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Natural analogue studies: present status and performance assessment implications

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Abstract

Studies of natural geological and archaeological systems as analogues to long-term processes, which are predicted to occur within a radioactive waste repository environment, have become increasingly popular over the last 10 years or so, to the extent that such studies form an integral part of many national programmes for radioactive waste disposal. There is now a common consensus that the natural analogue approach is a very useful scientific methodology to: (a) identify and understand processes and mechanisms analogous to those which could occur in the vicinity of a repository over realistic timescales, (b) derive input data which have been successfully used to test some of the laboratory-based models which form the basis of long-term repository performance assessment, and (c) to produce data which can be input directly to performance assessment models. Increasingly, analogues are playing an important role in public awareness, enabling the layman to understand better the concept of radioactive disposal and demonstrating the reliability of the disposal system over long periods of geological time.

The complexity of geological systems means that it is very often difficult and sometimes impossible to quantify precisely the physico-chemical boundary conditions necessary to model a particular geochemical process or mechanism. Consequently, the availability of quantitative analogue data is limited when repository performance assessments are considered. However, this in no way detracts from their value in building confidence by demonstrating that important processes do exist and by showing qualitatively that they behave in a way predicted by models based on laboratory-derived data.

The transfer of natural analogue data from the complexity of field studies to simplistic models which, by necessity, are used in performance assessments, is an area of activity which is presently being addressed. Field analogue studies are now being planned to interface with laboratory experiments and, ultimately, with in situ field experiments. This is a promising avenue of research

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which should provide a more quantitative use of natural analogue data in testing and further developing models used in (or supporting) repository performance assessments. © 1997 Elsevier Science B.V.

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1. Introduction

The study of natural analogues or natural geological and archaeological systems and their relevance to understanding the complexity of repository performance over long periods of time has been generally recognised, and analogue studies are now an integral part of most national programmes for the geological disposal of radioactive waste. This is reflected in the increasing number of completed and on-going national and international analogue studies described in the literature and the many articles relating such studies to repository performance assessments (e.g. see reviews and references therein by Chapman et al., 1984; Pearcy and Murphy, 1991; Miller et al., 1994; Smellie et al., 1995; McKinley and Alexander, 1996, and publications by the Commission of the European Communities, Natural Analogue Working Group – CEC NAWG, 1986a,b, 1989, 1991, 1994, 1996). There is now a common consensus that studies of natural systems or analogues form the basis of understanding repository processes and therefore play a major role in the derivation of performance assessment codes. Consequently, the analogue approach is a very useful methodology to: (a) identify and understand geological processes and mechanisms analogous to those which could occur in the vicinity of a repository over realistic timescales, (b) derive input data that have been successfully used to test some of the laboratory-based models which form the basis of (or provide input to) long-term repository performance assessment, and (c) produce data which can be input directly to performance assessment models (e.g. matrix diffusion depths). Furthermore, analogues are playing an increasingly important public relations and educational role through the use of brochures, video films, and travelling exhibitions etc., by enabling the layman to understand better the concept of radioactive waste disposal and by demonstrating the reliability of the disposal system over suitably long periods of time.

There is a general feeling, however, that natural analogue studies have now reached a threshold of usefulness and applicability to repository performance assessment. The geological and archaeological systems being studied are inherently complex, such that it is very often difficult and sometimes impossible to quantify adequately the physico-chemical boundary conditions necessary to model a particular geochemical process or mechanism. This in no way detracts from their major value in building confidence in the conceptual models by demonstrating that important processes do occur (both the expected and unexpected), and by showing qualitatively that most behave in a way predicted by models based on laboratory- and in situ-based data. Nevertheless, the apparent failure of natural analogue studies to impact quantitatively on performance assessment issues has to be recognised, and the reasons behind such a failure have to be addressed before further progress can be made.

2. Present use of analogues

2.1. Direct use

Few performance assessments have specifically referred to the direct use of analogue data; one major exception noted by McKinley and Alexander (1996) is the Nagra Kristallin I performance assessment (Nagra, 1994) where analogue input was referenced in sections relating to: (a) building confidence in the assessment, (b) development of assessment methodology and models, (c) engineered barriers, (d) matrix diffusion, etc. Other exceptions, to a lesser degree, include the SKB-91 assessment (SKB, 1992) and the PNC-H3 assessment (PNC-92, 1992). At the other extreme, Yucca Mountain assessments (e.g. Wilson et al., 1994) made no reference to direct analogue use.

Direct use of analogues in repository performance assessment tends to be considered under the general headings of quantitative (or hard), i.e. numerical input to performance assessments, qualitative (or soft) and public relations or awareness (Miller et al., 1994; Smellie et al., 1995). Quantitative or hard use is limited to: (1) corrosion rates of canister materials (from the study of archaeological metal artefacts), (2) the stability of the bentonite backfill/buffer (from studies of naturally occurring bentonite selected from varying temperature and pressure environments), (3) measuring the range of penetrative depths of natural radionuclide diffusion into crystalline rock matrices (which is a particularly critical parameter for performance assessment), and (4) check geochemical codes and thermodynamic databases used to provide solubility limits (another key performance assessment parameter set).

Qualitative or soft use (i.e. building confidence in the conceptual models by demonstration) is by far the major application of analogue data. Many examples have been documented, such as propagating redox front movement related to trace element mobility and retardation (MacKenzie et al., 1992; Hofmann, 1997), clay as a hydraulic barrier to groundwater flow (Cramer and Smellie, 1994), the radionuclide retention properties of clay (Hooker et al., 1985; Bros et al., 1993), and the present lack of evidence to support significant groundwater radionuclide transport by colloid material (e.g. Degueldre, 1991; Miekeley et al., 1992). Regarding public relations, the Cigar Lake uranium occurrence is a commonly used example since generalised disposal concept features (e.g. spent fuel, clay barrier, repository depths) can be conveniently related to the location and geometry of the deposit. Furthermore, the fact that there is no surface expression of the Cigar Lake deposit, which is one of the world's largest uranium deposits, located at repository depths (approx. 420 m) in water saturated sandstones, is a strong argument to the layman in support of the long-term reliability of a high-level waste repository.

Natural analogues can be used to study specific long-term evolutionary processes of importance, for example site saturation, geochemical modification of backfill/buffer materials, fuel dissolution, etc. Repository evolution can be described as a sequential series of geochemical processes comprising both transient and steady-state steps. This was well illustrated in the Poços de Caldas study (Chapman et al., 1992) where the evolution of redox front formation was detailed. The sequence of formation of the redox front involved both transient steps (before and during front evolution) and steady-state steps (following front evolution). By using a combination of time-related approaches (e.g. uranium decay series, rate of erosion, etc.) a good quantitative estimation of the evolutionary time for this phenomenon to occur was obtained.

2.2. *Indirect or hidden use*

Natural analogue data are also used indirectly in performance assessment. This is best exemplified in the systematic development of scenarios, where a large number of features, events, and processes (FEPs) of importance to the isolation of radioactive waste require to be identified and described (Andersson et al., 1989; Eng et al., 1994). Examples of FEPs include precipitation/dissolution, sorption/co-precipitation, radiolysis, physical properties of the waste package, physical properties of bentonite backfill and cement/concrete, gas production and migration, microbial activity, etc.

The role of natural analogues, together with laboratory- and in situ-derived data, is to support or otherwise the inclusion of different FEPs in scenario development. For example, a repository scenario case for nuclear criticality (i.e. due to fissionable ^{239}Pu or ^{235}U in spent fuel) was tested by comparison with the Oklo reactors in Gabon, even though the critical mass in spent fuel is much greater than at Oklo due to lower enrichment (Brehrenz and Hannerz, 1978). At Oklo, the fact that criticality did occur in nature, knowledge of the prerequisites for the nuclear reactions and the course of the criticality event etc. provided strong natural analogue input in these scenario discussions. Another example is the radiolysis of water at the exposed waste surface; this is very difficult to study experimentally at relevant dose rates and model, therefore, the assessment of the consequences of radiolysis in the repository is, to a large extent in some disposal concepts, based on observations from analogues such as Oklo (Curtis and Gancarz, 1983) and Cigar Lake (Karlsson et al., 1994; Smellie and Karlsson, 1996). Furthermore, the conclusion from laboratory experiments that humic and fulvic acids at low concentrations are relatively unimportant as complexing agents in deep groundwater is supported by numerous analogue studies. This can be compared with earlier opinions (e.g. KBS-2, 1978) when it was still assumed that natural organics could possibly influence spent fuel dissolution.

This increasing use of analogue data in scenario development is encouraging. It reflects both the fact that more analogue data are being published in the open literature and therefore available to the scientific community at large, and also the greater integration of performance assessment personnel in analogue programmes and vice versa.

3. Major obstacles to the use of natural analogues

As illustrated, although some performance assessments have integrated analogue data, albeit to a restricted extent, their use is not yet widely acknowledged. Several problem areas can be recognised: (a) the acquisition and transfer of analogue data suited to performance assessment requirements has been inadequate, (b) the difficulty of using complex natural analogue data as input to simple performance assessment models, and

(c) the need for closer integration between the geoscientific and performance assessment fraternities to improve dialogue and communication.

How best can these problems be addressed? There is first a necessity to increase dialogue and integration between the geoscientific groups, i.e. those responsible for collecting and interpreting field data, and the performance assessors who will ultimately model these data. Integration has improved greatly during the past 5 years or so, such that planned or on-going analogue projects in Mexico (Peña Blanca), Finland (Palmottu), Oklo (Gabon), and Japan (Tono) have increasingly involved performance assessor participation in the planning, execution, and evaluation of these analogue programmes. With increased dialogue, analogue studies can be efficiently structured both to provide the basic scientific data for conceptualising the natural geological and geochemical systems, and also to ensure the transfer of relevant input data to meet the requirements for models used in performance assessment. For example, field-derived data have often been unsuitable for such performance assessment models due to poorly selected samples or inadequately defined boundary conditions. On the other hand, existing performance assessment models are often, by necessity, either too simple or not robust enough to cope with the complexities of natural processes and mechanisms. This present dilemma facing natural analogue studies was expressed by Miller (1996) to the extent that: "Natural analogue studies provide information performance assessments cannot use: Performance assessments require information natural analogues cannot measure". Much remains to be resolved on both sides of the interface.

In order to address these difficulties, an interface group should be created within each natural analogue study/project. This should consist of geoscientific personnel who are familiar with the field and analytical data and also the use of such data in performance assessment, and performance assessment personnel who have been integrated into the scientific programme of analogue study from the outset. The major aim of such a group would be to ensure acquisition of suitable data for performance assessment, the successful transfer of such data, and the development and refinement of performance assessment models to represent better the systems being modelled.

Such improvement in dialogue and communication should lead to greater future recognition and use of natural analogue studies in repository performance assessments. Furthermore, development of more robust models should pave the way to reappraise existing analogue data in the light of this new experience. There is a considerable volume of published data from earlier analogue studies, for example Poços de Caldas, Cigar Lake, and Alligator Rivers where a full appraisal with respect to performance assessment has generally been frustratingly inadequate. This in part can be explained by unrealistically tight time schedules to complete and report the project, inexperience as to the data requirements for performance assessments, and little overall continuity in the integration of performance assessment groups.

The benefit of reappraising existing data based on present-day performance assessment experience and data requirements is illustrated by a recent exercise carried out by SKB on the Cigar Lake study (Smellie and Karlsson, 1996). Here, time and resources were given to a group of experts from various disciplines to review the available data. Although several of the performance assessment areas proved to have been adequately addressed, one issue that particularly benefitted from this re-analysis was radiolysis. In this case, a model for radiolysis was developed and tested, significantly narrowing the gap between calculated and predicted oxidant production. For example, calculations performed in the SKB-91 performance assessment (SKB-92), using radiolysis models developed to evaluate spent fuel leaching, showed that the entire Cigar Lake uranium body should have been oxidised in 18–170 Ma. At that time no attempt had been made to calculate the deposition of radiation; this has now been taken into consideration and the recalculations have resulted in a much more realistic interpretation of the Cigar Lake system. Considerable progress was also made in understanding and modelling the initial formation of the uranium deposit under hydrothermal conditions, and using this conceptual model to evaluate the changes that have subsequently occurred under ambient 'repository' conditions over geological timescales.

Furthermore, existing analogue data sources should be of great benefit by their ready availability and potential applicability to a variety of disposal concepts. This would be particularly relevant to many countries who, in the near-future, will be deciding on national disposal concepts. In such cases analogue programmes can be efficiently structured to supplement existing data, rather than implementing large-scale studies of rediscovery.

Irrespective of the issues discussed above, however, the prevailing situation is that the full potential of natural analogue studies is still not being utilised in performance assessments. One important area of uncertainty that still needs to be addressed is the necessity to constrain better the boundary conditions of processes and events relevant to performance assessment; more precise and quantitative data need to be derived. Imposing stricter physico-chemical constraints on analogue studies may be accomplished by: (1) returning to the laboratory, (2) taking the laboratory to the field, and (3) greater use of modelling in guiding the direction of natural analogue studies.

4. Integration of modelling, laboratory, and in situ studies

Few analogue studies to date have attempted to integrate fully laboratory, in situ, and modelling data in the planning, execution, and interpretation stages of the programme. In situ studies, such as tracer experiments, have been successfully performed in some analogue programmes to investigate hydraulic flow regimes as a part of the site characterisation stage, for example at El Berrocal (EC, 1995). However, it should be possible to go one step further and use the unique character of an analogue site to carry out in situ experiments relevant for the long-term stability of radioactive waste forms and the barriers employed to isolate them. For example, uranium deposits located in stable reducing or marginally oxidising environments could be used to test the isolating capabilities of backfill materials intended for use in the repository near-field. This may be conducted by emplacing bentonite or other backfill materials (or metals, or cements) in suitably monitored boreholes, and retrieving the material for examination after predetermined time intervals. Even though the timescales are still no better than laboratory-driven experiments, at least the simulated 'experimental' set up is more relevant to repository conditions.

In other cases, controlled disturbances could be used to perturb, for example, redox conditions or colloid concentrations in environments similar to initial repository conditions to see what may happen during the evolution of a repository near-field. If it is assumed that the natural analogue site is as close as possible to 'steady state' equilibrium conditions, then the time required to reestablish equilibrium conditions following perturbation provides a quantitative measurement of the robustness of the confining system. This in turn might allow the long-term stability of the system to be tested against current performance assessment models.

It is important that examples chosen for in situ experiments are carefully selected so that they clearly provide unique data which complement conventional laboratory and analogue studies. It is pleasing to report that progress is slowly being made, and already some integration of modelling, laboratory, and in situ studies is a feature of some of the planned and on-going large-scale analogue programmes; some examples are given below.

4.1. Peña Blanca, Mexico and Santorini, Greece

One of the on-going natural analogue programmes presently funded by the United States Nuclear Regulatory Commission (US NRC) couples information from two field sites to provide support for modelled predictions of repository conditions at the Yucca Mountain high-level waste candidate site, Nevada, during the next 10000 years or so. This study provides a good illustration of the use made of integrating laboratory studies into the analogue study to constrain boundary conditions of naturally occurring processes relevant to repository performance assessment at Yucca Mountain (Fig. 1).

The Peña Blanca field site, a uranium mineralisation hosted by Tertiary rhyolitic tuffs, is located near Chihuahua, Mexico (Calas, 1977). Its potential use as a natural analogue to Yucca Mountain was first documented by Ildefonse et al. (1990) and later

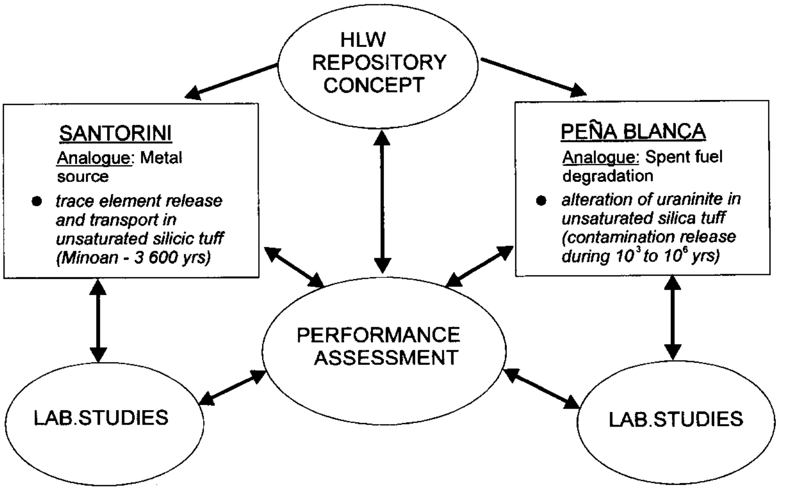

Fig. 1. Complementary analogue studies to a potential repository at Yucca Mountain, Nevada.

developed by Murphy and Pearcy (1992). Similarities with the Yucca Mountain site are striking; an arid to semi-arid climate, sequence of silca tuffs underlain by sedimentary carbonates, uranium mineralisation (waste package) in the oxidising, hydrologically unsaturated zone, etc.

A recent study by Pearcy et al. (1994) compared the observed alteration of natural UO_2 (uraninite) at Peña Blanca with laboratory studies of the degradation of spent nuclear fuel and non-irradiated UO_2. The latter study, to the extent of using ground-waters from the Yucca Mountain saturated zone, simulated post emplacement conditions anticipated to occur at the Yucca Mountain site. The main objective of the exercise was to evaluate the degree to which long-term alteration processes at Peña Blanca (e.g. 10^3–10^6 a) at ambient temperatures, and short-term laboratory experiments (e.g. 1–10 a) carried out from 85–90°C, reflect the long-term behaviour expected of spent nuclear fuel at the Yucca Mountain repository site. Comparison of results showed close similarities in the alteration pattern at the UO_2 crystal or grain boundaries caused by an advancing oxidation front, and also similarities in the alteration sequence of secondary reaction products (i.e. in both cases dominated by uranophane with subsidiary soddyite and other uranyl minerals). Generally, even when recognising the differences in the temperal and physico-chemical conditions involved, the study provides support for performance assessment models employed to predict long-term alteration of spent fuel in a Yucca Mountain repository environment.

The Santorini site is characterised by a thick deposit of silicic volcanic ash which resulted from a volcanic eruption of the island in Minoan times (ca 3600 a ago). Excavations have unearthed various metal artefacts within the unsaturated horizons and some bronzes have been used as a source term to investigate the extent of trace element release and migration through the host sediments. This approach can be considered analogous to predicting trace element release and migration from a corroding waste package through an unsaturated silicic tuff at the Yucca Mountain site (Murphy and Pearcy, 1994). Given the known boundary conditions at Santorini (i.e. location and timescale; measured material parameters in the laboratory such as porosity etc.), the distribution of the chemical species as a function of time can be calculated, and the extent of the trace element contaminant plume predicted. These modelled predictions have been tested by correlation with observed trace element distributions analysed from selected profiles through the surrounding sediments with some success (Murphy et al., 1997).

As illustrated in Fig. 1, the Peña Blanca and Santorini studies are complementary in the types of information that can be obtained and the relevance of this information to a performance assessment of a potential repository at the Yucca Mountain site. Integration of laboratory-oriented studies have greatly contributed to constraining the boundary conditions of these data, such that current performance assessment models can be quantitatively tested.

4.2. Palmottu, Finland

The Palmottu natural analogue site is a U–Th deposit hosted by Precambrian mica gneisses and granites. The uranium occurrences extend from an oxidising environment

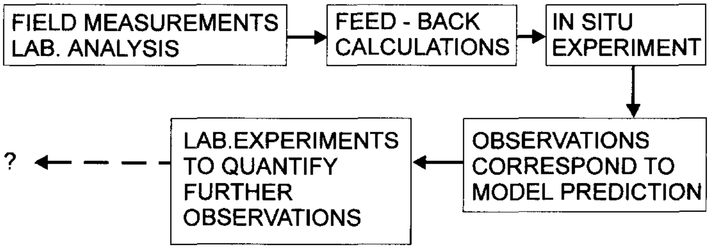

Fig. 2. Integration of field, in situ, and laboratory data in the Palmottu analogue project.

near the bedrock surface to reducing conditions at depth (Blomqvist et al., 1994). Field and laboratory investigations have been in progress since 1988; more recently studies have begun to focus on performance assessment issues. An important aspect of the Palmottu site is the potential to study the groundwater redox system, in particular the behaviour of uranium.

When routine surface field measurements of Eh–pH were linked with laboratory analysis of U(IV) and U(VI), a good correlation was indicated between the dissolved U(VI)/U(IV) ratio and the measured redox potentials. Modelling of the data showed that the soluble uranium species were in redox equilibrium with the groundwaters; the Eh–pH values plotted close to the stability fields of common uranium minerals and iron oxyhydroxides (Ahonen et al., 1993). This led to in situ tests being conducted at selected boreholes where the output groundwater pH was deliberately varied in a flow-through cell. The results showed a consistent change of Eh with pH which corresponded fairly well to the theoretical behaviour of the U(VI)/U(IV) redox pair, confirming that uranium, and not iron, is the dominant redox species at this location (Ahonen et al., 1994). The next step planned is a laboratory study, using uraninite crystals from the Palmottu fractures, to further support and quantify the field results.

This redox study well exemplifies the flexibility of analogue studies, where routine field measurements led to the unexpected observation that uranium (and not iron) is the dominant redox species at this locality. This was subsequently constrained by in situ tests closely integrated with predictive model calculations. Laboratory studies hopefully will further confirm and constrain the field observations (Fig. 2).

4.3. Maqarin, Jordan

It would be fair to state that, for many of the analogue studies performed to date, the main thrust has come from the geoscientific side, where something of significance to repository performance has been recognised in a natural system and subsequently pursued. In some cases, however, performance assessment criteria have been used to guide the direction of the natural analogue study. One good example of this is the testing of geochemical codes and associated thermo-dynamic databases (TDBs) carried out in several major analogue studies (e.g. Poços de Caldas, Cigar Lake, El Berrocal, Needle's Eye, etc.).

The first such test was carried out in the Oman study (Bath et al., 1987a,b), and the experience gained at this hyper-alkaline site was subsequently extended to Maqarin, Jordan, which is an extremely good geochemical analogue of a cementitious repository environment (Alexander et al., 1992; Khoury et al., 1992). The special problem of applying chemical thermodynamic models in such conditions is that most thermo-dynamic databases (TDBs) for high pH values are extrapolated from lower pH ranges and there are very little appropriate laboratory data against which to judge such estimations. This is liable to remain the situation for the foreseeable future because performing laboratory measurements under hyperalkaline conditions is not a trivial task and requires substantial effort and funding.

The approach taken in the Oman study was simple and robust. Assuming that the site is a good geochemical analogy of the hyperalkaline waters in a cementitious repository, it should be possible to predict the behaviour of a suite of trace elements in the natural system by using the codes and databases which will be employed in an actual repository performance assessment. A good correlation between the performance assessment prediction and reality (i.e. trace element concentrations actually present in the hyper-alkaline groundwaters) would indicate that the databases used were applicable to a cementitious repository. Obviously, poor agreement would mean that the extrapolation was somehow in error and a re-evaluation of the data would be required. According to Bath et al. (1987b), the predicted solubilities were consistent with the measured data (Table 1), although there were indications (for Pd and Ni) where the codes and databases would underpredict release from a cementitious repository.

Of utmost importance is the fact that the tests were carried out 'blind' (i.e. the modellers only had major element groundwater compositions without prior knowledge of the trace element concentrations on the associated mineralogy) as the difference between model prediction of the way any system will behave, and testing if a model can retrospectively simulate particular observations, is fundamental, although often not understood by the people carrying out the tests (Pate et al., 1994). In fact, model predictions resulting from the Oman study were published prior to the field sampling campaign (McKinley et al., 1987) and this practice was followed in the Maqarin study (Alexander et al., 1992).

In a formal repository safety assessment, safety will be demonstrated by means of a series of model predictions of how the repository will behave. To be confident of the robustness of such predictions, it is thus important to use models which have been shown to predict successfully the behaviour of similar systems, be they natural analogues or laboratory experiments, and not simply have been shown to simulate the results. This is all the more important for performance assessment where the assessors will have to use such codes and databases to predict, without prior knowledge, repository performance far into the future.

At Oman, studies were confined to hyperalkaline waters, whereas at Maqarin, studies were expanded to include detailed descriptions of the cement mineralogy (i.e. the source of trace elements of interest) and the secondary mineralogy of the water-conducting fractures (i.e. trace element sinks) and to attempt speciation measurements in the groundwaters. The mineralogical analysis have been so detailed that four previously undescribed minerals have been identified and several co-precipitation and solid solution relationships have been noted. The elements U, Th, Ra, Se, Pb, Sn, Ni, and Cr were

Table 1
Predicted (pre.) and observed (obs.) concentrations of trace elements (after Bath et al., 1987)

	Nizwa	Jebel	Bahla	Karku	Nidab
Se					
Pre.	$5e^{-3}$	$5e^{-3}$	$5e^{-3}$	$5e^{-7}$	$5e^{-7}$
Obs.	$< 3e^{-9}$	$< 3e^{-9}$	$< 3e^{-9}$	$< 3e^{-9}$	$< 3e^{-9}$
Pd					
Pre.	e^{-16}	e^{-10}	e^{-22}	e^{-22}	e^{-23}
Obs.	$2.8e^{-9}$	$6.6e^{-9}$	$2.8e^{-9}$	$2.8e^{-9}$	$3.8e^{-9}$
Sn					
Pre.	e^{-19}	e^{-19}	e^{-18}	e^{-18}	e^{-18}
Obs.	$< 2e^{-9}$	$< 2e^{-9}$	$< 2e^{-9}$	$< 2e^{-9}$	$< 2e^{-9}$
Zr					
Pre.	$5e^{-4}$	$5e^{-4}$	$5e^{-3}$	$2e^{-3}$	$1e^{-4}$
Obs.	$< 1e^{-9}$	$< 1e^{-9}$	$1.1e^{-9}$	$1e^{-9}$	$2.2e^{-9}$
Ni					
Pre.	$3e^{-7}$	$6e^{-7}$	$3e^{-7}$	$3e^{-7}$	$3e^{-7}$
Obs.	$< 1e^{-8}$	$< 1e^{-8}$	$2.7e^{-8}$	$2.0e^{-8}$	$3.4e^{-8}$
Th					
Pre. [a]	$5e^{-10}$	$5e^{-10}$	$5e^{-10}$	$5e^{-10}$	$5e^{-10}$
Pre. [b]	$1e^{-10}$	$1e^{-10}$	$1e^{-10}$	$1e^{-10}$	$1e^{-10}$
Obs.	$< 2e^{-10}$	$< 2e^{-10}$	$2e^{-10}$	$2e^{-10}$	$2e^{-10}$
U					
Pre. [a]	$2e^{-7}$	$8e^{-4}$	$1e^{-7}$	$1e^{-6}$	$6e^{-7}$
Pre. [b]	$2e^{-4}$	$5e^{-3}$	$3e^{-9}$	$3e^{-9}$	$2e^{-9}$
Obs.	$< 4e^{-11}$	$4.2e^{-11}$	$< 4e^{-11}$	$< 4e^{-11}$	$< 4e^{-511}$

[a] EIR database.
[b] NEA database.

examined and, as in the Oman study, most of the predictions of the solubility were found to be conservative. Unfortunately, the databases did not predict the minerals which were controlling the trace element concentrations very well, partly because such esoteric cement phases have rarely been studied and hence thermodynamic data are sparse, and partly because few databases or their codes can effectively handle complex situations, such as where the trace metal solubility is controlled by co-precipitation or co-dissolution (congruent/incongruent) or by solid solution. In other instances, important solid phases (several Se databases) and solute species (in most U databases) were missing and this obviously produced unrealistic predictions.

Studies of these type have produced something of a rift in the geochemical community in that academic geochemists feel the work to be superficial as the full reasons for the differences between predictions and the observations are not fully investigated. This is, however, forgetting the fact that in a repository safety assessment, if a code or database can be confidently shown to over-estimate releases of radionuclides to the biosphere under all expected conditions, then the problem is of no more interest to the safety assessors as they can confidently state that their predictions err on the cautious side.

Fig. 3 illustrates the various modelling stages carried out at Maqarin and how each iteration has helped to determine the amount of field sampling and analytical work

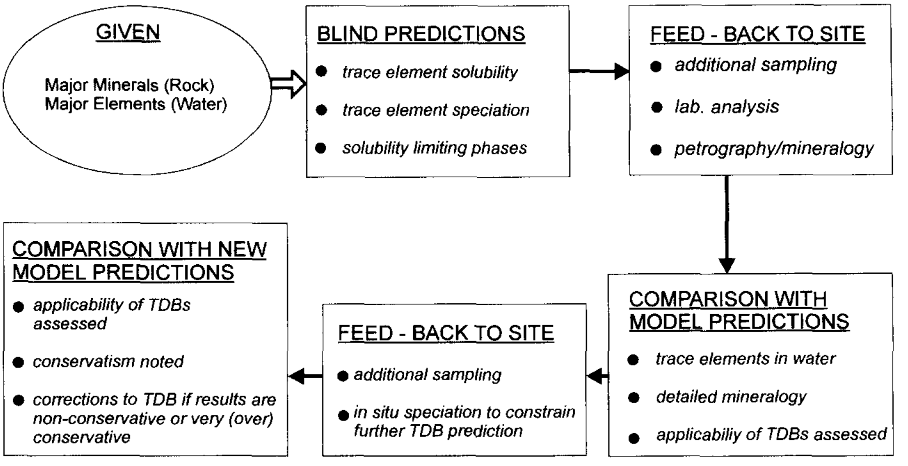

Fig. 3. Testing the applicability of thermodynamic databases (TDBs) to cementitious conditions in the Maqarin analogue project.

required for the next stage. Future work will involve laboratory studies to constrain further the observations, for example: (1) column experiments using Maqarin rock material to simulate marl/high pH–plume interaction to determine reaction kinetics and alteration rates and (2) investigation of radionuclide retardation processes by carrying out batch experiments to check sorption using a suite of safety-relevant trace elements similar to those used in the predictive modelling exercises.

5. Closing comments

To reiterate what was pointed out above, natural analogue studies have now reached a threshold of usefulness and applicability to repository performance assessment which can only be breached by trying to constrain further the physico-chemical conditions of the processes and events being studied and quantified. This may be accomplished by integration with carefully linked laboratory and in situ studies. If this is not successful, analogues will remain as they are today, important qualitative support for the features, events, and processes (FEPs) which are an integral part of scenario development, but failing to make a major impact on the long-term performance or safety assessment modelling of a repository. Consequently, the modelled input data will continue to be based on laboratory-derived data which neither realistically represents the timescales, nor the complexities, expected to be encountered during the lifespan of a repository.

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References

Ahonen, L., Ervanne, H., Ruskeeniemi, T., Jaakkola, T. and Blomqvist, R., 1993. Uranium mineral-groundwater equilibration at the Palmottu natural analogue study site, Finland. In: C. Interrante and R. Pabalan (Editors), Scientific Basis for Nuclear Waste Management XVI. MRS.

Ahonen, L., Ervanne, H., Jaakkola, T. and Blomqvist, R., 1994. Redox chemistry in uranium-rich groundwater of the Palmottu uranium deposit. Radiochim. Acta, 66/67: 115–121.

Alexander, W.R., Dayal, R., Eagleson, K., Eikenberg, J., Hamilton, E., Linklater, C.M., McKinley, I.G. and Tweed, C.J., 1992. A natural analogue of high pH pore waters from the Maqarin area of northern Jordan. II: Results of predictive geochemical calculations. J. Geochem. Exp., 46: 133–146.

Andersson, J., Carlsson, T., Eng, T., Kautsky, F., Söderman, E. and Wingefors, S., 1989. The joint SKI/SKB scenario development project. SKB Tech. Rep. (TR 89-35), Stockholm, Sweden.

Bath, A.H., Christof, N., Neal, C., Philip, J.C., Cave, M.R., McKinley, I.G. and Berber, U., 1987a. Trace element and microbiological studies of alkaline groundwaters in Oman, Arabian Gulf: a natural analogue for cement pore waters. Nagra Tech. Rep. (NTB 87-16), Baden, Switzerland.

Bath, A.H., Berner, U., Cave, M.R., McKinley, I.G. and Neal, C., 1987b. Testing geochemical models in a hyperalkaline environment. In: B. Côme and N.A. Chapman (Editors), Natural Analogues in Radioactive Waste Disposal. CEC Radioactive Waste Management Series, EUR 11037, CEC, Luxembourg, pp. 167–178.

Blomqvist, R., Suksi, J., Ahonen, L. and Niini, H., 1994. The Palmottu natural analogue study, Finland. In: CEC NAWG (Editors), Proceedings of the Fifth CEC Natural Analogue Working Group Meeting and Alligator Rivers Analogue Project (ARAP) Final Workshop, 5–9 October, Toledo, Spain. EUR 15176 EN, Luxembourg.

Brehrenz, P. and Hannerz, K., 1978. Criticality in a spent fuel repository in wet crystalline rock. SKB/KBS Tech. Rep. No. 108, Stockholm, Sweden.

Bros, R., Turpin, L., Gauthier-Lafaye, F., Holliger, Ph. and Stille, P., 1993. Occurrence of naturally enriched ^{235}U: implications for plutonium behaviour in natural environments. Geochim. Cosmochim. Acta., 57: 1351–1356.

Calas, G., 1977. Les phenomenes d'alteration hydrothermale et leur relation avec öles mineralisations uraniferes en milieu volcanique; le cas des ignimbrites Tertiaires de la Sierra de Peña Blanca, Chihuahua (Mexique). Sc. Geol. Bull., 30: 3–18.

CEC NAWG B. Come and N. Chapman (Editors), 1986a. Proceedings of the First CEC Natural Analogue Working Group (NAWG) Meeting, 5–7 November 1985, Brussels, Belgium. EUR 10315 EN, Luxembourg.

CEC NAWG B. Come and N. Chapman (Editors), 1986b. Proceedings of the Second CEC Natural Analogue Working Group (NAWG) Meeting, 17–19 June 1986, Interlaken, Swtizerland. EUR 10671 EN, Luxembourg.

CEC NAWG B. Come and N. Chapman (Editors), 1989. Proceedings of the Third CEC Natural Analogue Working Group (NAWG) Meeting, 15–17 June 1988, Snowbird, Salt Lake City, USA. EUR 11725 EN, Luxembourg.

CEC NAWG B. Come and N. Chapman (Editors), 1991. Proceedings of the Fourth CEC Natural Analogue Working Group (NAWG) Meeting and Poços de Caldas Project Final Workshop, 18–22 June 1990, Pitlochry, UK. EUR 13014 EN, Luxembourg.

CEC NAWG H. von Maravic and J. Smellie (Editors), 1994. Proceedings of the Fifth CEC Natural Analogue Working Group (NAWG) Meeting and Alligator Rivers Analogue Project (ARAP) Final Workshop, 5–9 October 1992, Toledo, Spain. EUR 15176 EN, Luxembourg.

CEC NAWG H. von Maravic and J. Smellie (Editors), 1996. Proceedings of the Sixth EC Natural Analogue Working Group (NAWG) Meeting, 12–16 September 1994, Sante Fe, New Mexico, USA. EUR 16761 EN, Luxembourg.

Chapman, N.A., McKinley, I.G. and Smellie, J.A.T., 1984. The potential of natural analogues in assessing systems for deep disposal of high-level radioactive waste. SKB Tech. Rep. (TR 84-16), Stockholm, Nagra Tech. Rep. (NTB 90-33), Baden, Switzerland.

Chapman, N.A., McKinley, I.G., Shea, M.E. and Smellie, J.A.T., 1992. The Poços de Caldas Project: natural analogues of processes in a radioactive waste repository, Part I. J. Geochem. Exp., 45: 1–24.

Cramer, J.J. and Smellie, J.A.T., 1994. The AECL/SKB Cigar Lake analog study: some implications for performance assessment. In: CEC NAWG (Editors), Proceedings of the Fifth CEC Natural Analogue Working Group (NAWG) Meeting and Alligator Rivers Analogue Project (ARAP) Final Workshop, 5–9 October 1992, Toledo, Spain. EUR 15176 EN, Luxembourg.

Curtis, D.B. and Gancarz, A.J., 1983. Radiolysis in nature: evidence from the Oklo natural reactors. KBS Tech. Rep. (TR 83-10), Stockholm, Sweden.

Degueldre, C., 1991. Microbial and colloidal populations in the maqarin groundwaters. In: W.R. Alexander (Editor), A Natural Analogue Study of Cement Buffered Hyperalkaline Groundwaters and their Interaction with Sedimentary Host Rock. Nagra Tech. Rep. (NTB 91-10), Baden, Switzerland.

EC, 1995. El Berrocal project: characterisation and validation of natural radionuclide migration processes under real conditions on the fissured granitic environment. Summary Report on Phase 1. Nuclear Science and Technology, EUR 15908 EN, Luxembourg.

Eng, T., Hudson, J., Stephansson, O., Skagius, K. and Wiborgh, M., 1994. Scenario development methodologies. SKB Tech. Rep. (TR 94-28), Stockholm, Sweden.

Hofmann, B., 1997. Geochemistry of natural redox fronts – a review. Nagra Tech. Rep. (NTB 95-07), Wettingen, Switzerland (in press).

Hooker, P.J., MacKenzie, A.B., Scott, R.D., Ridgway, I., McKinley, I.G. and West, J.M., 1985. A study of natural and long-term (10^3–10^4 year) elemental migtation in saturated clays and sediments, Part III. BGS Tech. Rep. (FLPU 85-9), CEC Radioactive Waste Management Series, EUR 10788/2, Luxembourg.

Ildefonse, P., Muller, J.-P., Clozel, B. and Calas, G., 1990. Study of two alteration systems as natural analogues for radionuclide release and migration. Eng. Geol., 29: 413–439.

Karlsson, F., Smellie, J.A.T. and Höglund, L.-O., 1994. The application of natural analogues to the Swedish SKB-91 safety performance assessment. In: CEC NAWG (Editors) Proceedings of the Fifth CEC Natural Analogue Working Group (NAWG) Meeting and Alligator Rivers Analogue Project (ARAP) Final Workshop, 5–9 October 1992, Toledo, Spain. EUR 15176 EN, Luxembourg.

KBS-2, 1978. Handling and final storage of unreprocessed spent nuclear fuel. KBS Final Rep., Vols. I–II, Stockholm, Sweden.

Khoury, H.N., Salameh, E., Clark, I.D., Fritz, P., Bajjali, W., Milodowski, A.E., Cave, M.R. and Alexander, W.R., 1992. A natural analogue of high pH cement pore waters from the Maqarin area of northern Jordan. I: Introduction to the site. J. Geochem. Exp., 46: 117–132.

MacKenzie, A.B., Scott, R.D., Linsalata, P. and Miekeley, N., 1992. Natural decay series studies of the redox front system in the Poços de Caldas uranium mineralisation. J. Geochem. Exp., 45: 289–321.

McKinley, I.G. and Alexander, W.R., 1996. The uses of natural analogue input in repository performance assessment: an overview. In: CEC NAWG (Editors), Proceedings of the Sixth EC Natural Analogue Working Group (NAWG) Meeting, 12–16 September 1994, Sante Fe, New Mexico, USA. EUR 16761 EN, Luxembourg.

McKinley, I.G., Berner, U. and Wanner, H., 1987. Predictions of radionuclide chemistry in a highly alkaline environment. In: H. von Maravic and J. Smellie (Editors), Chemie und Migrationsverhalten der Aktinide und Spaltprodukte in Naturlichen Aquatischen Systemen. PTB-SE-14, pp. 77–89.

Miekeley, N., Coutinho de Jesus, H., Porto da Silveira, C.L. and Degueldre, C., 1992. Chemical and physical characterisation of suspended particles and colloids in waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil. J. Geochem. Exp., 45: 409–438.

Miller, W., 1996. The value of natural analogues. In: CEC NAWG (Editors), Proceedings of the Sixth EC Natural Analogue Working Group (NAWG) Meeting, 12–16 September 1994, Sante Fe, New Mexico, USA. EUR 16761 EN, Luxembourg.

Miller, W., Alexander, W., Chapman, N., McKinley, I. and Smellie, J., 1994. Natural analogue studies in the geological disposal of radioactive wastes. Studies in Environmental Science 57, Elsevier, 395 pp.

Murphy, W.M. and Pearcy, E.C., 1992. Source-term constraints for the proposed repository at Yucca Mountain, Nevada, derived from the natural analog at Peña Blanca, Mexico. In: C.G. Sombret (Editor), Scientific Basis for Nuclear Waste Management XV. MRS, Pittsburg, pp. 521–527.

Murphy, W.M. and Pearcy, E.C., 1994. Performance assessment significance of natural analog studies at Peña Blanca, Mexico, and Santorini, Greece. In: CEC NAWG (Editors), Proceedings of the Fifth CEC Natural Analogue Working Group (NAWG) Meeting and Alligator Rivers Analogue Project (ARAP) Final Workshop, 5–9 October, Toledo, Spain. EUR 15176 EN, Luxembourg.

Murphy, W.M., Pearcy, E.C., Green, R.T., Prikryl, J.D., Mahanty, S., Leslie, B.W. and Nedungadi, A., 1997. A test of long term, predictive, geochemical transport modeling at the Akrotiri archaeological site. J. Contaminant Hydrology (in press).

Nagra, 1994. KRISTALLIN-I: safety assessment report. Nagra Tech. Rep. (NTB 93-23), Wettingen, Switzerland.

Pate, S.M., McKinley, I.G. and Alexander, W.R., 1994. Use of natural analogue test cases to evaluate a new performance assessment TDB. In: CEC NAWG (Editors), Proceedings of the Fifth CEC Natural Analogue Working Group (NAWG) Meeting and Alligator Rivers Analogue Project (ARAP) Final Workshop, 5– 9 October, Toledo, Spain. EUR 15176 EN, Luxembourg.

Pearcy, E.C. and Murphy, W.M., 1991. Geochemical natural analogs: literature review. Center for Nuclear Waste Regulatory Analyses, San Antonio, TX, NRC Contract NRC-02-88-005.

Pearcy, E.C., Prikryl, J.D., Murphy, W.M. and Leslie, B.W., 1994. Alteration of uraninite from the Nopal I deposit, Peña Blanca District, Chihuahua, Mexico, compared to degradation of spent nuclear fuel in the proposed U.S. high-level nuclear waste repository at Yucca Mountain, Nevada. Appl. Geochem., 9: 713–732.

PNC-92, 1992. Research and development on geological disposal of high-level radioactive waste. PNC TN1410 (93-059), Tokyo, Japan.

SKB, 1992. SKB RD and D Programme 92. Treatment and final disposal of nuclear waste. SKB Rep., Stockholm, Sweden.

Smellie, J.A.T. and Karlsson, F. (Editors), 1996. The Cigar Lake Analogue Project: A Reappraisal of Some Key Issues and Their Relevance to Repository Performance Assessment. SKB Tech. Rep., (96–08) Stockholm, Sweden.

Smellie, J.A.T., Karlsson, F. and Grundfelt, B., 1995. The potential use of natural analogue studies in radioactive waste disposal: a review. In: Geoval '94: Validation Through Model Testing, Proceedings of an NEA/SKI Symposium, 11–14 October 1994, Paris, France. NEA/OECD, Paris.

Wilson, M.L., Gauthier, J.H., Bernard, R.W., Barr, G.E. and Dockery, H.A., 1994. Total system performance assessment at Yucca Mountain – SNL second iteration (TSPA-1993). Sandia Rep. SAND 93-2675, Sandia Nat. Lab., Albuquerque, New Mexico, USA.