

Geochemical impact of seepage from a Canadian oil sands tailings pond: A radial diffusion cell study

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In Northern Alberta, Canada, the first of several oil sands tailings facilities has been constructed atop glaciofluvial outwash channels that are buried by surficial clays and till. Process-affected (PA) water from such ponds is expected to infiltrate through the low permeability sediments and affect the underlying sand channel aquifer(s). These channels are highly permeable and have the capacity to act as migration pathways, facilitating the release of tailings pond seepage into nearby surface water bodies. However, the nature and significance of this impact are not known.

In this study, radial diffusion cell experiments [1] were conducted to characterize the biogeochemical processes that control the composition of the ingressing PA seepage as it interacts with the glacial till sediments. The focus was on major ions contributing to salinization and the evolution of redox chemistry.

Following the addition of PA water into the aquitard sediment core, ion exchange led to a decrease of Na contained in the PA water and the release of pre-bound Ca, Mg and K. Elevated NO₂, NO₃ and high SO₄ concentrations were mitigated by reduction reactions – the latter in contrast with earlier findings from similar sediments [2]. Cl unexpectedly showed evidence of release from the sediments into the core reservoir, which is attributed to electrochemical migration to maintain charge neutrality.

[1] van der Kamp *et al.* (1996) *Water Resour. Res.*, **32**, 1815-1822. [2] Holden *et al.* (2011) *J. Contam. Hydrol.*, **119**, 55-68.

Measurement of four-isotope sulfur ratios on SHRIMP-SI

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The recent postulation that metabolic pathways may leave a detectable signal in the fractionation of the four sulfur isotopes (³²S, ³³S, ³⁴S & ³⁶S), potentially gives the geochemist another tool in the search for the earliest life on Earth and beyond.

However, accurate and precise measurement of the minor isotope ³⁶S presents significant analytical challenges, even for conventional gas-phase analysis. We have developed a multi-collector ion-microprobe analysis protocol that collects in-situ 4-isotope S data from both sulphates and sulphides. Valuable spatial information is maintained.

Data are acquired using a 3nA Cs⁺ primary beam focussed to a 25µm spot on the target. S isotopes are detected in faraday cups, which contain slit sizes appropriate to resolve any unwanted hydride interferences. Secondary S⁻ beam signals are determined using our new in-house Iflex temperature and humidity controlled electrometers. Each Iflex has 3 selectable resistors (10¹⁰Ω, 10¹¹Ω, 10¹²Ω) and a 27pF capacitor so that the detection system can be tuned to the appropriate beam intensity. Under such conditions pyrite targets yield approximately 2GHz ³²S, 16MHz ³³S, 88MHz ³⁴S, and 0.3MHz ³⁶S.

The low abundance ³⁶S isotope can be collected in either current or charge mode. Charge-mode detection eliminates the dead-time correction, drift in detector response and linearity issues associated with electron multipliers. In addition, response times are much faster than high (>10¹¹Ω) Ohmic resistors. Experimentation suggests that charge-mode delivers superior data quality over electron multipliers down to 50kHz, and 10¹²Ω resistors up to 1 Mhz and thus neatly bridges the “gap” between conventional electrometers and ion-counting.

Provisional data yields external 2 s.d. uncertainties for Δ³³S and Δ³⁶S that are better than 0.3‰ and 0.5‰ respectively, which are comparable to conventional analyses, but using several orders of magnitude less material. At this level of precision, documented anomalies of 2‰ can be easily resolved making SHRIMP a viable alternative to the protracted extraction procedures necessary for gas-phase analysis.