Tracing Ground-Water Movement in Abandoned Coal Mined Aquifers Using Fluorescent Dyes

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ABSTRACT

In shallow, essentially free-draining abandoned coal mine workings, quantitative ground-water tracing using the orange fluorescent dye Sulpho Rhodamine B (CI 45100) provides a powerful hydrogeological tool for determining ground-water flow regimes. However, this is not the case in deep, confined, abandoned coal mine workings where various dyes exhibit a nonconservative behavior due to adsorption onto ferric hydroxide deposits. This is a more significant problem than that of the effects of pH or acidity on fluorescence. Laboratory tests indicate that dyes with sulphonic functional groups should be selected in such situations and that dye concentrations need to be maintained at the highest level commensurate with aesthetic and toxicological conditions.

INTRODUCTION

The prediction of the hydrogeological behavior of coal mined aquifers is difficult because of the possibility of unrecorded workings, random collapse, and associated ponding, and uncertainty over the hydrological behavior of coal barriers (Aldous et al., 1986). However, there is a need for rapid and simple techniques to demonstrate the nature and directions of ground-water flow in such aquifers, for instance when planning the siting of sanitary landfills or assessing possible water inflows to opencast coal mine excavations. The direct investigation of ground-water flow using water tracing techniques is one possibility, but relatively few tracer studies have been previously reported.

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Parsons and Hunter (1972) and Siddle (1985) found Tritium a successful tracer in abandoned coal workings, while Merritt and Angerman (1972) have reported much less success using Fluorescein. Mather et al. (1969) also found Fluorescein unsuccessful when used to study fissure flow in sandstones above and adjacent to old mine workings. Positive results were, however, obtained using common salt (sodium chloride).

Fluorescent dye tracers offer advantages with respect to cost and ease of analysis compared with tritium, and detectability compared to sodium chloride. We have therefore conducted field trials using the fluorescent dye Sulpho Rhodamine B (CI 45100; dye nomenclature and sources are summarized in Table 2). These trials have shown that adsorption onto ferric hydroxide [$Fe(OH)_3$] [which is frequently precipitated on the walls and floor of mined voids (Frost, 1977)] proves a significant problem in the application of fluorescent dye tracer techniques. The results of laboratory experiments to assess the relative adsorption of different fluorescent dyes onto ferric hydroxide are also reported.

FIELD STUDIES

The study was undertaken in the Forest of Dean Coalfield, Gloucestershire, England. Extensive extraction of coal has occurred from 18 seams, of Upper Carboniferous age, which are folded into an elongated asymmetric basin underlain by rocks of the Carboniferous Limestone Series (Trotter, 1942). The Coleford High Delf coal seam was the most important coal worked, and is contained within a massive fractured sandstone, the Pennant Sandstone. Extensive workings occur in two hydrological situations. Those below the elevation of the major surface rivers are now totally water-filled and flow is confined by overlying shales. Those
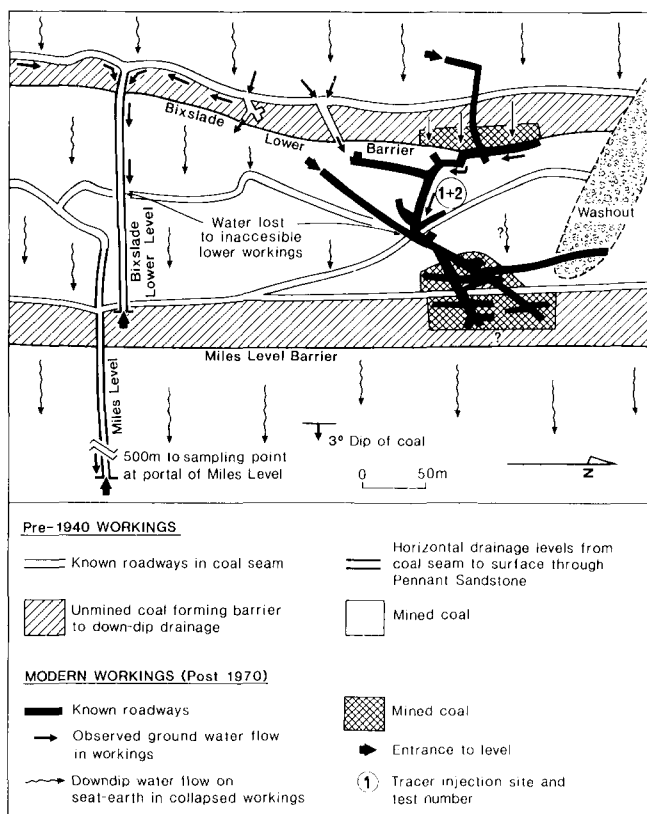
Fig. 1. Plan of workings in the Coleford High Delf coal seam in the catchment area of the Miles Level, compiled from available mine plans. Tracer tests 1 and 2.

above are drained by free-flowing, essentially horizontal drainage levels, discharging to the rivers and the workings are predominantly in the unsaturated zone (Aldous *et al.*, 1986). Three tracer tests were conducted using the fluorescent dye Sulpho Rhodamine B, and analyzed according to the methods described in Smart and Laidlaw (1977) using a Turner 111 filter fluorometer.

Tests 1 and 2: Free Drainage in the Unsaturated Zone

The first tracer tests were conducted under high and low flow conditions within the catchment area of a discharging mine adit known as Miles Level, which drains water from a complex of shallow abandoned workings in the unsaturated zone (Figure 1).

Downdip flow along the surface of the impermeable seat earth which floors abandoned and collapsed workings, is intercepted by major roadways along the strike. Water is diverted into these roadways by barriers of unmined coal, and discharged to the surface via horizontal levels excavated in the Pennant Sandstone. The coal barrier maintaining water flow into Bixslade Level has been perforated by several roadways and, at

the time of the tests, extensive leakage through the barrier was also observed underground in the post-1970 workings. These workings have also affected the Miles Level Barrier, but it was not known if this too had been penetrated, reducing the strike drainage to Miles Level from the north, and detrimentally affecting low flow conditions in the Cannop Brook surface stream (Aldous *et al.*, 1986). The lower workings are inaccessible, and thus the hydrological connections between the accessible workings and the discharge at Miles Level are unknown. Two tracer tests were therefore conducted using 500 ml solutions containing 5 g of Sulpho Rhodamine B dye. These were injected underground in an abandoned mine 0.5 km from Miles Level where a stream (discharge 9.6 ls^{-1} high flow, 2.4 ls^{-1} low flow) disappeared into collapsed workings (Figure 1). No ponding of the water was visible, suggesting that free flow continued beyond the collapsed workings. Samples were collected from Miles Level using an automatic water sampler (48 interval sampler, Rock and Taylor Ltd).

In both tests the tracer was transmitted rapidly to the sample site with relatively little dispersion (Figure 2), indicating that concentrated flow in a channel or conduit continued beyond the collapsed workings.

Using the principles outlined by Stanton and Smart (1981), the channel must be predominantly water-filled because the additional discharge at high flow is accommodated wholly by an increase in velocity, [assuming the width (w) and depth of water (d) in a submerged conduit are constrained, $Q = w \cdot d \cdot v$]. The volume of the conduit may also be calculated using the volume of water discharged from the adit between the time of injec-
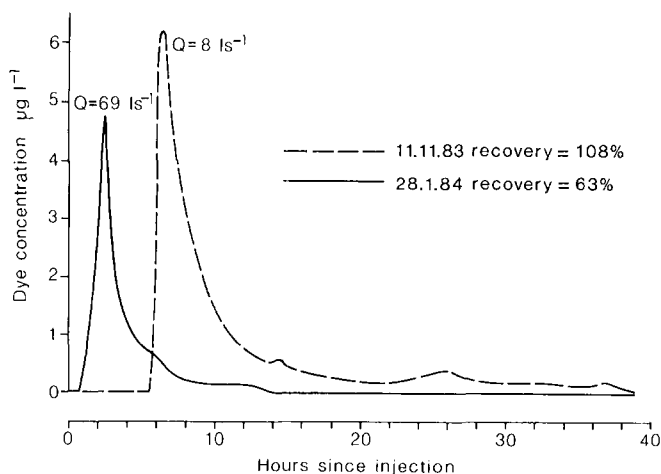

Fig. 2. Time versus concentration curves for tracer tests 1 and 2 in coal mine workings in the unsaturated zone.

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tion and tracer centroid (time at which 50% of the injected tracer passed the sample point). Where there is an increase in discharge down the conduit (in this example, from 9.6 to 69.0 and from 2.4 to 8.0 ls^{-1}), the true volume lies between the value calculated using the minimum (input) and maximum (output) discharge. In this case the calculated volume lies between 500 m^3 and 70 m^3 for high flow conditions and 285 m^3 and 86 m^3 for low flow conditions.

The strike roadways which are tributary to the head of the Miles Level contribute the majority of the portal discharge, the section cut through the Pennant Sandstone yielding relatively little additional flow. Of the total 0.85 km flow path, 0.6 km is downstream of the level head tributaries. Thus, the portal discharge is the most appropriate one to use in the volume calculation. The average for the two tests yields a volume of 390 m^3. For the 0.6 km flow path, this suggests a passage cross-sectional area of 0.65 m^2 compared with the portal value of 0.4 m^2. The significant parts of the remaining flow path must contribute to the conduit volume. One possibility is that the traced water follows the post-1970 roadways downdip into a ponded section cut into the Miles Level Barrier (Figure 1). The difference between high and low flow volume estimates may therefore represent a seasonal change in this ponded volume, and the significant dye loss (see below) observed at high flow may be due to overflow of the barrier in the overlying sandstones into the deeper basin mine workings.

The dye recovery at low flow is complete; the figure is in excess of 100% (108%), suggesting an overestimate of flow from the gauging structure (probable accuracy ±10%). As all the tracer entering the inaccessible workings was discharged at Miles Level, no water can have been lost through the barrier, thus proving its integrity at low flow. However, at high flow the much lower recovery of 63% cannot be explained by gauging error, and a flow distributary must occur (Brown and Ford, 1971). One possibility is that ponding occurs at high flow, permitting water to overflow into adjacent workings which do penetrate the barrier.

Test 3: Water-Filled Mine Workings (Saturated Zone)

Given the success of the initial tests, a third test, using 5 kg of Sulpho Rhodamine B dye, was undertaken in flooded coal mine workings in the saturated zone. This was injected at the bottom of a 3 m diameter, 130 m deep abandoned mine shaft (surface level 100 m AOD) with a standing water
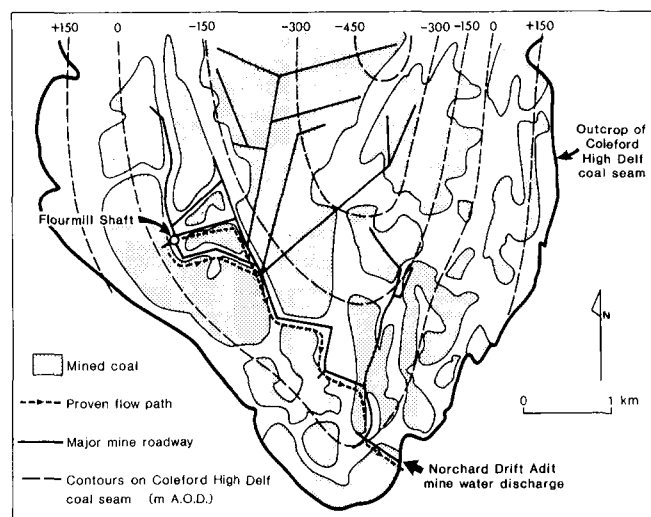

Fig. 3. Plan of workings in the Coleford High Delf coal seam, compiled from abandonment plans, and showing the results of tracer test 3.

level at 26.5 m AOD (Figure 3). Unfortunately, the base of the shaft was choked by 9 m of fallen debris, which precluded direct injection into the workings, which were offset to the side of the shaft.

Access at the surface was limited to a 20 cm diameter vent pipe. The dye was introduced as a powder, and lowered to -19 m AOD before release. It was then flushed into circulation using 28 m^3 of water (equivalent to 6.5% of the total flooded shaft volume) injected via the surface vent pipe from a water tanker. No fluctuations in water levels occurred during the injection period, suggesting a direct connection to the workings.

Samples were collected from the mine water discharge at the Norchard Drift Adit some 3.6 km distant from the injection shaft, using an automatic water sampler. This is the only major outflow draining the deep workings in the Forest of Dean basin. The dye was first detected after seven days (Figure 4), and remained detectable for only 32 hours at the sampling point. This rapid transmis-
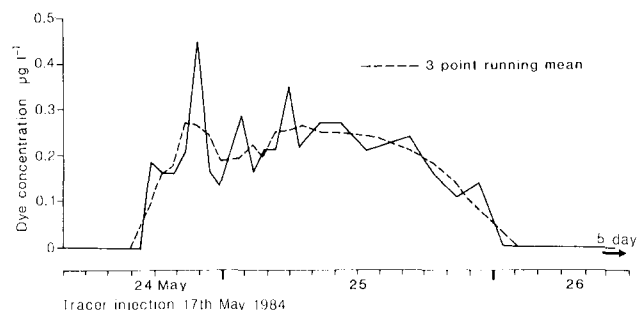

Fig. 4. Time versus concentration curve for tracer test 3, in coal mine workings in the saturated zone.

Table 1. Results of Tracer Tests Conducted in Coal Measures Aquifers

Location	Tracer	Injection site	Tracer quantity	Distance km	Recovery %	Travel velocity m/d
Forest of Dean Coalfield, UK (this study)	Sulpho Rhodamine B	Underground stream	5.0 g	0.5	108	1840
	Sulpho Rhodamine B	Underground stream	5.0 g	0.5	63	16000
	Sulpho Rhodamine B	Shaft	5.0 kg	3.6	1	460
South Wales Coalfield, UK (Parsons and Hunter, 1972)	Fluorescein	Shaft	?	1.7	ND	—
	Tritium	Shaft	50 Ci	1.7	97	363-162
South Wales Coalfield, UK (Mather et al., 1969)	Fluorescein	Borehole	1.4 kg	0.1	ND	—
	Fluorescein	Borehole	1.4 kg	0.15	ND	—
	Fluorescein	Borehole	13.6 kg	0.2	NC	921
	Fluorescein	Borehole	15.9 kg	0.35	ND	—
	Sodium Chloride	Borehole	152 kg	0.1	ND	—
	Sodium Chloride	Borehole	1016 kg	0.15	62	570
	Sodium Chloride	Borehole	2032 kg	0.35	15.3	88

ND — not detected; NC — not calculated.

sion indicates conduit flow; and the flow velocity is comparable to the rates reported in other tracer studies from coal mine workings (Table 1). The flow velocities are lower than those measured in the free drainage zone. (This would be expected as a lower hydraulic gradient exists.) However, the very rapid clearance of the dye indicates remarkably little longitudinal dispersion during transmission through the workings, which suggests conduits with relatively uniform dimensions, few dead zones and a high discharge (see discussion in Stanton and Smart, 1981). Therefore, it can be concluded that only the major roadways remain open as ground-water conduits. The adjacent mined areas, which were unsupported longwall or pillar and stall workings, are now largely collapsed, and contribute little to water transmission. The breakthrough curve (Figure 4) is bimodal suggesting the overlap of two separate pulses of dye transmitted through separate conduits with different travel times. Inspection of coal mine abandonment plans (Figure 3) shows that two major haulage roadways interconnected the discharge adit and the injection shaft. The roads bifurcated at the base of the shaft and rejoined 0.4 km later.

The dye recovery in this third test is very low (1%), and is unlikely to be easily explained by dis-

charge of dye via an alternative outlet. The lack of a significant low concentration tail on the dye breakthrough curve suggests that after the initial water injection into the shaft, little additional dye entered the ground-water circulation. This was confirmed on May 25 when 31% of the dye injected was still present within the injection shaft. In general, continuous flow at the tracer injection site is desirable to ensure movement of the tracer into the regional ground-water flow.

Sixty-eight percent of the injected tracer still remains unaccounted for, and given the failure of the other tracer tests using fluorescent dyes reported in the literature (Table 1), the low recovery indicates a nonconservative behavior of the tracer. In the case of Fluorescein, this could be due to reduction of dye fluorescence by the low pH of many mine waters, but Sulpho Rhodamine B is not affected until pH values fall below 3.5 (Laidlaw and Smart, 1982). Since typical pH values for the Norchard Drift are between 6.7 and 7.0, it must therefore be concluded that dye adsorption onto mineral surfaces is responsible for this non-conservative behavior. Laboratory experiments have demonstrated relatively small contrasts in adsorbence onto different mineral types (Smart and Laidlaw, 1977), and a field rate of dye loss

Table 2. Common Names, Colour Index Number, Generic Name and Manufacturer of the Fluorescent Tracer Dyes Tested

Fluorescent dye	CI[1]	CI[2]	Manufacturer
Lissamine Yellow FF	56205	Acid Yellow 7	Brico Commercial Chemicals Co. Ltd.
Fluorescein	45350	Acid Yellow 73	Brico Commercial Chemicals Co. Ltd.
Pyranine	59040	Solvent Green 7	Bayer Dyestuffs Ltd.
Sulpho Rhodamine G	45220	Acid Red 50	Farbwerke Hoechst AG
Sulpho Rhodamine B	45100	Acid Red 52	Farbwerke Hoechst AG
Intracid Rhodamine WT	—	Acid Red 388	Crompton and Knowles Ltd.
Tinopal CBS-X	FB351	—	Ciba-Geigy UK Ltd.

FB — Fluorescent brightener.
CI[1] — Colour Index Constitution number.
CI[2] — Colour Index Generic name as given in the Colour Index (SDC & AATCC, 1971-1982).

comparable to the 2.5% per day quoted for limestone conduits by Stanton and Smart (1981) for Rhodamine WT dye might be expected. The much higher rate actually found in coal mined aquifers (approximately 7.5% per day) may therefore be due to strong adsorption onto ferric hydroxide precipitated onto the walls of the mined voids (Frost, 1977). A series of laboratory experiments were undertaken to investigate this possibility.

THE ASSESSMENT OF DYE ADSORPTION BY FERRIC HYDROXIDE

Seven fluorescent dyes (Table 2) were compared in laboratory experiments, to assess their adsorption potential onto ferric hydroxide [$Fe(OH)_3$]. Two variables were used: adsorbent concentration and dye type. Two different adsorbents were used, freshly prepared ferric hydroxide and kaolinite [British Pharmocopeia Clay (Evans Medical)]. The ferric hydroxide was prepared by neutralizing (to a pH of 7.0 ± 0.1) a known concentration solution of ferric chloride with sodium hydroxide. A known weight of adsorbent and dye of selected concentration (prepared in distilled water), was sealed in a bottle, kept in the dark, shaken every 12 hours and left for 48 hours until a true equilibrium was established. The temperature was constant at 20°C ± 1°C. Blanks of both dye and sediment were also prepared. The blanks of dye alone were used to correct for any decay of the dye solution with time, while those of ferric hydroxide and kaolinite permitted subtraction of the background fluorescence. Blanks constituted about 20% of all samples run in the experiment.

The effects of varying ferric hydroxide concentration on adsorption of the seven fluorescent dye tracers with a solution concentration of 100 μg/l are shown in Figure 5A. These results

demonstrate that even at low ferric hydroxide concentrations, adsorption is present, but to a similar extent as that observed for identical concentrations of kaolinite (Figure 5B). At ferric hydroxide con-
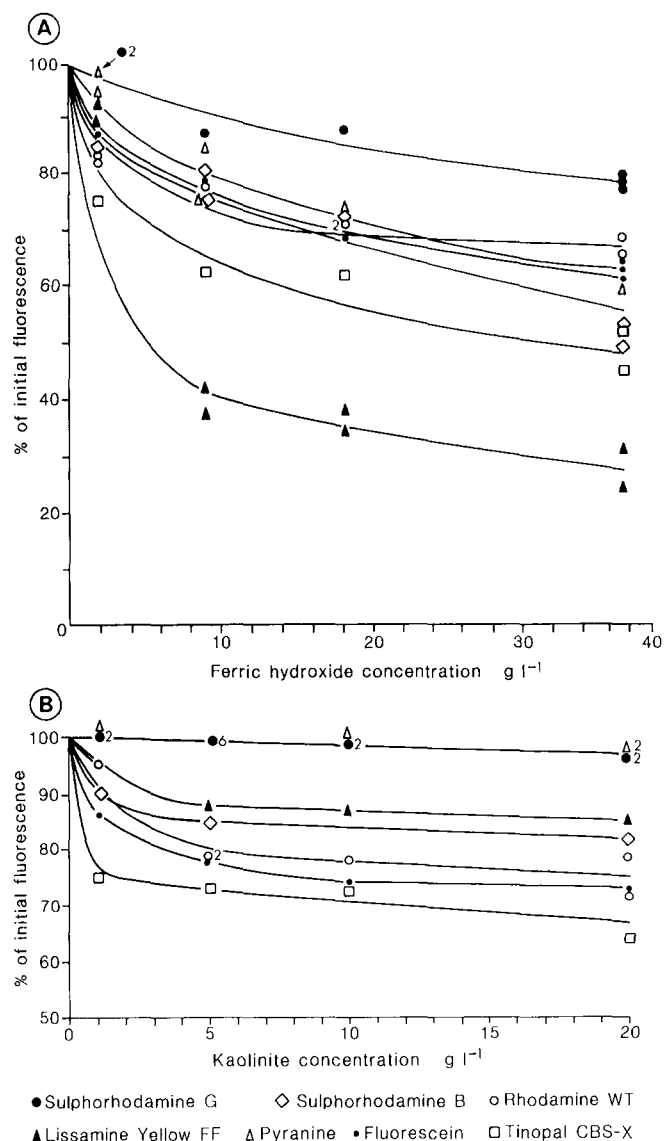

Fig. 5. Comparison of fluorescent tracer dye adsorption on ferric hydroxide (A) and kaolinite (B).

• Sulphorhodamine G ◇ Sulphorhodamine B o Rhodamine WT
▲ Lissamine Yellow FF △ Pyranine • Fluorescein □ Tinopal CBS-X

centrations of 9.5 g/l Tinopal CBS-X, Sulpho Rhodamine G and Pyranine all show increased absorbence by the ferric hydroxide in comparison to kaolinite. At high concentrations, ferric hydroxide adsorbed more dye than kaolinite for all the fluorescent tracers tested. For Sulpho Rhodamine G, the absorbence was about seven times higher than for kaolinite at 20 g/l. This dye has the highest resistance to adsorption onto ferric hydroxide of those tested, while Sulpho Rhodamine B (the dye used in our field trials), Rhodamine WT, Pyranine, and Fluorescein have only moderate resistance to adsorption. The most readily adsorbed dye was the green fluorescent dye Lissamine Yellow FF, whose losses were as high as 70% at a ferric hydroxide concentration of 38 g/l. In comparison, at the same ferric hydroxide concentration, average losses were 40% for Fluorescein, Pyranine, Rhodamine WT, Sulpho Rhodamine B, and Tinopal CBS-X. Dye losses were typically 20-25% greater than those observed for kaolinite at high ferric hydroxide concentrations and 5-10% greater at lower concentrations.

A second experiment under identical conditions was conducted, using a constant concentration of ferric hydroxide of 38 g/l and varying concentrations of the seven dyes ranging between 2.5 μg/l and 50,000 μg/l. This experiment demonstrates that percentage losses of the dyes in batch systems increase as dye concentrations decrease (Figure 6). Thus the greater tracer dilution in field test 3 probably also contributed to the low recovery reported. Dye concentrations therefore need to be maintained at the highest level commensurate with aesthetic considerations (visible colouration ca. 30 μg/l) and safety. A maximum design concentration of about 10 μg/l is recommended on toxicological grounds by Smart (1982, 1984).
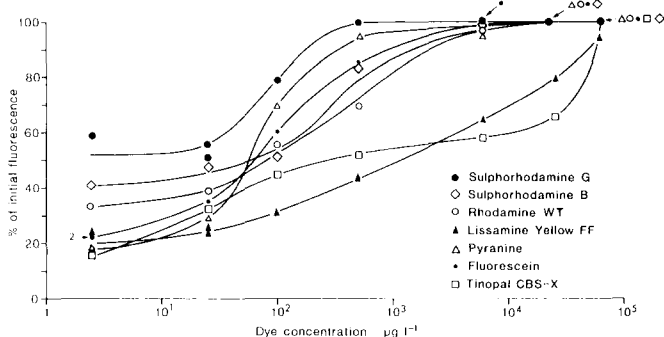

Fig. 6. Effect of dye concentration on percentage adsorption on ferric hydroxide at a constant concentration of 38 g/l.

DISCUSSION

The field tests reported here have confirmed earlier studies reported from the literature, and demonstrate that concentrated conduit flow can occur through mined voids in Coal Measures aquifers. The hydraulic characteristics of these voids are comparable to those of the natural cave conduits observed in karstified limestone aquifers which have similarly high flow velocities (Smith and Atkinson, 1972). They report a mean value of 3500 m/d for 40 tracer tests in the White Limestone of Jamaica and 7400 m/d for the 23 tests in the Central Mendip Hills, England. Similar interpretation techniques may therefore be used for the tracer tests, yielding information on network geometry, passage configuration and volume, and the extent of flooding. The field studies presented have illustrated some of these applications.

Fluorescent dyes cannot be considered as conservative tracers in mined Coal Measures aquifers because there is substantial adsorption of them onto the ferric hydroxide which frequently coats all surfaces of the mined voids and which may also be in suspension in the mine waters. Such sorption of dye is in contrast to their behavior in karstified limestone aquifers. This problem is more significant than pH effects due to the acidity of mine waters, providing dyes with sulphonic acid functional groups are selected (Smart and Laidlaw, 1977). Of the seven fluorescent dyes examined, Sulpho Rhodamine G appears to offer the best resistance to adsorption onto ferric hydroxide, and will be the subject of future tests.

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