AL(OH)₃ CLOGGING IN SALT INTERCEPTION SCHEME BOREHOLES AT BOOKPURNONG, MURRAY BASIN: THE ROLE OF PYRITE AND HYDROXY-SULFATE MINERALS IN ANCIENT COASTAL ACID SULFATE SEDIMENTS

Paul Shand[1], Julianne James-Smith[2], Todd Hodgkin[2], Rob Fitzpatrick[1], Stuart McClure[3], Mark Raven[3], Andrew Love[2], Mick Stadter[2], Tony Hill[2]

[1] CRC LEME/CSIRO Land and Water, PMB 2, Glen Osmond, Adelaide, SA 5064
[2] Department of Water, Land and Biodiversity Conservation, Grenfell Centre, Grenfell Street, Adelaide, SA 5000
[3] CSIRO Land and Water, PMB 2, Glen Osmond, Adelaide, SA 5064

INTRODUCTION

Clogging of boreholes by an amorphous white precipitate, identified as amorphous aluminium hydroxide, occurred during pump testing of salt interception scheme (SIS) boreholes in the Loxton Sands at Bookpurnong in the Murray Basin (AWE 2004; Harrington 2004). The clogging, which did not occur during previous testing of boreholes at Loxton, caused a decrease in efficiency of around 80% and led to significant clogging of pumps and impellers (Figure 1).


Figure 1. Clogging of pump and impellers by amorphous Al(OH)₃ (from James-Smith *et al.* 2005).

Aluminium is amphoteric i.e. it is soluble under both acidic and alkaline conditions. The solubility of gibbsite is shown on Figure 2, along with the dominant species at different pH. High dissolved Al concentrations are well known in association with acid mine drainage (AMD) and disturbed acid sulfate soil (ASS) environments where associated waters are very acidic (pH often < 2-3). Other areas include acidic surface waters in poorly buffered hard-rock catchments (Shand *et al.* 2005). Although Al is theoretically soluble under high pH conditions, under natural conditions dissolved Al is often much lower than equilibrium concentrations due to complexation reactions. The groundwaters that were affected by clogging were slightly acidic to neutral in terms of pH, where Al should only be present at a few μg l⁻¹.

An earlier study, using the limited mineralogical data available, proposed that the Al was derived from the oxidation and hydrolysis of Fe^{2+}, which was present in the upper Loxton Sands (Harrington 2004):

$$Fe^{2+} + 2H_2O + 0.5\ O_2 + e^- \rightarrow Fe(OH)_3 + H^+$$
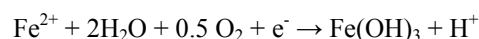
The origin of acidity by hydrolysis of Fe^{2+} has also been postulated as the driving mechanism for acid generation in the low pH Lakes of Western Australia (McArthur *et al.*, 1991). Several criteria were suggested, based on results from the initial study site, for predicting potential occurrences of clogging: (i) high dissolved Fe (> 25 mg l⁻¹); (ii) low buffering species; and (iii) Al in an available form e.g. sorbed to minerals or organic matter (Harrington 2004). However, a borehole with low concentrations of dissolved Fe and high buffering capacity was subsequently found to clog and the model was called into question.
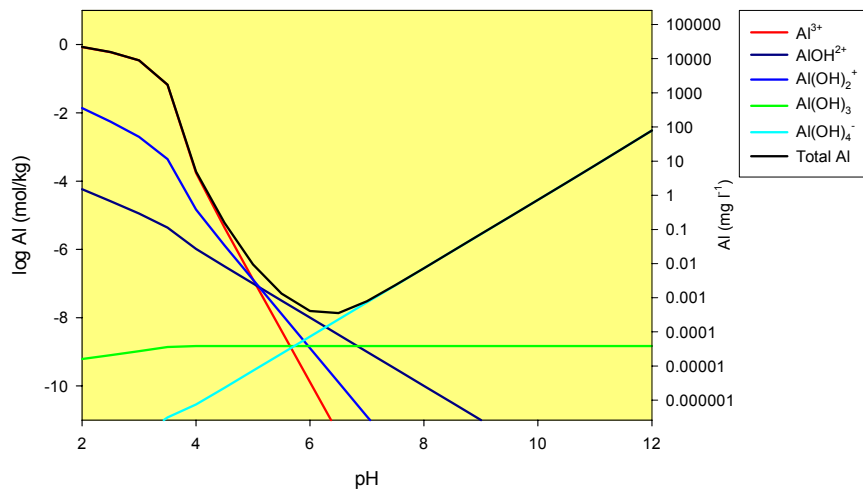
Figure 2. Solubility of gibbsite ($Al(OH)_3$) under varying pH conditions (calculated using PHREEQC2). Total solubility is high under acidic and alkaline conditions with minimum solubility at circumneutral pH.

Oxidation of pyrite is one of the most acid producing reactions in nature. However, it was not considered as a potential source of acidity at Bookpurnong because it was not detected in core material using X-ray diffraction. Pyrite oxidation is complex a mechanism and proceeds by a variety of steps, but the overall reaction is as follows:

$$2FeS_2 + 15/2O_2 + 5H_2O \rightarrow 2FeOOH + 4SO_4 + 8H^+$$
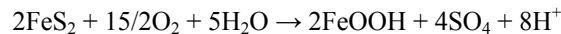
The aim of the current study is to re-evaluate the existing model and assess other potential sources of acidity using hydrochemical data and scanning electron microscopy. The following three boreholes were studied in detail: borehole A, where clogging was first observed and most extensive; borehole B, in which clogging did not occur during initial testing but occurred subsequently (where the groundwater had high buffering capacity and low dissolved Fe), and borehole C, where clogging was not observed.

GEOLOGICAL BACKGROUND
The Loxton Sands are of Late Miocene to Late Pliocene age and comprise a sequence of lower and upper shoreface, beach, estuarine, dune and back-barrier lagoonal sediments, forming a relatively thin (10-20 m) but extensive sedimentary sequence (Hill *et al.* 2004; Munday *et al.* 2004). There is an overall coarsening upwards sequence in the Loxton Sands, typically from offshore shelf mud to relatively upper shore facies coarse sands.

Groundwater mounds have formed beneath irrigation districts close to the River Murray leading to mobilisation of salt and higher fluxes to the river (Hill *et al.* 2004). Consequently, salt interception schemes are planned close to the Murray River to intercept and abstract saline groundwater from the Loxton Sands at Loxton and Bookpurnong. Conceptual models for the geology and aquifer characteristics were developed using drill-core lithological characterisation, ground and airborne geophysics, and hydrogeological testing (AWE 2004; Munday *et al.* 2004), aiding in the optimum design and location of SIS.

RESULTS

Hydrochemical data
The groundwaters in the Loxton Sands aquifer at Bookpurnong are saline and of Na-Cl type. A pronounced redox boundary is present in the aquifer at Bookpurnong (James-Smith *et al.* 2005), close to the water table and at the transition from shallow coarser orange-red sands to deeper finer-grained grey silty sands. This boundary has been used to separate the Loxton Sands into upper (ULS) and lower units (LLS). Downhole logging results showed that the aquifer is strongly stratified, with higher electrical conductance (EC) in the Lower Loxton Sands (Figure 3), the change occurring close to the redox boundary. The limited hydrochemical data from samples collected during pump tests at boreholes A and B showed that water chemistry changes, becoming less saline with time. The data from borehole A (using data from AWE 2004) are shown on Figure 4. The borehole was screened across the redox boundary at this site and the results show that the source of groundwater changed from mainly LLS initially to ULS over the duration of pumping.

There was also an overall decrease in pH during pumping, and an increase in SO_4/Cl ratio at the time of clogging to values above that found in both units prior to pumping. Pump testing at borehole B also showed a decrease in pH and EC, but no overall trend in SO_4/Cl.
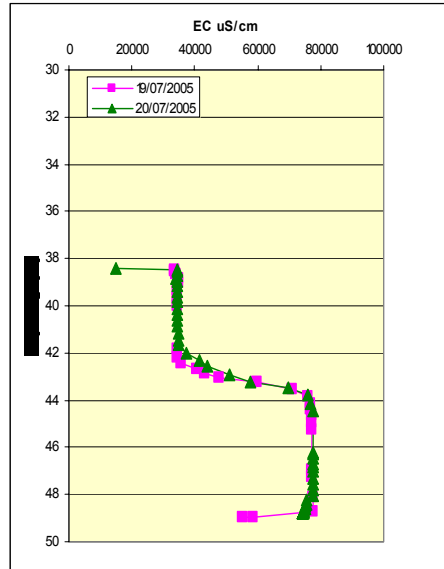
Figure 3. Downhole electrical conductance profiles of groundwater in borehole B showing lower EC in the upper Loxton Sands above ca. 42 m depth (from James-Smith & Shand, 2005).
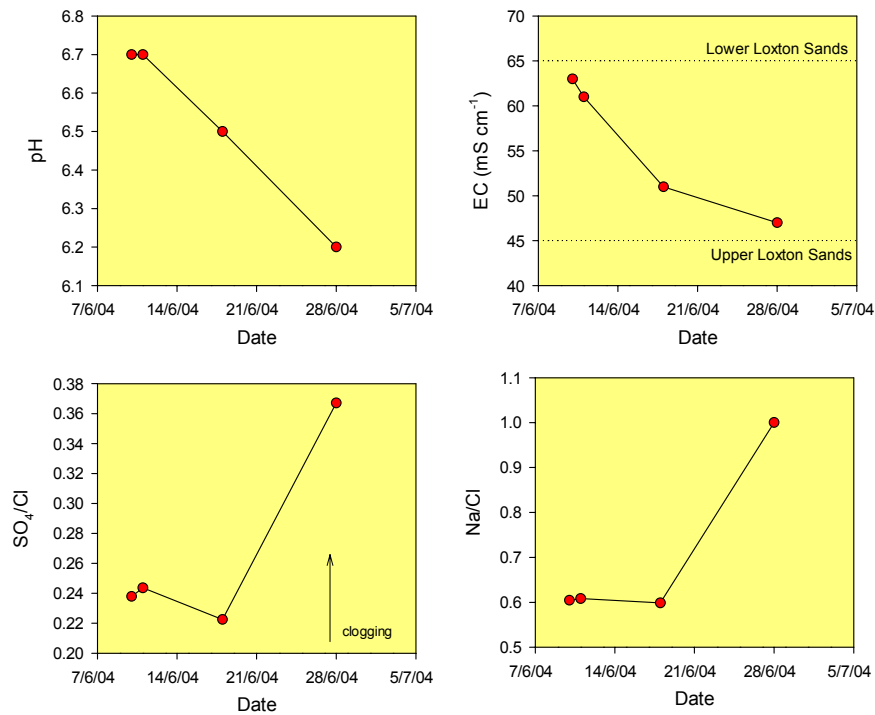

Figure 4. Hydrochemical data collected during a pump test of borehole A. Dotted lines show EC of upper and lower Loxton Sands groundwater.

Scanning electron microscopy (SEM)

Samples for SEM were collected from stored core material at the three sites, mounted on aluminium stubs and evaporatively coated with carbon. The specimens were placed in a Phillips XL30 FEG-SEM with an attached EDAX DX4 energy dispersive X-ray system, using primary electron beam energy of 10-20 KeV. Imaging was performed using the secondary electron (SE) signal where information about surface topography was required, and the back scattered (BSE) signal where information about chemical composition was required. Energy dispersive X-ray (EDX) analyses were completed to determine the chemical composition of individual points on mineral surfaces. Selected images, from different depths at each site, are shown on Figures 5 to 7.

Samples from above the redox boundary in borehole A were an orange-brown colour and sand grains were coated with Fe oxyhydroxide minerals (Figure 5). Occasional euhedral crystals of a hydroxy-sulfate mineral with a composition intermediate between alunite ($KAl_3(SO_4)_2(OH)_6$) and jarosite ($KFe_3(SO_4)_2(OH)_6$) (Al:Fe 2:1) were present in association with Fe oxyhydroxide coatings. Pseudomorphs of Fe oxyhydroxides, with the texture of framboids, indicate alteration of original pyrite. Below the redox boundary at ca. 45 m, pyrite was abundant, forming both framboids and octahedra (Figure 5). Secondary sulfate minerals were also abundant, forming coatings on grains (in close association with pyrite) and as lath shaped crystals forming bridges between sand grains. EDX analysis indicated that these grains were natrojarosite ($NaFe_3(SO_4)_2(OH)_6$), in contrast to alunite-jarosite at shallower depth. Preliminary X-ray diffraction data has confirmed the presence of natrojarosite as well as jarosite and szomolnokite ($FeSO_4.H_2O$) in this sample. Pyrite and hydroxysulfate minerals were also abundant at 52 m depth, but the sulfate minerals here were intermediate between natrojarosite and natroalunite ($NaAl_3(SO_4)_2(OH)_6$). The presence of these hydroxyl-sulfate minerals, which are only stable at very low pH and under very oxidising conditions, indicate previous episodes of sulfide oxidation. The Eh-pH stability fields of pyrite and alunite/jarosite do not overlap and their presence together represents a case of extreme disequilibrium. Samples from the fossiliferous Lower Loxton shells beneath the LLS at 60 m depth, contained abundant calcite as well as framboidal pyrite, but no sulphate minerals. Siderite ($FeCO_3$) was also relatively abundant especially below the redox boundary.
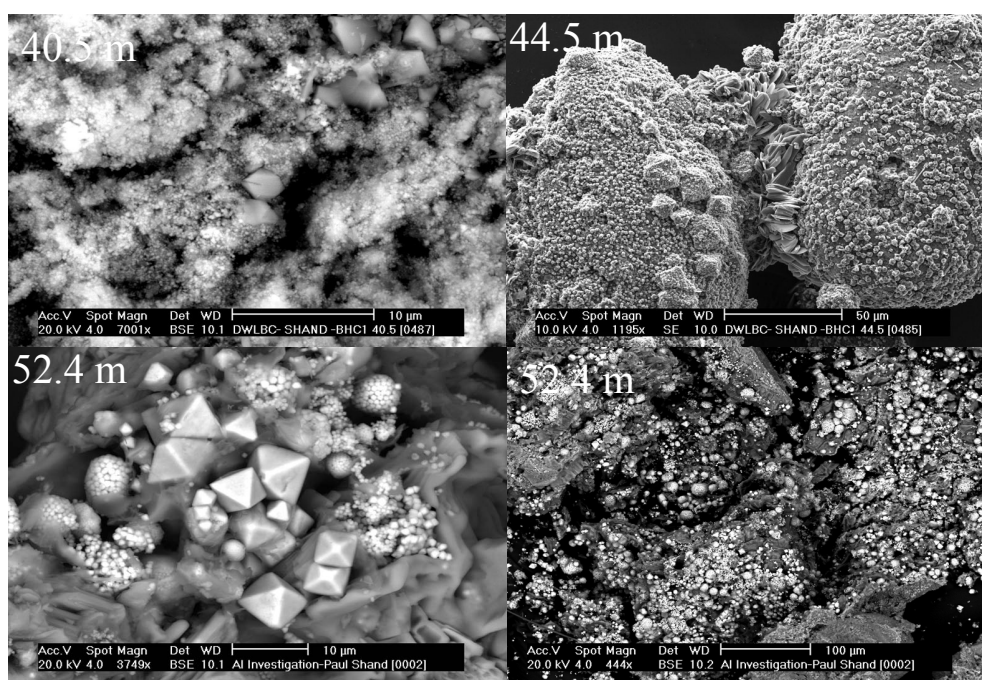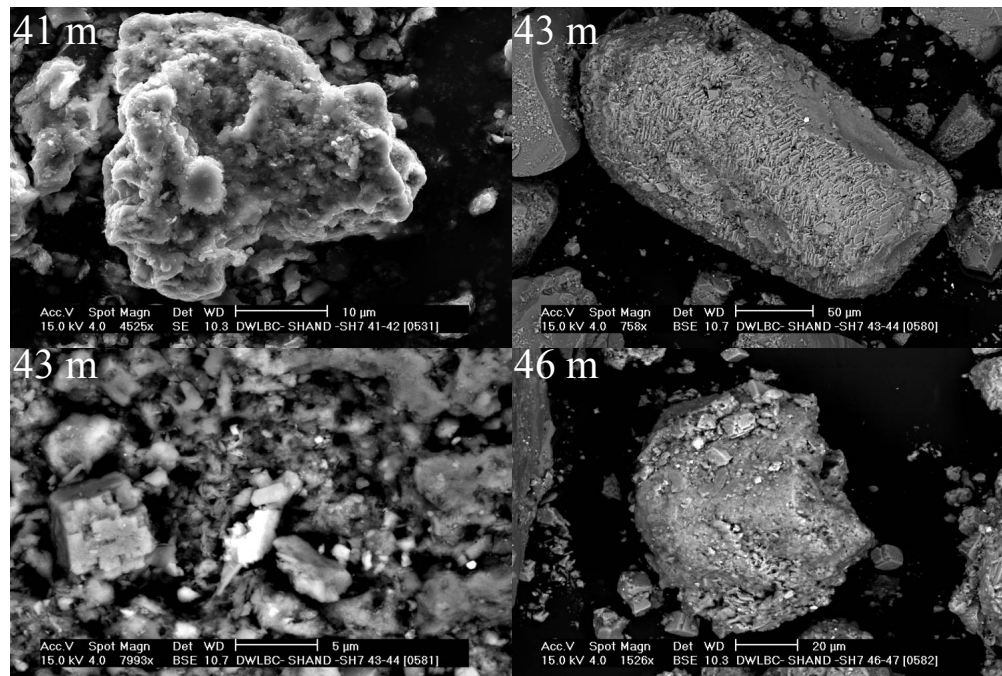

Figure 5. SEM images of samples from borehole A (sample depths shown in metres). 40.5 m: Fe oxyhydroxide coating of sand grains with euhedral to subhedral crystals of alunite-jarosite; 44.5 m: two sand grains coated with abundant euhedral (cuboid and octahera) pyrite and bridging laths of hydroxysulfate mineral (natrojarosite); 52.4 m (left image) framboidal and octahedral pyrite intermixed with natrojarosite-natroalunite; (right image) abundant framboidal pyrite (bright) on sand grains.

SEM images from borehole B are shown on Figure 6. Pyrite was mainly present as framboids, although not as abundant as borehole A, and no secondary hydroxysulfate minerals were identified. Gypsum was occasionally found, forming subhedral crystals as well as siderite (Figure 6). Pyrite was difficult to find in

samples from borehole C, but was present as occasional framboids (Figure 7). In contrast to the other samples, calcite was relatively abundant both as detrital grains and shelly material (probably aragonite).
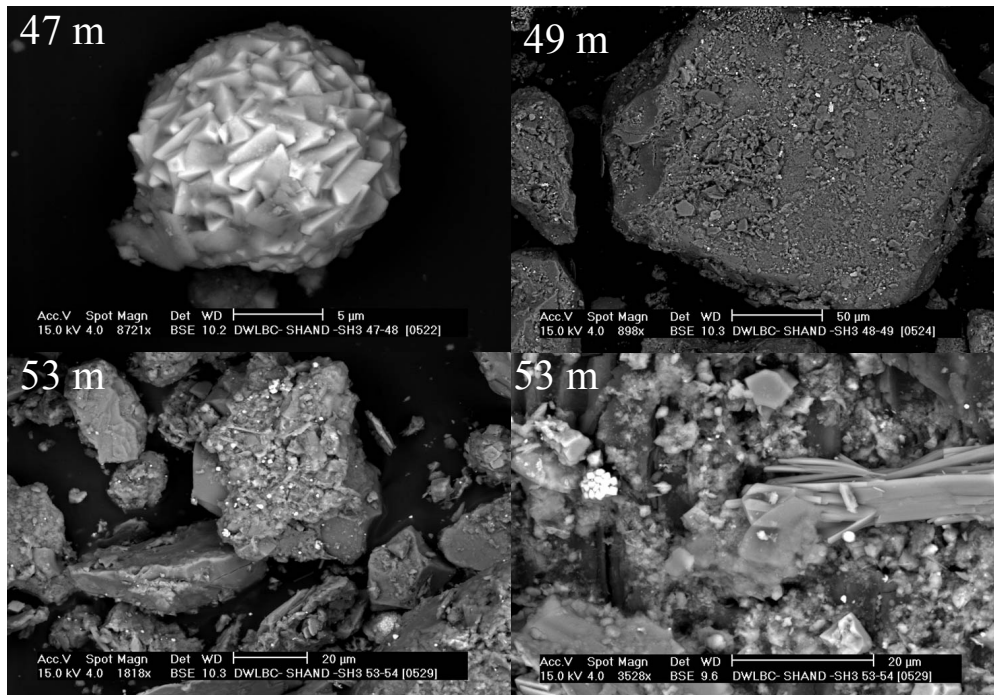
Figure 6. SEM images of samples from borehole B (sample depths shown in metres). 47 m: pyrite framboid; 49 m: two sand grain with pyrite (bright) on surface; 53 m (left image) small grains of pyrite and framboid (lower right); (right image) framboidal pyrite (left), gypsum (right) and siderite (lower right centre).

Figure 7. SEM images of samples from borehole C (sample depths shown in metres). 41 m: sand grain coated in Fe oxyhydroxide; 43 m: large calcite grain with minor pyrite (bright); 43 m: siderite (centre left), illmenite (large bright crystal, centre) and minor disseminated pyrite (small bright grains); 46 m: minor pyrite (bright) on sand grain.

DISCUSSION AND SUMMARY

The presence of pyrite and secondary hydroxysulfate minerals (which act as stores of acidity) provide a basis for reassessing previous models for Al mobilisation and transport in the Loxton Sands at Bookpurnong. Whereas previous models did not account for a full mass balance for hydrogen ions, the presence of pyrite and minerals of the alunite-jarosite group provide a primary source of acidity, capable of mobilising Al. Two observations must be taken into account in the formulation of a conceptual model: (i) clogging did not occur initially and (ii) pH in discharge water was not low enough to dissolve high amounts of Al. This implies that pumping induces acidification and/or mobilisation of Al and, in addition, that the transport must be localised and not controlled by the ambient pH conditions as represented by discharge water. A conceptual model has been developed whereby cavitation and lowering of the water table towards the redox boundary introduced oxygen and induced acid production and Al mobilisation at the redox boundary itself. Mixing of this locally-derived acidic groundwater with circumneutral pH water from above and below the boundary induces rapid Al precipitation on borehole screens and in particular at the pump inlet. This model explains the delay in clogging as well as the conflicting hydrogeochemistry (high Al concentrations at circumneutral pH). Mobilisation of hydroxysulfate minerals, noted only in borehole A, is also indicated by the large increase in SO_4/Cl ratios at this site. The presence of these minerals as a source of both acidity and Al, as well as the presence of pyrite, needs to be taken into account in future predictions of clogging at SIS schemes.

The variety of pyrite forms and the differences in hydroxysulfate mineralogy are likely to be controlled by a range of environmental factors including redox environment, solution chemistry, different degrees of S saturation, differences in solid phase mineralogy etc. Little is known about the controls on pyrite micromorphology but differences in precursors (e.g. polysulfides or monosulfides) may play an important role. Knowledge of these processes will help provide useful indicators for assessing the changing environmental conditions, which give rise to such complex mineral assemblages and allow better predictions of their response to new imposed environmental conditions.

REFERENCES

AWE 2004 Bookpurnong Salt Interception Scheme: Clogging Investigations. November, 2004.

HARRINGTON, N. 2004 Investigation into the precipitation of Al-hydroxide during pumping of bores at Bookpurnong (Western's Highland site) in relation to groundwater quality in the Loxton Sands aquifer. DWLBC Report 2004/40.

HILL, A.J., HOPKINS, B.M., MUNDAY, T.J., HOWES, N.M., JAMES-SMITH, J.M., YAN, W., WILSON, T.C., BERENS, V., RAMMERS, N., TELFER, A.L. & HOWLES, S.R. 2004 Loxton-Bookpurnong salt interception schemes – taking a multidisciplinary approach to the refinement of an informed hydrogeological model. The 9th Murray-Darling Basin Groundwater Workshop, 2004.

JAMES-SMITH, J. & SHAND P. 2005 Aluminium hydroxide clogging of boreholes in a Tertiary sand aquifer adjacent to the River Murray, Bookpurnong, South Australia. Abstract, "Where Waters Meet" Conference, NZHS-IAH-NZSSS Auckland 2005.

JAMES-SMITH, J., SHAND, P., HODGKIN, T., HILL, T., STADTER, M. AND LOVE, A., 2005 Aluminium hydroxide clogging of wells, Bookpurnong, South Australia: Conceptual model and Environmental risks. South Australia. Department of Water, Land and Biodiversity Conservation. DWLBC Report 2005/40.

MCARTHUR, J.M., TURNER, J.V., LYONS, W.B., OSBORN, A.O. & THIRLWALL, M.F. 1991 Hydrochemistry on the Yilgarn Block, Western Australia: Ferrolysis and mineralisation in acidic brines. *Geochimica et Cosmochimica Acta*, **55**, 1273-1288.

MUNDAY, T.J., HILL, A.J., WILSON, T., HOPKINS, B., TELFER, A.L., WHITE, G.J. & GREEN, A.A. 2004 Combining geology and geophysics to develop a hydrogeological framework for salt interception in the Loxton Sands aquifer, Central Murray Basin, Australia. CRC LEME Open File Report 180.

SHAND, P., HARIA, A. H., NEAL, C., GRIFFITHS, K. J., GOODDY, D.C., DIXON, A. J., HILL, T., BUCKLEY, D.K. & CUNNINGHAM, J. E. 2005 Hydrochemical heterogeneity in an upland catchment: further characterisation of the spatial, temporal and depth variations in soils, streams and groundwaters of the Plynlimon forested catchment, Wales. *Hydrology and Earth System Sciences*, **9(6)**, 611-634.