on top of the RAPS upper layer.
- 10cm upper layer of municipal (peat-free) compost.
- 60cm mixed layer of 50:50 vol.% municipal compost and Carboniferous limestone gravel.
- lower layer of 10cm of Carboniferous limestone gravel.
- an underdrain, comprising silica gravel and embedded drainage pipes, of design thickness of 22.5 cm to the base of the embedded pipes. The drainage pipes feed the water into an outflow pipe.

The total RAPS thickness is thus around 1 m. The RAPS has a top surface area of around 280 m² as an oval shape approx 30m by 10m (although the liquid surface area is dependent on flow rate: if the inflow is low, the downflow through the RAPS can exceed the inflow, resulting in a drop in supernatant water level and in small areas of shoreline becoming exposed). The calcitic limestone gravel was derived from two local quarries (Ammanford and Penderyn) in the Carboniferous limestone. The gravel clast size ranged from 5 to 40 mm, with a median of just less than 20 mm. Around 180 tonnes limestone gravel were used in the RAPS (Atkins, 2007), representing $3.6 \times 10^9$ meq neutralising capacity. Based on the general characteristics of Welsh Carboniferous limestone, it is not unreasonable to assume a relatively high degree of limestone purity (Harrison, 1993).

The outflow from the RAPS is via a flexible pipe, the level of whose mouth can be adjusted. This alters the head difference across the RAPS, which can, in turn, affect the throughflow rate and the level of standing water on top of the RAPS, up to a maximum freeboard of c. 30 cm. The supernatant water level in
the RAPS thus depends on the head gradient (the controlled level of the
outflow pipe), the hydraulic conductivity of the RAPS media and the flow
entering the system.

On leaving the RAPS, the water flows through a series of aeration cascades
and three aerobic sedimentation basins, before discharging, via an aerobic
wetland, to the Afon (River) Cathan (Figure 1).

After the RAPS commenced operation, it became evident that some iron
oxidation and ochre precipitation was occurring in the supernatant water of the
RAPS. However, by comparing the raw mine water with the RAPS effluent, it
is clear that the RAPS is fulfilling its primary function of raising the pH and
alkalinity of the water, converting it to a net alkaline condition. The effluent
water is almost saturated with respect to calcite and, of course, it contains
elevated concentrations of calcium. Further, it contains depleted
concentrations of sulphate, suggesting sulphate reduction (-26.4 mg L\(^{-1}\) or -
0.55 meq L\(^{-1}\), on average) is being facilitated by the compost in the RAPS
media. The effluent water also contains decreased concentrations of iron (-
39.5 mg L\(^{-1}\) or -1.4 meq L\(^{-1}\)), manganese and aluminium, suggesting
hydroxide precipitation on top of (and possibly within) the RAPS, in addition to
losses due to iron sulphide precipitation. See Atkins (2007), Watson et al.
(2009) and Geroni (2011) for further details.

1.3 **Decline in Hydraulic Conductivity**

Assuming an average flow rate of 2 L s\(^{-1}\) (Table 1), and dividing this by the
RAPS area, this implies an average Darcy velocity down through the RAPS of:

\[
0.002 \text{ m}^3 \text{s}^{-1} / 280 \text{ m}^2 = 7.1 \times 10^{-6} \text{ m s}^{-1} = 0.62 \text{ m d}^{-1}
\]  

(4)

Dividing this figure by the vertical hydraulic gradient across the RAPS (i.e. the
head difference between the supernatant water and the outflow pipe) yields
an estimate of bulk composite vertical hydraulic conductivity. As the flow rate
and head difference are regularly monitored, this allows systematic changes
in hydraulic conductivity to be identified. Watson et al. (2009) report the apparent progressive deterioration of the hydraulic conductivity of the Tan-y-Garn RAPS system over the course of several years. Figure 2 illustrates the decline in apparent hydraulic conductivity, as calculated by throughflow per unit area (Darcy velocity) divided by hydraulic gradient. By June 2008, the bulk vertical hydraulic conductivity had declined to some 0.25 m d\(^{-1}\). As hydraulic conductivity decreases, several things happen in order to maintain RAPS throughflow:

- It becomes necessary to lower the level of the outflow pipe to increase the hydraulic gradient down through the RAPS.
- The freeboard of supernatant water above the RAPS increases (thus also increasing hydraulic gradient).
- Eventually the maximum freeboard of 30 cm is exceeded and untreated mine water begins to overflow, bypassing the RAPS, and discharging directly to the aerobic treatment lagoons (this also occurs if mine water flow rates increase beyond the RAPS capacity for meteorological reasons - i.e. high rainfall).

![Figure 2. Estimated change in vertical hydraulic conductivity with time for RAPS (after Watson et al., 2009).](image)
It is recognised that RAPS hydraulic performance (bulk vertical hydraulic conductivity) can decrease with time, due to the following potential factors:

- post-construction compaction
- accumulation of iron oxyhydroxide (ochre) in the supernatant layer
- mineral precipitation and biofouling within the RAPS itself.

1.4 Previous Tracer Tests

Tracer tests have previously been successfully used to elucidate hydraulic conditions and modal and mean residence times in mine systems and RAPS (Aldous and Smart, 1988; Diaz-Goebes and Younger 2004; Wolkersdorfer, 2002; 2008; Wolkersdorfer et al. 2005, in press; Watson et al. 2009). During the years 2006-2008, around ten tracer tests were carried out at Tan-y-Garn (Atkins, 2007; Watson et al., 2009) using lithium bromide, sodium chloride or fluorescein as quasi-conservative tracers. The tests showed the expected inverse linear relationship between flow rate \((Q)\) through the RAPS and time \((T_p)\) to peak tracer concentration in effluent (Figure 3a). Given that

\[
\frac{H}{T_p} = \frac{V_D}{n_e}, \text{ then } \frac{V_D}{(1/T_p)} = Hn_e
\]

(5)

where \(H\) = the thickness of the RAPS = 1.025 m

\(n_D\) = specific discharge or Darcy velocity (m d\(^{-1}\))

\(n_e\) = effective porosity of the RAPS

The above assumes that the RAPS medium is relatively homogenous and that \(T_p\) represents a mean conservative tracer travel time. We should note that \(T_p\) for a conservative tracer actually corresponds to a modal or dominant residence time of the system, which may not be the same as a mean residence time (Kusin et al., 2012), especially if there are significant matrix diffusion effects or a multi-modal porosity distribution.
Thus, the gradient of the graph (Figure 3a) = 0.3279 m = 1.025 m x \( n_e \), suggesting an effective RAPS porosity \( n_e \) of around 32%. Alternatively, we can calculate effective porosity (\( n_e \)) from each individual test (Figure 3b). From these calculations, we obtain a first estimate of the effective bulk porosity of the RAPS at 32-35%, although this may be an overestimate, due to the finite volume of the partially ochre-filled supernatant water layer.

![Graph showing results of hydraulic tracer tests](image)

Figure 3. Results of 10 hydraulic tracer tests performed 2006-2008; 9 tests used NaCl tracer, 1 test used LiBr (marked). The tests with the highest flow rates were generally the earliest tests. \( T_p \) = time to peak tracer concentration in effluent. Specific throughflow is calculated as throughflow divided by RAPS area of 280 m². In the lower diagram, there is no discernable trend: thus, the
marked “trendline” should be understood as an average. Based on data presented in Watson et al. (2009).

Figure 3b exhibits a large variance in derived values, but fails to demonstrate any systematic trend or decline in calculated effective porosity. The fact we observe a decline in hydraulic conductivity (Figure 2) without a clear decline in effective porosity (Figure 3b) should not be too surprising, as hydraulic conductivity is controlled by the aperture of the throats (Doyen, 1988; Rezaee et al., 2006), connecting pore spaces, which can become clogged very easily, rather than by the aperture of the pores themselves (Heiderscheidt et al., 2008). The spread of values in Figure 3b also provides some impression of the accuracy of the hydraulic data obtained from analysis of these tracer tests, approximately 30% around the mean value.

2. Methods and Materials

2.1 Objective

The initial objective of the June 2008 tracer test described in this section was to carry out a combined hydraulic and thermal tracer test, by the injection of a conservative chemical (sodium chloride) and thermal signal (cool water) into the RAPS system (Taylor, 2008). The thermal behaviour of the RAPS represents a separate scientific thread and is reported in a companion paper to this (Taylor et al., in prep.). This paper focuses on an integrated presentation of the hydraulic and chemical behaviour of the RAPS.

2.2 Combined Tracer Test: June 2008

At 13:10 on 25th June 2008, a combined sodium chloride and thermal tracer (cool water) test was initiated.

Prior to the test, the influent mine water had an electrical conductivity of 460 µS/cm, while the effluent water from the RAPS was more mineralised and had
an electrical conductivity of 650 µS/cm. At the time of the test, the flow rate through the RAPS was lower than the typical flow rate (cited above as around 2 L s\(^{-1}\)), reflecting the low recharge to the mine system during summer. During the 72 h period following the commencement of the tracer test, the flow varied between extremes of 0.62 to 1.13 L s\(^{-1}\), with an arithmetic mean of 0.87 L s\(^{-1}\), a standard deviation of 0.09 L s\(^{-1}\), but with no systematic increasing or decreasing trend.

For the test, an empty 200 L drum was placed adjacent to the access chamber L1 (Figure 1) down-gradient from the mine entrance from which the water emerges. 15 kg of sodium chloride (common salt, corresponding to 256 moles: 5.9 kg sodium and 9.1 kg chloride) was initially placed in the drum. From upstream of a temporary impoundment in the chamber, around 0.65 L s\(^{-1}\) of the mine water flow were pumped into the drum, which was stirred manually, dissolving the NaCl rapidly. When the drum was full, after some 300 s, the saline water from the drum was allowed to overflow via a hose back to the access chamber, downstream of the impoundment, re-joining the total mine water flux (to result in the narrow spike in electrical conductivity at L1 - Figure 4).

### 2.3 Monitoring

The test was monitored by four electronic loggers (Schlumberger Water Services Diver\(^\text{®}\) type) installed at the site (Figure 1) at the following locations:

- **B1** in the open air adjacent to the RAPS, measuring ambient air temperature and barometric pressure (Baro-Diver\(^\text{®}\)). The readings from diver B1 were used to compensate divers L1 to L3 for atmospheric pressure.

- **L1** in the “inflow chamber” receiving mine water from the mine tunnel entrance, recording water level and influent water temperature and electrical conductivity (CTD-Diver\(^\text{®}\), with a manufacturer-cited accuracy in conductivity of ±1% and a resolution of ±0.1%).
• L2 in the RAPS supernatant water, measuring water level and water temperature (Mini-Diver®), located near downstream end for reasons of access.
• L3 in the RAPS outflow chamber, measuring water level, water temperature and electrical conductivity (CTD-Diver®). A 28°4’ angle v-notch weir (Atkins, 2006) was installed in the chamber, allowing flows to be calculated from water levels in at L3, using a conversion algorithm provided by the Coal Authority. Manual readings were taken at the weir board at regular intervals to confirm logged data.

No density compensation was made to loggers L1 to L3 as the electrical conductivity at the NaCl tracer peak in the RAPS effluent only reached 750 µS cm\(^{-1}\) and the total variation over the course of the test was only 100 µS cm\(^{-1}\) (Figure 4)

2.4 Automated sampling and analysis
An automated sampler was set up at the RAPS outflow (L3), programmed to take 500 mL water samples by activating a peristaltic pump at a frequency of 1 per hour. Samples were downloaded from the autosampler twice daily and filtered using a syringe-driven 0.2 µm cellulose acetate filter into 50 mL sample vials. Water samples were returned and submitted for analysis:

• of total alkalinity immediately using a portable titration kit.
• for the anions Cl\(^-\), NO\(_3\)\(^-\) and SO\(_4\)\(^{2-}\) at the Oxford University Centre for the Environment, using a Dionex Ion Chromatograph, with a sodium carbonate eluant.
• for the elements Ca, Na, Mg, K, Sr, Mn, Fe, Ba by inductively coupled plasma optical emission spectrometry (ICP–OES) at the School of Geography, University of Leeds using a Perkin Elmer Optima 5300 DV.
3. Results and Interpretation

3.1 Hydraulic Tracer Test

In the case of the 25th June 2008 tracer test, monitoring of electrical conductivity shows initial breakthrough of the salt tracer after 6 hours, with a peak conductivity after \( T_p = 23 \) hours (Figure 4). Consideration of \( T_p \) implies an apparent modal or dominant tracer velocity of around \( 1.24 \times 10^{-5} \) m s\(^{-1}\) or \( 0.0446 \) m h\(^{-1}\). Conductivity has returned to background after a period of 160-170 hrs. Applying equation (5) with the prevailing flow rate of 0.87 L s\(^{-1}\) (specific discharge of 0.0112 m h\(^{-1}\)) yields an apparent effective porosity of 25%.

Figure 4(a) Electrical conductivity measurements during tracer test of June 2008 (conductivity uncorrected for temperature). Note that the peak measured conductivity in the mine water inflow chamber (L1) was around 7670 µS/cm. Tracer injection at \( t = 0 \). R denotes probable rainfall events diluting the mine.
water. (b) Hourly rainfall measurements for Mumbles Head meteorological station (OSGB36 Grid reference SS 627 870, approximately 23 km due south of Tan-y-Garn).

### 3.2 Hydrochemical Observations

Concentrations of major ions were regularly sampled at the outflow of the RAPS (Figure 5). These were converted to “normalised” concentrations by subtracting the “background” concentrations prior to the commencement of the tracer test (Figure 6). The mass recovery of chloride within \( t = 170 \) was calculated at c. 6.7 kg (74%); that of sodium as 4.2 kg (71%), although these figures are dependent on the accuracy of the flow determinations.

![RAPS effluent (L3) water chemistry: tracer test June 2008](image)

Figure 5. Concentrations (mg L\(^{-1}\)) of Cl\(^-\), Na\(^+\), Ca\(^{++}\) and Mg\(^{++}\) in RAPS effluent outfall water during tracer test of June 2008. Also shown is estimated cumulative recovery of Cl\(^-\) and Na\(^+\) (cumulative recovery corrected for background concentrations).
Assuming chloride to be the most conservative tracer parameter, Figure 6 suggests that sodium is very slightly retarded relative to the breakthrough of chloride. More surprisingly, an earlier breakthrough of an excess of calcium (and, to a lesser extent, magnesium) is noted. This calcium excess is followed after an elapsed time of c. 50 hours by a relative depletion in calcium. As calcium was not applied as a tracer, these excess and deficit concentrations must relate to calcium being released or absorbed within the RAPS. The Na/Ca meq ratio rises throughout the course of the tracer test. This pattern is strongly suggestive of the pulse of sodium tracer being absorbed onto ion exchange sites (and retarded) in the RAPS matrix and displacing calcium and magnesium (which would be expected to saturate ion exchange sites in a limestone-rich environment). As the salt pulse passes, sodium desorbs from exchange sites and calcium would then be expected to be re-sorbed. Further support for the Ca-Na exchange hypothesis (see also Appelo and Postma, 2005; De Vries, 2007) comes from Figure 7, where the cumulative recovery of Na\(^+\)+Ca\(^{2+}\) (in equivalents) closely matches the Cl\(^-\) recovery curve.

Figure 6. Excess concentrations (normalised relative to background) of Cl\(^-\), Na\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\) in RAPS effluent outfall water during tracer test of June
2008, in meq L\textsuperscript{-1}. Also shown is Na/Ca meq ratio (also corrected for background).

![Cumulative recovery of Cl, Ca and Na as equivalents, June 2008 tracer test](image)

Figure 7. Cumulative recovery (corrected relative to background) of Cl\textsuperscript{-}, Na\textsuperscript{+} and Ca\textsuperscript{++} in RAPS effluent outfall water during tracer test of June 2008, in equivalents of charge. Calcium was not, of course, applied as a tracer, so the “recovery” is simply calculated as the excess concentration discharged from the RAPS during the course of the test.

4. Modelling the Tracer Test

Modelling of the tracer test was attempted using three modelling approaches of increasing complexity. The third approach (Section 4.3) is arguably more demanding, in terms of parameterisation, than the available data are able to support. For this reason, even more complex modelling was not felt to be justified.

4.1 Simple advection-dispersion model
A 1-dimensional dispersive-advective model (Equation 6) with retardation was
selected as a “first pass” algorithm to simulate salt transport downwards
through the RAPS. This model was discussed by, e.g., Enfield et al. (1983),
and was codified by Banks (1984) and used to simulate the transport of an
“initial square-wave” pulse or “slug” of cations through the basal liner of a
landfill (conceptually, very similar to the RAPS). The model assumes
homogeneity in matrix properties, constant flow velocity and a discrete “slug”
of solute of finite length entering the system:

\[
C(z,t) = \frac{C_0}{2} \left[ \text{erf} \left( \frac{z + z_0 - v_s t}{2\sqrt{Dt/R}} \right) - \text{erf} \left( \frac{z - v_s t}{2\sqrt{Dt/R}} \right) \right]
\]

where

\( C(z,t) \) = concentration of solute at depth \( z \) and time \( t \)
\( C_0 \) = initial concentration in slug at \( z=0 \) and \( t=0 \).
\( z_0 \) = the initial length of the slug of solute input at the top of RAPS (m)
\( z \) = the depth coordinate (m)
\( v_s \) = the apparent velocity of the solute (m s\(^{-1}\)) = \( v/R \), (or simply \( v \) for chloride)
\( v \) is the mean linear hydraulic velocity. We have assumed, in the first instance,
that the modal velocity \( H/T_p \) (1.025 m / 23 h = 0.0446 m h\(^{-1}\) = 1.24 x 10\(^{-5}\) m s\(^{-1}\))
is a reasonable approximation to the mean hydraulic velocity.
\( \text{erf} \) = the error function
\( R \) = retardation factor
\( D \) = dispersion coefficient (m\(^2\) s\(^{-1}\))
\( t \) = time (s) elapsed since tracer injection

Parameter \( R \): The model was parameterised assuming that \( R \), the retardation
factor, for chloride was 1 (i.e. a conservative, non-retarded tracer).

Parameters \( v \) and \( v_s \): From the tracer test, if the peak travel time is 23 hrs and
if we assume that this dominant travel time is a first approximation of the
mean conservative solute travel time in the mobile pore water fraction, then we can estimate \( v = v_s \) for chloride as around \( 1.24 \times 10^{-5} \, \text{m s}^{-1} \).

Parameter \( C_0 \): The initial concentration of the tracer in the supernatant water lagoon is not known. From Figure 4, we can see that the initial spike of salt has an electrical conductivity of c. 7200 \( \mu \text{S cm}^{-1} \), relative to background, which corresponds to c. 4000 mg L\(^{-1}\) salt at L1 (assuming that c. 550 mg L\(^{-1}\) salt is equivalent to 1000 \( \mu \text{S cm}^{-1} \); Hem 1985; Misstear et al. 2006). \( C_0 \) can also be estimated using a very simple mixing model. The injected mass of salt was 15 \( \times \) 10\(^6\) mg into an estimated RAPS supernatant water volume 280 m\(^2\) \( \times \) 0.1 m = 28 m\(^3\) = 28000 L. If mixing were instantaneous, this would result in an average concentration of 536 mg L\(^{-1}\) salt (211 mg L\(^{-1}\) Na\(^+\) and 325 mg L\(^{-1}\) Cl\(^-\)).

Parameter \( z_0 \): The initial length of the slug \( z_0 \) is also highly problematic to parameterise, but one could take two ‘extreme’ approaches: (i) assume all the salt entered the lagoon, sunk as a dense layer to the base of the lagoon and mixed into a ‘bottom layer’ of water during the first hour of the test (injection volume = 0.87 L s\(^{-1}\) \( \times \) 3600 s = 3.132 m\(^3\)), giving an average thickness of 3.132 m\(^3\) / 280 m\(^2\) = 1.12 cm, or (ii) assume that the salt mixed throughout the entire c. 0.1 m depth of supernatant water in the lagoon. If the effective porosity of the RAPS is 25%, then we could either postulate (i) a short concentrated slug of length, say, 0.0112 m / 0.25 = 0.0447 m (Figure 8a,b) or (ii) a less concentrated, longer slug of 0.1 m / 0.25 = 0.4 m (Figure 8c,d).

Parameter \( D \): As regards the dispersion coefficient, \( D \), it is not uncommon (Gelhar et al., 1992; Delleur, 1998) to assume a value of c. 0.1 \( \times \) L \( \times \) v, where L is the characteristic transport length being considered (in this case \( H = 1.025 \) m). This approach would yield a starting value of 1.27 \( \times \) 10\(^{-6}\) m\(^2\) s\(^{-1}\) (assuming chemical diffusion is negligible, compared with mechanical dispersion).

Clearly, the application of such a simple 1-D analytical model is optimistic. Nevertheless, Figure 8 demonstrates that it is possible to obtain a good fit to the early portion of the breakthrough curve with \( D \) in the range 1.2 to 2.2 \( \times \) 10\(^{-6}\).
and an $R$ of 1.15 to 1.2 for sodium. To obtain a fit to the maximum peak height, it is possible either:

- to set $C_0$ in the range 1250-1700 mg L$^{-1}$ NaCl (492 - 669 mg L$^{-1}$ Na$^+$ and 758 - 1031 mg L$^{-1}$ Cl$^-$) with a short slug, or
- to set $C_0$ in the range 147-200 mg L$^{-1}$ NaCl (58-79 mg L$^{-1}$ Na$^+$ and 89-121 mg L$^{-1}$ Cl$^-$) with a long ($z_0 = 0.4$ m) slug. In this latter case, the velocity has to be increased through the RAPS (to $1.49 \times 10^{-5}$ m s$^{-1}$) as the long slug takes a longer time to enter the RAPS.

Figure 8. Modelled versus actual normalised (corrected relative to background) concentrations of (left - a,c) Cl$^-$ and (right - b,d) Na$^+$ in RAPS effluent water ($z = 1.025$ m) during tracer test of June 2008, using the
algorithm of Enfield et al. (1983). Four simulations are shown. Simulation 1 (a) and (b): \( C_0 = 1700 \text{ mg L}^{-1} \text{ NaCl}, R = 1.2 \) for sodium and dispersion = \( 2.2 \times 10^{-6} \text{ m}^2 \text{ s}^{-1} \); Simulation 2 (a) and (b): \( C_0 = 1250 \text{ mg L}^{-1} \text{ NaCl}, R = 1.15 \) for sodium and dispersion = \( 1.27 \times 10^{-6} \text{ m}^2 \text{ s}^{-1} \); Simulation 3 (c) and (d): \( C_0 = 200 \text{ mg L}^{-1} \text{ NaCl}, R = 1.2 \) for sodium and dispersion = \( 2.2 \times 10^{-6} \text{ m}^2 \text{ s}^{-1} \); and Simulation 4 (c) and (d): \( C_0 = 147 \text{ mg L}^{-1} \text{ NaCl}, R = 1.15 \) for sodium and dispersion = \( 1.27 \times 10^{-6} \text{ m}^2 \text{ s}^{-1} \). For (a) and (b), slug length \( z_0 = 0.0447 \text{ m} \) and hydraulic velocity \( v = 1.24 \times 10^{-5} \text{ m s}^{-1} \), for (c) and (d) \( z_0 = 0.4 \text{ m} \) and \( v = 1.49 \times 10^{-5} \text{ m s}^{-1} \). In all cases \( R = 1 \) for chloride.

This model produces a poor fit for the latter part of the curve and underestimates the total recovered tracer mass. This poor fit to the late data is unsurprising and is most likely due to three factors:

(i) too little tracer injected in simulations - the real tracer injection profile to the RAPS is unknown and likely quite complex, potentially with a long, low concentration tail due to mixing (see (ii) below).

(ii) the fact that the model assumes a discrete, well-defined “square wave” slug of tracer uniformly entering the top of the RAPS. In reality, as the tracer initially entered the RAPS, one would have had a localised pulse of high salt concentration entering the RAPS, followed by a more widespread pulse at lower concentration as the salt mixed and diffused throughout the RAPS supernatant water body.

(iii) the likelihood of chemical diffusion of the tracer into micropores within the matrix of the RAPS (i.e. multiple porosity distribution)

Thus, this initial modelling approach might be expected to potentially produce realistic output for the initial tracer breakthrough from the test, but would not be expected to simulate the later (mixing / matrix diffusion-dominated) portion of the test, for which more sophisticated models would be required.

4.2 Diaz-Goebes and Younger (2004) matrix diffusion model
Diaz-Goebes and Younger (2004) produced a 1-dimensional model (which is summarised in Equations 7-10), which simulates matrix dispersion effects and allows the user to partition flow between (i) a conventional “macro-porous” medium flow domain and (ii) an equilibrium matrix diffusion domain, via a partition coefficient (which they term \( \psi \)). The model was successfully tested by Diaz-Goebes and Younger (2004) on two British RAPS tracer tests and is deemed appropriate for use also at Tan-y-Garn.

\[
C(z,t) = \Psi \left[ \frac{M}{n_e \sqrt{4 \pi D_L t}} \right] \exp \left[ -\left( \frac{z - v_D t}{n_e} \right)^2 \right] + (1 - \Psi) \left[ \frac{M}{n_e \sqrt{4 \pi D_L t}} \right] \exp \left[ -\left( \frac{z - \frac{v_D t}{n_e R_{mat}}}{n_e} \right)^2 \right] \]

(7)

\[
R_{mat} = 1 + \left( \frac{n_{mat}(1 - n_e)}{n_e} \right)
\]

(8)

\[
D_e = D_L + \frac{\pi^2 v^2 n_{mat}(1 - n_e)}{12 F_n R_{mat}^2}
\]

(9)

\[
F_n = \frac{\pi^2 D_D}{b^2}
\]

(10)

where parameters are explained in Table 2 and where \( C(z,t) \) = concentration of solute (in one dimension - i.e. mass per unit depth) at time \( t \) and depth \( z \) (kg m\(^{-1}\)).

Like Equation (6), the model assumes homogeneity of the properties of the porous medium within the two domains and a constant flow velocity. Unlike equation (6), the model assumes that the entire tracer (salt) input enters the RAPS instantaneously as a “spike” at time \( t = 0 \) and depth \( z = 0 \). Even by applying a 65% recovery correction to the 15 kg salt input and by assuming that 650 mg L\(^{-1}\) salt equates to 1000 µS cm\(^{-1}\) conductivity, one is only able to broadly approximate the shape of the conductivity signal in the effluent water (Figure 9).
Table 2. Parameterisation of the Diaz-Goebes and Younger (2004) matrix diffusion model, with explanations of parameters in Equations (7) to (10) and best estimate parameterisations required to yield the curves in Figures 9 and 10. The selected value of $D_D = 0.0006 \text{ m}^2 \text{ h}^{-1}$ ($1.67 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$) is that recommended by Diaz-Goebes and Younger (2004) for other UK salt tracer tests.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Figure 9. Instantaneous “spike” model of input</th>
<th>Figure 10. Mixing tank model of input</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\psi = \text{partition coefficient between standard advective-dispersive porous medium flow (}\psi = 1\text{) and matrix diffusion influenced flow (}\psi = 0\text{)}$</td>
<td>0.3</td>
<td>0.3</td>
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<tr>
<td>$M = \text{mass of tracer injected (kg)}$</td>
<td>9.75 kg</td>
<td>9.75 kg</td>
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<tr>
<td>$n_e = \text{effective porosity of conventional “macro-porous” domain (dimensionless) = } \nu_D / \nu$</td>
<td>25%</td>
<td>19%</td>
</tr>
<tr>
<td>$n_{\text{mat}} = \text{porosity of stagnant micro-porous (matrix) domain (dimensionless)}$</td>
<td>30%</td>
<td>30%</td>
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<tr>
<td>$\nu_D = \text{specific discharge (Darcy flux) (m s}^{-1} )$</td>
<td>$0.00087 \text{ m}^3 \text{ s}^{-1} / 280 \text{ m}^2$ = $3.11 \times 10^{-6} \text{ m s}^{-1}$</td>
<td>$0.00087 \text{ m}^3 \text{ s}^{-1} / 280 \text{ m}^2$ = $3.11 \times 10^{-6} \text{ m s}^{-1}$</td>
</tr>
<tr>
<td>$\nu = \text{linear (hydraulic) water flow velocity (m s}^{-1} ) = 1.025 \text{ m} / T_p$</td>
<td>$0.0446 \text{ m h}^{-1}$ = $1.24 \times 10^{-5} \text{ m s}^{-1}$</td>
<td>$0.0603 \text{ m h}^{-1}$ = $1.67 \times 10^{-5} \text{ m s}^{-1}$</td>
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<tr>
<td>$T_p = \text{dominant transit / residence time in RAPS (time to peak concentration)}$</td>
<td>23 h = 82800 s</td>
<td>17 h = 61200 s</td>
</tr>
<tr>
<td>$D_L = \text{coefficient of longitudinal hydrodynamic dispersion (m}^2 \text{ s}^{-1} )$</td>
<td>$1.27 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$</td>
<td>$1.27 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$</td>
</tr>
</tbody>
</table>
$D_e = $ enhanced dispersion coefficient due to effects of matrix diffusion (m$^2$ s$^{-1}$)

$D_D = $ coefficient of molecular diffusion within matrix blocks (m$^2$ s$^{-1}$)

$R_{mat} = $ apparent retardation factor due to matrix diffusion (dimensionless - not chemical sorption)

$b = $ characteristic dimension (spacing) of rapid flow domain (m)

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value 1</th>
<th>Value 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_e$</td>
<td>$4.33 \times 10^{-6}$ m$^2$ s$^{-1}$</td>
<td>$2.34 \times 10^{-5}$ m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$D_D$</td>
<td>$1.67 \times 10^{-7}$ m$^2$ s$^{-1}$</td>
<td>$1.67 \times 10^{-7}$ m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$R_{mat}$</td>
<td>1.90</td>
<td>2.28</td>
</tr>
<tr>
<td>$b$</td>
<td>0.4 m</td>
<td>0.8 m</td>
</tr>
</tbody>
</table>

**Figure 9. Output from Diaz-Goebes and Younger (2004) model of Tan-y-Garn tracer experiment, with following input data. Mass of tracer added: 15000 g x 65% = 9750 g, mean solute transport time in conventional macroporous domain 23 hrs, RAPS thickness 1.025 m. The “corrected” trace incorporates fluctuations in influent mine water conductivity measured at L1.**
4.3 **Diaz-Goebes and Younger (2004) model with mixing tank**

The matrix diffusion model (Figure 9) successfully simulates the general shape of the effluent breakthrough and the “tailing” effect that can be ascribed to matrix diffusion, but still tends to overestimate initial conductivity.

One possible reason for this could be that all tracer is assumed to enter the top of the RAPS at \( t = 0 \). Thus, the original Diaz-Goebes and Younger (2004) was modified slightly to incorporate a mixing tank effect to the model input. The mixing tank model was based on conventional exponential decay of an initial excess tracer concentration \( C_0 \) (9750 g / 280 m\(^2\) / 0.1 m = 348 g m\(^{-3}\) = 348 mg L\(^{-1}\)) by applying a throughflow \( Q \) of 0.87 L s\(^{-1}\) water and a volume of supernatant lagoon water \( V_{\text{wat}} = 280 \text{ m}^2 \times 0.1 \text{ m} = 28 \text{ m}^3 \).

\[
\ln[C(0,t)] = \ln(C_0) - \frac{Qt}{V_{\text{wat}}} \tag{11}
\]

The new supernatant excess input concentration \( C(0,t) \) for a series of 1 hr time slices was calculated and the Diaz-Goebes and Younger (2004) model was applied for each time slice. The outputs from each slice were then superimposed to produce a final result.

The number of parameters that are potentially adjustable in this model are considerable and therefore, a unique “best fit” solution could not unambiguously be identified. However, the solution in Figure 10 provides a very satisfactory fit to the real data. It will be noted that the mean solute travel time for the conventional macroporous domain had to be reduced from 23 to 17 hrs to obtain a fit. This (as was the case for the long “slug” of tracer in the initial model in Section 4.1) is due to the fact that tracer is entering the RAPS over a prolonged period, leading to the peak effluent tracer concentration apparently being shifted to a later time relative to the start of the tracer application. Thus, failure to account for mixing in the supernatant water initially led to the tracer velocity being underestimated and the travel time being overestimated by around 35% (23 hrs as opposed to 17 hrs).
Figure 10. Output from combined mixing tank / Diaz-Goebes and Younger (2004) model of Tan-y-Garn tracer experiment. (Top) Modelled conductivity of supernatant input water to RAPS by mixing tank model; (bottom) modelled effluent conductivity, with following input data: mass of tracer added: 15000 g x 65% = 9750 g, mean solute transport time in conventional macroporous domain 17 hrs, RAPS thickness 1.025 m. The “correction” in both diagrams shows corrections due to fluctuations in influent mine water conductivity measured at L1.
5. Discussion and Conclusions

It is important to understand the residence time of water being treated in a RAPS unit in order that the performance can be assessed against design expectations, and that future designs may be improved, e.g. by optimising the design residence time (Kusin et al. 2012; Kusin 2013). RAPS operators need to understand how residence time varies with varying flow rates. Previous tracer tests indicate that the Tan-y-Garn RAPS exhibits a predictable pattern (Figure 3a), with residence times decreasing proportionately to increasing flows.

During the operational lifetime of the RAPS there is a possibility that hydraulic “short circuits” (preferential flow pathways through the RAPS matrix) could develop or that porosity and hydraulic conductivity could be reduced by compaction or clogging. Changes in hydraulic conductivity can be monitored by simple application of Darcy’s Law, by monitoring bulk water throughflow rates and hydraulic head gradients (influent less effluent head) across the RAPS. The existence of short circuits and changes in porosity can be monitored by repeat tracer tests, and by comparing results with the early-life correlation of residence time versus flow rate. Alternatively, such tracer tests could be replaced by monitoring of natural tracer signals such as temperature (Taylor et al., in press).

The RAPS Tan-y-Garn has performed very satisfactorily at its main task, injecting on average some 2.9 meq L\(^{-1}\) alkalinity, and 3.9 meq L\(^{-1}\) calcium to the mine water. The RAPS does not behave entirely passively regarding the other components, however: it removes on average 0.55 meq L\(^{-1}\) sulphate from the water, suggesting that sulphate reduction is taking place within the RAPS. Iron has decreased on average by around 1.4 meq L\(^{-1}\) through the RAPS, possibly by precipitation as oxyhydroxides at the RAPS top or as sulphides within the RAPS. During the course of its operation, RAPS bulk
vertical hydraulic conductivity decreased from around 4 m d$^{-1}$ in 2006 to 0.25 m d$^{-1}$ in 2008.

A sodium chloride tracer test carried out at Tan-y-Garn in June 2008 resulted in peak salt concentrations being detected in RAPS effluent 23 hours after salt injection to the raw mine inflow. A retardation of sodium (by a factor of 1.15 to 1.2) relative to chloride was observed, due to reversible cation exchange in the RAPS matrix, resulting in displacement of calcium from ion exchange sites to the effluent water, with concurrent absorption of influent sodium onto exchange sites.

The tracer tests allowed broad estimates of effective porosity (c. 19 - 32%), hydraulic conductivity (c. 0.25 m d$^{-1}$), and solute dispersion (1.2 to 2.2 x 10$^{-6}$ m$^2$ s$^{-1}$) to be deduced. A simple advection/dispersion model was found adequate to simulate the early portion of the tracer breakthrough curve. A more complex model (Diaz-Goebes and Younger, 2004), which accounted for matrix diffusion processes, was necessary to simulate the long tail of the curve, however. It appears that matrix diffusion processes are of great importance in the RAPS, potentially influencing up to 70% of the solute throughflow. Modelling has further demonstrated that lack of consideration of mixing and dilution processes in the supernatant water can lead to overestimation of real residence times and porosity and underestimation of solute throughflow velocities (in the case of Tan-y-Garn, by a factor of at least some 35%). The real mean throughflow time of the mobile pore water fraction was estimated to be of the order of 17 hours (rather than 23 hours), due to this effect. Ideally, conductivity or chemical monitoring of the supernatant water during the course of the test would have assisted in defining the tracer input signal.

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Meteorological data used in Figure 4b supplied by the UK Met Office under terms of licence 010070604.

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