

# Chemical characterisation of core pore-waters for deep borehole investigations at Sellafield, Cumbria

M. Cave  
S. Reeder  
R. Metcalfe

*Analytical Geochemistry Group, Fluid Processes Group, British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK.*

## Introduction

A site near Sellafield, north-west England, is currently being assessed by UK Nirex Ltd for its suitability to host a radioactive waste repository. At this site, a sequence of relatively permeable sedimentary cover rocks, consisting mainly of Permo-Triassic red beds, overlies a sequence of low permeability Ordovician volcanic basement rocks, the Borrowdale Volcanic Group (BVG). A major part of the investigation has been the chemical characterisation of the groundwaters in these varied lithologies, in order to aid the interpretation of groundwater flow paths and water-rock interaction. This has involved sampling groundwaters from deep (up to ca. 2km) boreholes. However, the coverage of such sampling is restricted by the relatively low frequency of fractures from which groundwater flow can be induced and from which waters can be collected. This means that often only relatively large-scale hydrochemical variations down a borehole may be resolved using samples obtained from these zones. It is therefore desirable to construct continuous geochemical profiles down the boreholes using alternative sources of data as an additional interpretation tool. One source of such data are geophysical logs. However, these usually allow only an indication of gross salinity variations down a borehole. Chemical data may also be extracted from core samples collected from down the borehole. The purpose of the present paper is to describe the evaluation of such data using (a) pore-water extraction from relatively low porosity sandstones by inert, heavy liquid displacement centrifugation and (b) aqueous leaching of residual solutes.

## Methods

Core samples were preserved at approximately 25m intervals by wrapping in plastic film and aluminium foil then coating with a thick layer of wax immediately on removal of the core from the borehole. On return to the laboratory, the samples were unwrapped and the outer 1–2cm annulus trimmed from the core and discarded. The

remaining material was broken into fragments of cm diameter and separated into three subsamples. The first aliquot was used to determine the sample moisture content by heating at ca. 110°C for in excess of 12 hours. The second portion of sample was preserved by the addition of the inert heavy liquid 1,1,2-trichloro-1,2,2-trifluoroethane and subsequently centrifuged, using the heavy liquid to displace any pore-water. Finally, an aliquot of the core was milled to <350µm diameter and dried at ca. 110°C for a minimum of 12 hours before accurately weighing ca. 5g into a centrifuge tube. 30ml of distilled water was then added and the sample shaken at room temperature for approximately 24 hours. The supernatant leachate was then centrifuged, filtered and preserved for subsequent chemical analysis. Determinations carried out on the pore-waters and aqueous leachates were: pH and alkalinity by automated titration; Na, K, Ca, Mg, Si, Ba, Sr, Mn, Fe, Al and Li by ICP-AES; Cl, SO<sub>4</sub>, NO<sub>3</sub> and Br by ion chromatography; total organic and inorganic carbon by TOC analyser.

## Results and Discussion

Chemical analysis of these pore-waters and aqueous leachates gives data comprising of a combination of the *in-situ* pore-waters and associated contaminants. For the displaced waters, the contamination arises from infiltration of drilling fluid (containing a lithium tracer) into the core material. For the aqueous leachates, the sources of contamination are more complex, as there is a significant contribution arising from dissolution of the rock matrix as well as contamination derived from the infiltrating drilling fluid. The aqueous leachates must also be corrected using the original sample moisture content in order to obtain *in-situ* compositions.

For simple two-component systems, in which only true pore-water solutes and contaminant drilling fluid were present, the raw data have been reconstructed by a simple mathematical reduction. This involved the subtraction of a component representative of the contaminant composition and proportional to the extent of

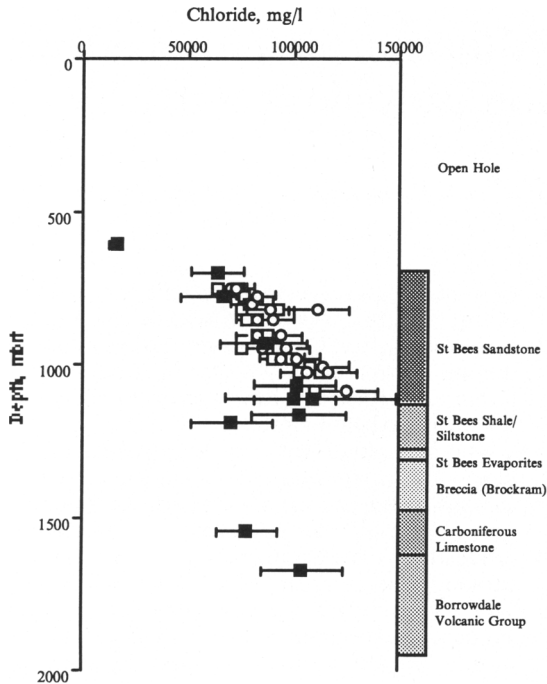


FIG. 1. Pore-water chloride

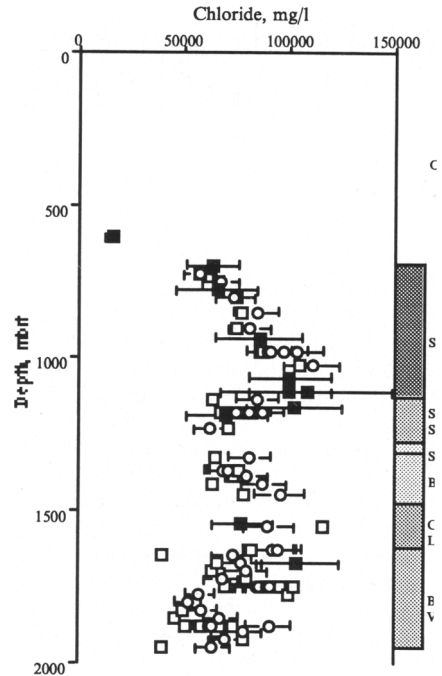


FIG. 2. Aqueous leachate chloride

contaminant contribution (estimated from the Li concentration). This approach is only valid for the reconstruction of the extracted pore-waters and conservative elements in the aqueous leachates, e.g. Cl and Br.

For the more complex systems, a novel methodology that uses Principal Component Analysis (PCA) has been applied to the data to resolve the pore-water contribution from the drilling fluid contamination and dissolution products. Target Factor Analysis (TFA), using independently derived groundwater data, has been used to validate the PCA model. These multivariate statistical analysis techniques have also been applied to the simple two-component systems in order to compare reconstruction methods.

Figs. 1 and 2 represent chloride compositions obtained from extracted pore-waters and aqueous leachates respectively. Data reconstructed by simple mathematical reduction (open circles) and multivariate statistical analysis (open squares) are shown, as well as groundwater data obtained from hydraulic tests (closed squares)

These profiles indicate that both pore-water extraction and aqueous leachate test data, when corrected by either of the reconstruction methods, produce chloride compositions which show excellent agreement with those obtained from discrete

flowing groundwaters. However, whilst some other reconstructed determinands (e.g. Br, Na and possibly Mg, Ca, Sr and  $\text{SO}_4$ ) also agree closely with corresponding groundwater compositions, others (e.g. Si, K and  $\text{HCO}_3$ ) give compositions that are enhanced with respect to expected values.

### Conclusions

Data obtained for pore-water extracts are relatively easy to reconstruct and derive reliable results for a wide suite of determinands. However, pore-water extraction was possible only from the more porous sandstones from the cover sequence (Fig. 1) and, therefore, the applicability of the technique is limited. Aqueous leaching, however, can be carried out on all types of test material, although the data require more complex analysis in order to quantify the residual solute component. Further work is required to understand the mechanisms of the leaching process in order to provide an insight as to why some determinands have elevated concentrations in the pore-waters and leachates compared to groundwaters sampled directly. However, the techniques described here have the potential to allow the reconstruction of more detailed chemical profiles than would normally be possible using conventional data.