Semail Ophiolite (Oman)

Description: The Semail Ophiolite in Oman natural analogue has been used to collect data and information on chemical and microbiological controls in high pH systems analogous to the cement interstitial waters. The natural analogue is constituted of unusually high pH springs (pH = 11.5 at 34°C) derived from the alteration (serpentinization) by percolating groundwaters of ultramafic minerals (olivine, pyroxene) contained in the Semail Ophiolite Nappe (Lippard et al., 1986). The serpentinization reaction, schematically written as (Bath et al., 1987a) :

$$1.8\ Mg_{1.85}Fe_{0.16}SiO_4\ (\text{olivine}) + Mg_{0.892}Ca_{0.018}Fe_{0.09}SiO_3\ (\text{pyroxene}) + 3.17\ H_2O$$

$$\text{===>}\ 1.39\ Mg_3Si_2O_5(OH)_4\ (\text{serpentine}) + 0.375\ Fe(OH)_2 + 0.018Ca^{2+} + 0.0306\ OH^-$$

combined with the leaching of trapped sea salts drives the dilute meteoric recharge waters to moderately saline Na-Cl-Ca-OH spring waters. These spring waters show in addition a marked reducing character (Eh ~-300 mV) with high partial pressures of hydrogen and sulfide contents in the 20 ppm range. These hyperalkaline waters undergo rapid modifications in the vicinity of the springs, by dissolution of carbon dioxide and precipitation of calcite and by mixing with other surface groundwaters, which leads to the precipitation of calcite, brucite and serpentine minerals.

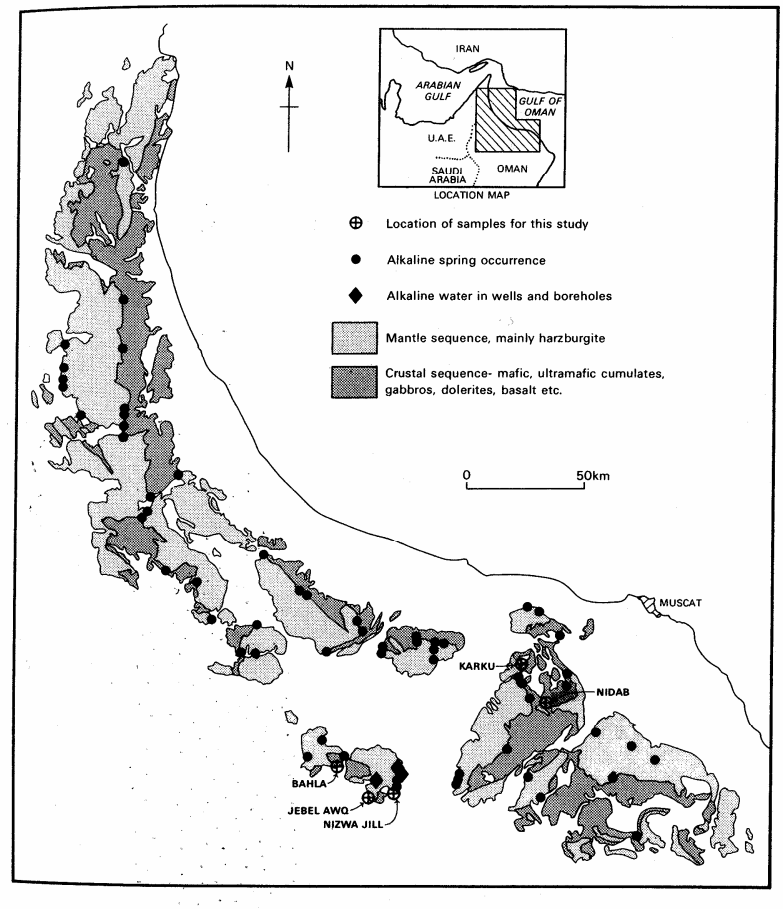

Figure 1: Distribution of ophiolites and hyperalkaline springs in northern Oman. The name and location of the five sampling sites (7 springs) is indicated. (After Bath et al., 1987a)

Several spring waters were sampled and studied in 1986 within a project funded by UK Nirex and Nagra (McKinley et al., 1988). The main topics of interest were :

– the comparison between measured and predicted concentrations of several key elements (U, Th, Ni, Pd, Se, Sn, Zr) and the evaluation of uncertainties in speciation modelling

– the identification of microbial populations or species that are active in this high pH environment
– the potential role of colloids in high pH waters

Table 1 reports typical values for pH, Eh and major elements found in the hyperalkaline springs.

pH	Eh (mV)	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	S^{2-}	HPO_4^-
11.44	-363	258	11.2	72	<0.1	351	2.39	26	0.95

Table 1: Measured parameters and concentrations in the spring water from the Karku site. The water temperature is 35.7°C and concentrations are given in mg/l (after Bath et al., 1987).

The confrontation between measured and predicted concentrations of trace elements has raised several important issues addressing both basic science and methodology. Trace elements of interest were generally below the state-of-the-art detection limit of 1986. One of the important issues is the assessment of the redox state of traces, provided that several major redox couples are not in equilibrium or miss important species (eg polysulfides). The case of U is particularly interesting and observations from the Karku site suggest significant U association with colloidal material.

A wide range of microorganisms is found to have adapted to the natural alkaline groundwaters, although the counts of bacteria remain low (< 10^3 ml^{-1}). Growth and activity limiting factors seem to be both high pH and low availability of specific nutrients like phosphate in particular. The observation of active sulphate-reducing bacteria associated with clostridia type bacteria is an important finding because of the potential impact of SRB on steel corrosion.

Relevance: The pH level of the Oman springs corresponds to pH levels that will be encountered in degraded cements but not in fresh or slightly altered concrete (pH ~13 during the alkali period and then pH ~12.5 as long as portlandite buffers the system). An interesting feature is the marked reducing character of the spring waters. The residence time of waters is not specified or bracketed in the reports but is probably much longer than what can be achieved in the laboratory : concentration data of metals are thus expected to be closer to equilibrium than in short term tests.

The Oman springs waters give thus access to specific intensive parameters (concentration level of metals, etc) in a unique window of water composition that is relevant for a high pH cementitious near-field. These data can be checked against the state of the art in speciation modelling and against thermodynamic databases. Information on U association with colloids and on active microbes in hyperalkaline environments is also relevant for qualitatively supporting PA scenarios of a cementitious near-field.

Position(s) in the matrix tables: Cement, near field

Limitations: The Oman natural analogue suffers several important limitations :
– several elements of interest (e.g. Zr) are probably source limited in the system and this moderates the operational conclusions that can be driven
– the dataset is rather limited due to the few sampling campaigns

Modelling attempts conducted in this study also have several limitations :
– the basic knowledge of trace element speciation has evolved since 20 years and the conclusions of this study need reassessment in this respect
– the solubility modelling is based on pure mineral phases of the traces ; actual control of traces could also be sorption or co-precipitation

Quantitative information: Important quantitative information on the range of viable microorganism concentration at pH ~11. This information needs to be scaled as a function of available nutrients in an actual repository. Solubility models based on pure mineral phases are shown to be conservative.

Uncertainties: Because trace element concentration levels in the spring waters were in general below detection limit, it is not possible to conduct a complete evaluation of speciation/solubility calculations. Chemical data on the source rocks and fracture mineral is also needed in order to check possible source term limitations.

Time-scale: The lack of information on the residence time of waters is a problem for scaling the data to laboratory or repository scale. Some insight about seasonal variations of water flow and chemistry could be useful.

PA/safety case applications: The Oman study has been used to test a number of geochemical codes and databases used to predict radionuclide solubility in safety assessments.

Communication applications: None known.

References:

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Added value comments: None

Potential follow-up work: The Oman alkaline springs deserve further investigation with respect to following aspects:

- since 1986, the knowledge of actinide speciation in reducing conditions has evolved a lot and the modelling exercices should be conducted again. In the same way, trace analysis techniques have been improved and resampling of the sites is of potential interest
- other trace elements solubility should be included in the future modelling exercices : in particular Fe, As, Cr, REE, Ra, Pb
- the initial findings on U bearing colloids need further field sampling combined with lab experiments on colloïds
- compare viable SRB in Oman with Maqarin microbes

Keywords: Cement, near field, speciation, solubility, U, Th, Ni, Pd, Se, Sn, Zr, colloids, microbiology, hyperalkaline, sulphate-reducing, SRB, modelling, Oman

Reviewers and dates: Laurent Trotignon (CEA) (October 2004).