

14th INESON meeting, Thursday 25th November 2004: Programme

14.00 – Registration and afternoon tea

14.45 Introduction to the Ineson Meeting 2004.

Mike Rivett, Hydrogeological Group of the Geological Society.

14.50 Predominance and mineral stability diagrams revisited.

Dr. David Kinniburgh, British Geological Survey

Garrels and Christ (1965) introduced the concept of predominance and mineral stability diagrams to geochemistry. These diagrams have appeared in every textbook of geochemistry since then. The procedure used for calculating the diagrams did not solve the chemical speciation problem directly but was based on simplified linearised equations. This meant that it was necessary to ignore certain processes completely, including some that are of interest to environmental geochemists, such as adsorption, ion exchange and solid solution formation. This reduces the usefulness of the diagrams especially for trace elements. It is now feasible to calculate the diagrams using a full chemical speciation, e.g. with PHREEQC2, thereby including all of these processes. This makes the diagrams more believable. They are particularly useful for understanding complex 'real-world' situations where it can be difficult to appreciate the interplay between the many interactions involved. Much is familiar in the new diagrams but there are some surprises too! The new approach should find application in environmental geochemistry, aquifer management, water treatment and corrosion science.

15.20 Predicting mine water pollution from first principles.

Professor Steve Banwart, Sheffield University

Source term modeling is a critical part of environmental risk assessment for mine water pollution. Such modeling requires the prediction of the rate of mineral weathering reactions that generate and attenuate the dissolved loads of metals from mine water discharges. A long-standing discrepancy in observed weathering rates between observations made in laboratory experiments on single minerals and weathering at catchment scale is also observed for mine sites. This discrepancy is important because it creates significant uncertainty, both in the conceptualization of reactive transport processes, and consequently in the quantitative prediction of contaminant source strength and attenuation that underpins environmental assessment. One consequence of this discrepancy for mine sites is their suitability as geological observatories to study weathering processes in detail. If the discrepancy could be resolved for mine sites, this would shed light on factors that could be general and significant for catchments and aquifers as well.

Field studies at Europe's largest copper mine at Aitik, Sweden have demonstrated that weathering rates of rock at the field site are to a large degree predictable from just a few, readily-available, critical, bulk-averaged physico-chemical characteristics. Fundamental descriptions of mineral dissolution reactions, based on the transition-state theory of chemical kinetics, proved essential to the extrapolation to field scale of mineral dissolution rates observed in lab studies. This suggests that existing compilations of mineral dissolution rate laws and rate constants obtained in lab studies may be applicable for *a priori* estimation of field weathering rates. Recent research that attempts to address some of the complexity inherent in field sites shows that mineral dissolution rates observed from studies of individual minerals do not necessarily show the same behaviour when reacting within whole-rock, polymineralic assemblages. Current research also demonstrates that the impact of spatially-variable flow and solute transport plays a significant role in the scale-discrepancy between lab and field weathering rates, and needs to be conceptualized and quantified in reactive transport models for risk assessment of mine sites.

Chair: John Chilton, IAH British National Committee

15.50 Professor Stephen Foster, New President, IAH

Ineson Lecture 2004

15.55 Geochemistry, groundwater and pollution – learning by modelling.

Dr. Tony Appelo, Amsterdam.

Hydrogeochemistry is a difficult subject because many chemical and physical processes interact to form the quality of groundwater. Generally, interpretation starts with setting up a hydrogeological framework that provides basic ideas about the flowlines through the subsoil, the residence times in various units, the infiltration areas, and the likely variations in time and space that may have affected water quality. However, the hydrogeological information is often scanty and a hydrogeologist will maintain that tracers are necessary for delineating the flowpath of water in the hidden subsoil. To ensure that his information is consistent with only one law (Darcy's), a hydrogeologist uses and needs numerical groundwater models. It goes without saying that a hydrogeochemist, who in addition relies on Fick's laws for calculating diffusion and dispersion, on Guldberg and Waage's law of mass action for equilibria, on the law of mass balance in general, and on kinetic laws which are indefinite, also cannot do without a numerical model. He is fortunate to have PHREEQC for the intricate job of modeling water quality along a flowline. PHREEQC can combine the calculation of equilibria among water and minerals, exchangers and complexing surfaces, and of any kind of irreversible or kinetic reaction with advective and diffusive/dispersive transport. A graphical user interface allows direct plotting of the results on-screen, making it a learning tool that enables testing of ideas, in addition to being a professional instrument for checking interpretations and predictions.

In the lecture, the procedures of modeling groundwater quality are illustrated. First, a case is discussed of tritium/helium dating of groundwater which shows the effects of dispersion and mixing in a phreatic aquifer. Second, the concept of retardation is revisited. Linear retardation has often been applied in hydrogeochemical transport models and the formula is useful for guessing, but incorrect for a substance with a curved sorption isotherm. It is even invalid when various species interfere in the sorption reaction, as will be shown for a case of acid mine drainage with transport of U(6) and precipitation of reduced U(3) in confining layers that contain pyrite. Third, it will be discussed that the model is not finished. Notably, the chemical database needs critical inspection and extension. For surface complexation of heavy metals, the database stems from laboratory experiments in which CO₂ is carefully excluded, but in which then also HCO₃⁻, the dominant anion in fresh water, is removed. Actually, HCO₃⁻ is quite important for sorption of oxyanions like arsenate and arsenite. In Bangladesh, the high alkalinity of groundwater may displace sorbed As from iron-oxyhydroxide and increase the concentration of As to far beyond the drinking water limit. Also, sorption of HCO₃⁻ will affect ¹⁴C dating of groundwater by retardation. For example, oxyhydroxides in the Bunter sandstone in the East Midlands (Sherwood) aquifer may contain as much HCO₃⁻ sorbed, as is dissolved in the groundwater, implying that the conventional (uncorrected) ¹⁴C ages of water could be twice higher than the hydraulic residence time.

Examples and input-file templates for PHREEQC are available at: www.xs4all.nl/~appt/index.html

17.00 Discussion

17.15 Wine reception and finger buffet (£8.50 payment at reception)