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Humic Substances in Performance Assessment of Nuclear Waste Disposal: Actinide and Iodine Migration in the Far-field

(HUPA)

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Foreword

This is the final report of the European Commission project Humic Substances in Performance Assessment of Nuclear Waste Disposal: Actinide and Iodine Migration in the Far-field (HUPA). The report presents the project and the outcome of scientific technical investigations from general conclusions towards progressive detail. After the introduction and project objectives, the partners and project structure are given. Thereafter objectives of the work packages, the overall outcome of the project and pending issues provide an overview of the achievements and present status of development. The scientific technical results are then given in some detail followed by an overall summary of progress.

Detailed scientific technical results are documented in the form of three technical progress reports [5-7]. The project builds on a series of European Commission co-funded projects, especially the preceding Effects of Humic Substances on the Migration of Radionuclides: Complexation and Transport of Actinides (HUMICS). The technical progress reports and the final report of this project [1-4] help in providing an understanding for the overall development in this field.

The present report is based on the scientific technical contributions of a large number of co-workers at the project partners' and additional scientists from other institutions by joint contributions. The outcome of the project thus rests on the contributions of these many scientists, listed in Annex I “Contributors to scientific technical reporting within the HUPA project”.

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1. Introduction

The present project is one in a series of research activities supported by the European Commission on the role of humic substances for the long-term safety of nuclear waste disposal. These activities started in the mid-eighties within the MIRAGE project (MIgration of RAdionuclides in the GEosphere) with the most recent project prior to the present one being Effects of Humic Substances on the Migration of Radionuclides: Complexation and Transport of Actinides (HUMICS). The HUMICS project was conducted within the fourth framework programme of the European Commissions. It started January 1997 and had a duration of three years. The results of the HUMICS project can be found in three open technical progress reports and a final report [1-4].

The present HUPA project is conducted within the Commissions fifth framework programme. It started November 2001 and had a duration of three years. Also for this project, detailed scientific technical results can also be found in technical progress reports [5-7]. By this approach, in addition to publication in various scientific journals and conference proceedings, detailed scientific technical results are available to interested parties in a compact form. Furthermore, some of the more preliminary and/or detailed results are not likely to appear in scientific journals and proceedings. Therefore, persons interested in detailed scientific technical results of the present and the foregoing projects dealing with the influence of humic substances on the migration of radionuclides in the geosphere need to consult these technical progress reports.

The overall approach of the HUPA project is to provide process understanding resting on a solid scientific ground, rationalising the developed state of knowledge in the form of models, and visualisation of the impact of humic colloid mediated actinide and iodine transport via migration cases. Application of the knowledge developed within the project to specific radioactive waste disposal strategies is the task of responsible national organisations and not within the scope of this project.

The scientific technical objectives were to generate knowledge about the impact of humic substances on the migration of actinides and iodine in the far-field of a nuclear waste repository. In the beginning, focus was rather on the potential enhancement due to humic colloid mediated radionuclide transport. Thereby, sources, inventory, stability and mobility of dissolved humic substances in their colloidal form formed a key topic. Other key topics were the interaction with actinides and iodine, transport studies under near-natural conditions in the laboratory, rationalisation of knowledge in models and application to three migration cases for visualisation of the overall outcome. Changes relative to the original objectives were given by moving emphasis of natural chemical analogue studies from the question of kinetic exchange constants for different inventories in natural and laboratory systems to the study of anthropogenic actinide contaminants in the Irish Sea. Furthermore, by the involvement of a Marie-Curie grantee, the question of additional sources from the high alkaline natural clay near-field was brought into the project.

The overall objectives of the project cover (i) generation of relevant scientific-technical results, (ii) visualisation of the concerned impact on performance assessment, (iii) provision for knowledge transfer, and (iv) provision of a European dimension and training, especially in view of the EU enlargement during the project implementation period. The project is divided into eight different work packages, reflecting the different elements required in order to achieve the overall scientific technical project objectives. These work packages are (i) “Critical assessment of experimental methods”, (ii) “Generation and characterisation of humic substances”, (iii) “Radionuclide humate interaction data by designed system investigations”, (iv) “Characterisation of radionuclide humate complexes”, (v) “Natural chemical analogue studies”, (vi) “Radionuclide transport experiments”, (vii) “Model development”, and (viii) “Performance assessment”. The EU enlargement during the project phase was also reflected by the inclusion of an additional partner, namely the University of Cyprus.

The present project builds on the long foregoing development of experience and scientific basis. It distinguishes itself from previous activities by, amongst others, inclusion of iodine next to the highly radiotoxic and long-lived actinides. As the key role of kinetics became obvious, the past project experienced a strong shift in work deviating from initial intentions. This is also reflected in the present project where a main objective is clarification of processes responsible for the wide range of dissociation kinetics observed. Results have been generated from systems varying from the laboratory scale up to anthropogenic actinide contaminants in the Irish Sea with contact times over several decades and real system analysis of natural aquifer systems.

One important objective is related to the description of the actinide humic acid interaction. There is a large number of “models” argued for in the literature. These “models” reflect some aspects of available experimental data but fail to enclose other aspects and experimental observations. The present project has proven successful in developing a description that, taking different especially recently available information into account, turns out to be relatively simple and plausible.

Access to and continuous development of advanced analytical methods is a key element in providing for continued progress. Examples of such advanced analytical techniques making previously inaccessible information available are synchrotron radiation based spectroscopy and microscopy, development and application of advanced mass spectroscopy techniques and continued refinement of time resolved laser fluorescence spectroscopy.

The principle approach to the report is to give key information in the beginning, followed by discussion of the progress within individual work packages in some detail. The structure of the report thus goes from extracted short information towards more detail. Further details on scientific-technical results are given in the form of three technical progress reports [5-7].

2. Objectives

Nuclear energy is an important element in the energy supply in Europe. Continued use of nuclear energy contributes to a stable socio-economic development and contributes to the overall European strategic objective of lowering dependency on energy import. A key objective of the Commission's support for research in this field is providing for continued acceptance of nuclear energy by demonstrating that residues can be managed appropriately, including providing trust in the capability of safe disposal. The present project contributes to this overall objective by establishing a trustworthy scientific basis for predicting the impact of humic substances on the mobility of long-lived actinide ions and iodine in case of release from a repository in a distant future.

The direct objective of the project is to develop tools for quantification, or justification for exclusion of humic colloid mediated radionuclide migration in performance assessment (PA). It falls within the overall objective of decreasing uncertainty in long-term safety assessment of nuclear waste disposal. For this purpose, the necessary data and adequate process understanding for the radionuclide humic colloid interaction and mobility of humic colloids in natural aquatic systems are developed. The impact of humic colloid mediated radionuclide migration on PA of nuclear waste disposal is visualised by predictive modelling on real site migration cases. The project focuses on radionuclides relevant for the long-term safety of radioactive waste disposal, i.e. the actinides and iodine.

3. Partners and project structure

The project has nine partners from six European countries (Table 1). In addition, a Marie-Curie fellowship was a temporary contributor, reporting through the project. The project structure is based on eight work packages (Table 2). The first six of these work packages are of experimental character. Work package no. 7 is model development where knowledge is rationalized for application to various systems and conditions. Work package no. 8 is aiming at visualizing the impact of humic colloid mediated radionuclide transport under three different specified conditions, defined as three migration cases. There is no work package specifically dealing with the origin and mobility of humic substances. Analysis of natural aquifer systems and the conversion of clay organic matter show that this is an issue that needs considerable attention. This issue is dealt with within work package no. 8 because it is related to definition of the system conditions. The project structure is shown in Figure 1, with the interrelation between the different work packages.

Table 1: Project partners

Partner no.	Partner
1	Forschungszentrum Karlsruhe GmbH (FZK/INE), DE (Coordinator)
2	Forschungszentrum Rossendorf (FZR-IfR), DE
3	GSF-National Research Centre for Environment and Health (GSF), DE
4	Commissariat à l'énergie atomique (CEA-DPC), FR
5	University of Nantes - Présidence (U-Nantes), FR
6	University of Manchester (U-Manch), UK
7	Technical University of Prague (CTU), CZ
8	Fodor Joszef National Centre of Public Health, Frederic Joliot-Curie National Research Institute of Radiobiology and Radiohygiene (FJC), HU
9	University of Cyprus (UCY), CY
Temporary contributor	Francis Claret, FZK/INE, through EC Marie-Curie Fellowship (MCFI-2001-01983)

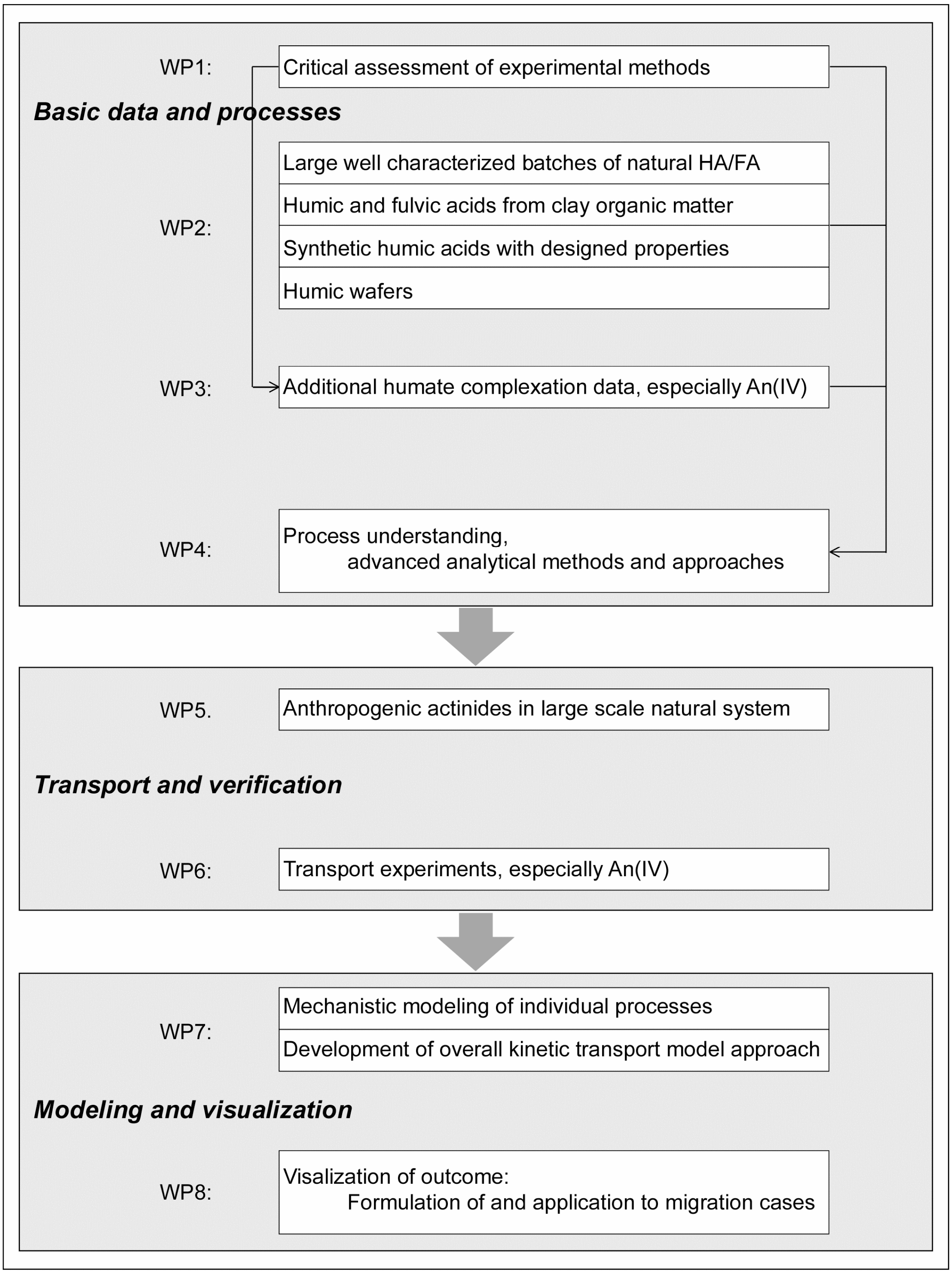

Fig. 1: Structure of RTD work within the project and interrelation between different work packages. In addition to the top-to-bottom flow of information shown in the figure, back-feed was an important element for the continuous development of the work programme

4. Objectives of the work packages

WP 1. Critical assessment of experimental methods

The objectives of this work package are to provide understanding for processes involved in application of different experimental methods used for obtaining radionuclide humate interaction data. By this exercise, radionuclide humate interaction data are given a broad basis providing trust in their correctness. The knowledge generated provides the basis for judging upon the reliability of published data, thus allowing extension of the database without separate experimental investigations.

Table 2: Project structure/work packages

Work package	**Title**	**Lead contractor** (Partner no. cf. Table 1)
1	Critical assessment of experimental methods	7
2	Generation and characterisation of humic material	2
3	Radionuclide humate interaction data by designed system investigations	4
4	Characterisation of radionuclide humate complexes	1
5	Natural chemical analogue studies	1
6	Radionuclide transport experiments	2
7	Model development	6
8	Application to Performance Assessment	6

WP 2. Generation and characterisation of humic material

The objectives of this work package are to ensure availability of appropriately purified and well characterized natural humic and fulvic acids and generate humic material with specified properties for certain purposes. The latter includes humic acid where specified functional groups are blocked, synthetic humic substances with designed properties and silica wafer and other minerals coated, especially with covalently bound humic acid. The purpose of generating material with specified properties is to enable specific insight in metal ion interaction processes.

WP 3. Radionuclide humate interaction data by designed system investigations

The objectives are to ensure accessibility to metal ion humate interaction data for different metal ions and metal ion complexes, including generation of ternary complexes, required for providing the basis for adequate understanding of the interaction process. Interaction equilibrium data are insufficient in many systems because of the finding that kinetic data need to be applied. The data from “equilibrium investigations”, nevertheless, are required for definition and selection of kinetic data and are a prerequisite for adequate process understanding. This also implies the close association with WP4, i.e. characterisation of complexes.

WP 4. Characterisation of radionuclide humate complexes

The objectives of this work package are to ensure appropriate interpretation of the radionuclide humate interaction process and thus provide the basis for the required process understanding. This is a key issue for providing trust in the capability to conduct predictive modeling of humic colloid mediated radionuclide transport, and thus for providing trust in the overall outcome of the project. A key element in this work is development and use of frontier analytical techniques.

WP 5. Natural chemical analogue studies

The objectives of this work package were originally tailored towards generation of kinetic data for different metal ion inventories. The key question originated from the observation that radionuclides show a number of kinetic dissociation modes. Contrary to investigations on laboratory systems, the inventory of natural trace metal ions shows part of the inventory dissociating so slow that it so far has not been possible to quantify this kinetics. The key question arising from comparison of the outcome of these individual studies is to which extent actinide ions in long contact with a natural system will mimic the behavior of the natural inventory of natural actinide ions, including natural chemical analogues, or if the description of their behavior can be extrapolated from laboratory system studies. For this purpose, the objectives were amended to anthropogenic actinide contaminant studies in the Irish Sea.

WP 6. Radionuclide transport experiments

The objectives of this work package are to provide transport data for radionuclides by near-natural laboratory system investigations. Several such investigations have been conducted in the past. Consequently, the present work focuses on systems where data are scarce and specific investigations tailored towards development of general fundamental process understanding. The studies also provide an in-put for visualisation of humic colloid mediated transport via migration cases (WP 8).

WP 7. Model development

The objectives of this work package are to rationalize "radionuclide interaction data", "complex characterisation", "natural chemical analogue studies" and “radionuclide transport experiments” (cf. above) and bringing them into consistent mathematical descriptions. These descriptions serve the basis for predictive modeling, but also for testing and feed-back to experimental work.

WP 8. Application to Performance Assessment

The objective is to provide scientifically justified simplifications of detailed process understanding and associated models. These scientifically justified simplifications are tailored for direct application in PA codes. Application to real sites in the form of three migration cases is used for visualisation of the impact of humic colloid mediated radionuclide transport on PA. Origin, stability and mobility of humic substances, both natural and additional sources (from chemically amended repository conditions), are also treated within this work package.

5. Overall outcome of the HUPA project

The state of knowledge in key areas prior to the HUPA project and corresponding main achievement of the project is given. After that, the overall outcome with respect to PA is given.

5.1. Status prior to the project and key achievement

The status with respect to key topics prior to the HUPA project, key objectives and key achievement are shown in Table 1. The information is structured according to the work packages of the project. More detailed information on the project objectives is given under section 4 and on the progress within the different work packages within section 7.

Table 1: Status prior to the HUPA project, key objectives and key achievements structured according to the project work packages (cf. Table 2)

WP	Key problem (status prior to HUPA)	Key objectives	Key achievements
1	Large number of partly conflicting humate complexation data published from application of different experimental methods.	Identify limitations of various experimental methods applied.	Thorough experimental study and documentation of key problems with a large number of experimental methods applied.
2	(i) Variety of humic and fulvic acids used in different published work, frequently without thorough characterisation of the material. (ii) Difficulties to distinguish the impact specific characteristic elements and functionalities on various processes involved. (iii) Unclear relation between hydrophobic clay organic matter as a potential source material and extracted/ hydrolyzed aquatic/hydrophilic humic and fulvic acids. (iv) In homogeneous solution, An(IV) complexation studies are very difficult, and characterisation of complexes by surface sensitive methods of highly hydrolyzing metal ions in general is not possible.	(i) Generate new large well characterized batches of humic and fulvic acids from the Gorleben groundwater Gohy-573, in order to allow continued intercomparision of results from this well characterized material from this source (used in EC projects since the eighties). (ii) Generate synthetic humic acids with designed properties. (iii) Investigate/characterize clay organic matter and humic and fulvic acids generated from that material under alkaline conditions. (iv) Generate humic wafers with covalently surface bound humic acid on very flat surfaces.	(i) Very large batches of both humic and fulvic acid from this groundwater generated, thorough characterisation well beyond common standards, and documentation in technical progress report. (ii) Synthetic humic acids generated with, amongst others high redox capacity and blocked phenolic groups. (iii) Characterisation of both source material and the aquatic humic and fulvic acids by a series of advanced analytic methods, resulting in clear correlation between the sources and the resulting hydrophilic humic and fulvic acids. (iv) Humic wafers generated with thorough characterisation of the entire synthesis route and outcome.
3	Some complexation data missing, especially for the tetravalent actinide ions.	Generate trustworthy humate complexation data for the tetravalent actinide ions.	Objectives partly achieved. Modeling and characterisation shows some progress, but also that the interaction with hydrolyzed species and the formation of An(IV) colloids requires further studies and development of further advanced analytical methods.
4	Large number of complexation and kinetic data for the actinide humate interaction available. No general agreement on the thermodynamic approach for description of the interaction process. As a consequence, only limited trust in the application of data for long-term transport predictions.	Make use of, and develop new, advanced analytical methods and approaches in order to provide the basis for actinide humate interaction process understanding.	Considerable progress, especially in a new thermodynamically plausible approach for description of the interaction process, taking recent characterisation data into account. The progress coupled with advances in and development of analytical methods, very much reflected in the consortium.

Table 1 *(continued 1)*: Status prior to the HUPA project, key objectives and key achievements structured according to the project work packages (cf. Table 2)

WP	Key problem (status prior to HUPA)	Key objectives	Key achievements
5	Kinetic approach to modeling of actinide transport under laboratory and dipole scale conditions shown to be successful. Application to larger spatial and time scales missing.	Demonstrate the principle applicability of the kinetic approach to large-scale natural anthropogenic actinide contamination in the Irish Sea.	Applicability of kinetic approach to anthropogenic large-scale system demonstrated, including key information on distribution of actinides between different kinetic modes after long contact times.
6	Adequate transport experiments under near-natural conditions in the laboratory and in dipoles have been conducted for all actinides, with exception for plutonium.	Complement the experimental basis on actinide transport experiments in humic colloid rich systems by investigations with plutonium.	The desired transport experiments have been performed. The interpretation still suffers under the lack in process understanding, including lack in unambiguous determination of the plutonium redox state.
7	(i) Actinide humate interaction: There is a large number of approaches published reflecting the lack in process understanding. (ii) Humic colloid mediated actinide transport in the far-field: During the HUMICS project, a kinetic approach was developed that was shown to successfully describe the humic colloid mediated transport in a large number of column experiments with widely varying conditions. Demonstration of validity in large scale systems pending (cf. WP 5).	(i) Reflect the progress in process understanding by interactive model development in order to identify processes and document the state of knowledge (ii) Test applicability of the basic kinetic approach to actinide transport on anthropogenic contamination in the Irish Sea (cf. WP 5).	(i) A variety of processes have been formulated and tested for their applicability in relation to experimental findings. An important step was a surprisingly simple formulation of the overall reaction reflecting recent basic findings on the nature of humic and fulvic acid. Some questions remain open, especially an unambiguous answer to the question of possible complex formation induced association of humic molecules already at low metal loading. (ii) Validity of basic kinetic approach demonstrated (cf. WP 5).

5.2. Key achievements with respect to application to PA

5.2.1. Generalisation of humic substances properties

In a first approximation, characteristic properties of humic substances can be generalized. Despite individual differences, definition of humic substances over a large number of common characteristics, varying within limits, is possible. If more detailed results are required, however, knowledge about specific properties is needed. This is specifically true for differences between aqueous/dissolved humic substances and the stationary/sedimentary organic material partially containing humic substances, but also precursors of aquatic humic substances and additional organic compounds.

The complexation properties are shown to partly depend on the specific nature of humic and fulvic acids of different origin. More problematic, however, is that a correlation between different properties and the interaction kinetics is still an open issue. This specifically refers to the question of the relatively large basically irreversibly bound part of the inventory of trace metal ions found in natural humic colloids. Contrary to this, only a small fraction of actinide ions added under near-natural laboratory conditions and time-scales show dissociation kinetics so slow that it cannot be quantified by laboratory column transport experiments. In this context, especially the potential role of inorganic/mineral constituents has not yet been clarified.

Table 1 *(continued 2)*: Status prior to the HUPA project, key objectives and key achievements structured according to the project work packages (cf. Table 2)

8	(i) Origin, stability and mobility of humic colloids in a variety of relevant natural systems has already been investigated. The origin of humic colloids was shown to be microbial turn-over of soil organic matter, peat and brown coal sand in deep groundwater. However, knowledge is missing about: - Additional sources from geochemically modified conditions, especially from clay organic matter and organic components of the waste and waste forms in the near-field, and - Mobility of humic colloids in relation to the origin and associated differences in properties. (ii) In the HUMICS project, via two migration cases initial work was done on visualizing the consequence of humic colloid mediated actinide transport. The two migration cases were both for saturated sandy aquifer systems with advective flow. Verification of the basis for formulating these migration cases and application to other situations was still missing.	(i) Further develop the understanding of origin, stability and mobility of humic colloids in relevant systems - Investigate if there are possible differences in the mobility of humic colloids of different origin in groundwater over salt gradients, and if so, relate these differences to differences in characteristic properties - Investigate the potential for additional source from clay organic matter under alkaline cement dissolution near-field conditions. (ii) Improve the two existing migration cases by inclusion of new information and formulate migration case for uranium mining and milling rock-pile. Visualise the impact of humic mediated actinide migration on these three migration cases by application of the kinetic approach at its further developed status.	(i) - In the Gorleben aquifer system with its salt gradient reaching from fresh recharge near surface groundwater to deep salt saturated brines, fulvic acid from recharge is shown to be mobile over the entire depth (and salt gradient), whereas fulvic acid from in-situ generation (microbial turn-over of Miocene brown coal sand in deep groundwater) is not penetrating into the salt saturated brines. This means that a priori statements concerning the mobility of humic colloids are not possible, especially not for additional sources from the near-field with their very much unknown properties. - Large amounts of humic and fulvic acids are generated by alkaline hydrolysis of clay organic matter under cement dissolution near-field conditions. Despite some variations in characteristic properties, depending on the origin, principle actinide complexation behavior is the same as for typical humic acids. The mobility of the humic colloids from this additional source still needs to be investigated. (ii) The impact of humic colloid mediated actinide transport was visualised on the three migration cases. The impact cannot be disregarded under these advective flow groundwater and rock-pile conditions.

Another issue is the question of mobility of dissolved humic substances in its natural colloidal form. Investigations in real systems ((isotope-)geochemical analysis of groundwater systems) show that humic colloids in general are stable (directly shown for up to 15.000 years) and mobile like ideal tracers. One exception is the Gorleben aquifer system, where fulvic acid from deep groundwater in-situ generation is not mobile into high ionic strength groundwater near the salt dome, whereas fulvic acid from recharge is. For the recently identified potential additional source of dissolved humic substance from high pH influence in the clay near-field, such a prediction of their mobility over relevant time and spatial scales is not yet possible (no natural chemical analogue available).

5.2.2. Applicability of laboratory data

The principle agreement between laboratory transport studies and the anthropogenic actinide contaminant studies in the Irish Sea shows, that there is an agreement between laboratory and large scale anthropogenic systems. However, the short-term laboratory studies and the chemical environment in the Sea may not adequately reflect natural groundwater conditions and the time-scales involved. This may be specifically true for chemically amended near-field conditions and the potential for actinides to become built into humic colloids in a comparable fashion as found for the natural trace element inventory, presumable in mineral inclusion form. When it comes to prediction of mobility in the aqueous phase, only real system analysis provides trustworthy information, presently missing for the clay near-field and other additional sources (cf. above).

5.2.3. Impact of humic colloid mediated transport versus mineral bound humics/organics

The kinetics of radionuclide interaction with the aqueous humic inventory (humic colloids) is comparably well known. In the present approach, the slow dissociation kinetic mode leads to an enhanced actinide transport irrespective of the nature and concentration of sorbing sites on the sediments. The magnitude of the impact is determined by the groundwater flow rate relative to the magnitude of the slow dissociation kinetics, and may be negligible especially in diffusion controlled systems. Where the radionuclide has already interacted with the sediment, the increase in mean residence time in the mobile phase, due to the slow dissociation mode, is also relevant at considerable groundwater flow rates.

Corresponding radionuclide interaction data for the stationary organic/humic inventory is not known. Characterisation of clay organic matter shows that humics and humic precursors are present. The solubilization and release of humic matter from this source is very much associated with formation of carboxylic groups. This means that distinction between the two inventories (mobile and stationary organics/humics) is not the result of sorption/desorption equilibrium exchange but reflects structural differences, especially the lower content of complexing carboxylic groups in the stationary inventory. Furthermore, solubilization is associated with breaking of strong bonds to the mineral surfaces (not only sorption through the less hydrophilic nature). This clear distinction in the two inventories by their very different nature is also reflected in the capability to perform ^{14}C groundwater dating by dissolved fulvic acids.

In summary, adequate knowledge about the stationary humic/organic inventory is still missing, especially the radionuclide interaction kinetics required for application to PA.

5.2.4. Amendment of mineral surface properties

As mentioned above, organic/humic substances are bound to mineral surfaces. This leads to an amendment of mineral radionuclide sorption properties. Organic coating may be found on less active surfaces, changing the chemical properties, but will have a more specific impact by sorption on otherwise active sites. Determination of this impact of organic substances on the mineral surface properties is still at an infant stage.

5.2.5. Overall importance of humic substances

With respect to humic colloid mediated transport enhancement, humic substances appear to be important for the long-term assessment of a repository in many systems. With respect to the interaction with stationary organic/humic substances, the situation is not yet clear, however, the radionuclide retention by minerals will be strongly influenced by the organic coating and sorption on active sites. Consequently, for a large number of systems, as a minimum the impact of humic substances should be considered and brought into comparison with other possibly more important impacts.

5.2.6. Availability of knowledge, data and models

Actinide humate interaction data is available with exception for the tetravalent ions in the relevant pH range, some other mixed/ternary complexes and description of the competition impact by other cations. Ranges of kinetic radionuclide humic colloid interaction data are available.

With reference to the HUPA project, interaction of iodine with humic substances gives partly contradicting results, and thus the potential retention via the stationary humic/organic substances is still not resolved.

To some extent, models and associated data are available for trustworthy prediction of the humic colloid mediated actinide transport. This especially refers to the agreement between the "several decades long migration case" with anthropogenic contaminants at the shore of the Irish Sea and other sources of knowledge and data. Transport codes for the modeling of column experiments under near-natural conditions are available, correctly predicting the magnitude of the "ideal tracer mobile fraction". The capability to predict the transport of the residual inventory still is not fully demonstrated. This especially refers to decoupling of the unknown dissociation kinetics from the stationary phase and the transport enhancement in the mobile phase.

5.2.7. Implementation in PA

For the purpose of application to PA, a broad basis of data and knowledge is available, reaching from progress in detailed complex coordination to large scale real system analysis. At the end, however, data that will enter into PA will probably be restricted to overall description of humic colloid sources and their mobility, and the radionuclide interaction kinetics with both humic colloids and the stationary inventory. The sorption on and coating of mineral surfaces will probably be included via the sorption behavior of the minerals. Introduction of the kinetics in the exchange of radionuclides between different compartments in an element along a potential flow path is possible in PA codes. The underlying mechanisms, however, are still unclear and trustworthy data for stationary organic/humic substances are missing. Therefore, confidence in long-term predictions over many thousands of years remains hampered.

6. Remaining main uncertainties

Uncertainties are still given with respect to:

- Lack in process understanding resulting in lack in trust in long-term predictions,
- The problem of selecting processes observed in different types of experiments under different types of conditions and by different systems investigated, for their regard or disregard in the predictive long-term modeling,
- The potential for incorporation of actinides into humic colloids in a comparable fashion as found for the natural trace element inventory, especially under geochemical conditions deviating from those typically found in natural groundwater systems, such as those found in the near-field,
- The magnitude of some interaction data is still unsatisfactorily, especially (i) the lack in trustworthy data for the tetravalent actinide ions forming ternary complexes under relevant conditions, and (ii) lack of adequate data for some other ternary complexes,
- The impact and treatment of cation competition is unclear, especially with metal ions abundant in natural groundwater systems,
- The potential differences between the frequently studied aquatic humic and fulvic acids, and the basically unknown properties of their sediment organic carbon precursors of aquatic humic substances, key substances for actinide retention, still needs to be resolved,
- Potential additional sources need to be quantified, especially under non-natural near-field conditions,
- Stability and mobility of humic substances depending on their properties/origin, especially in view of potential additional sources for which no natural chemical analogues are available, and
- Stationary humic/organic substances as a potential source for retention of iodine is still not clear.

Based on the great progress within the HUPA project, including the established knowledge network(s) where the foundations have been laid also during earlier EC supported RTD activities/programmes, these topics will be subject to further studies beyond the present project, especially the integrated project Fundamental Processes of Radionuclide Migration (IP FUNMIG), starting January 2005 and with a duration of four years.

7. Progress within work packages

7.1. WP 1 (Critical assessment of experimental methods)

7.1.1. Progress within experimental programme

Analytical methods and approaches for complexation studies may be divided into three different types:

- Separation of different species by size, charge, … . Examples are dialysis, ultrafiltration, (ultra-)centrifugation, size exclusion chromatography and electrophoresis. Examples of potential problems arising are shift in equilibrium, insufficient species separation and loss of species.

- Indirect speciation via additional complexing agents, ion exchange or ion selective electrodes. Examples of potential experimental problems are complexity of data analysis relying on additional input data, generation of additional unintended species and unintended processes that may influence equilibrium.
- Direct speciation via spectroscopy has a limited sensitivity range. In the case of fluorescence spectroscopy, the behavior of excited states may deviate from that of the ground state and photodynamic processes need to be well understood.

Analytical methods representing the first two groups are investigated.

Experimental conditions the intercomparison of the experimental methods were defined with respect to temperature, pH, ionic strength, humic acid concentration, equilibration time and metal ion to humic acid ratios. In order to have a common basis for the intercomparison of different experimental methods, one batch of Aldrich humic acid is used. Purification and the thorough characterisation are documented well in order to establish a good basis for intercomparison within the exercise as well as comparison with well documented published data. Analytical data showed that the purification was successful.

Results of the analysis of different experimental methods may be summarized as follows:

i. Dialysis

Different membranes were used with different material and nominal cut-off of 500, 1000 and 10,000 Dalton. General trends expected for the complexation were observed, namely that the free metal ion concentration decreases with increasing pH, with decreasing ionic strength and humate ligand loading.. With large pore-sizes humic acid is transported across the membrane, and thus the required separation of species is not obtained. With small pore-sizes equilibration is slow. In all cases sorption of the free metal ion takes place.

In summary, slow establishment of equilibrium, large sorption of the metal ion and trustworthy humate complexation data can only be obtained when experimental setup and conditions are well chosen. This restricts the method to narrow analytical windows.

ii. Cation exchange

In this method the system consists of three components, namely the metal ion, the humic acid and a cation exchanger added in order to define the free metal ion concentration. For this purpose, Amberlite IR-120 was used.

The general expected trends were observed, such as increase in the free metal ion concentration with decreasing pH. Furthermore, the effect of pre-equilibration was found to be small and variable. The kinetic behavior of europium humate as reported in the literature was verified. A considerable problem, however, is that the interaction between the free metal ion and the added cation exchanger is non-linear. Evaluation of data thus has to take into account this non-linear interaction. If this is done, trustworthy results are obtained. With respect to making use of published data, it must be ensured that the isotherm used as input data for the distribution between non-complexed metal ions and the cation exchanger is adequately investigated.

An additional difficulty was also encountered during the investigations, namely the general problem of regarding formation of polymeric species. The U(VI) humate complexation was studied by ion-exchange method as a function of pH, ionic strength and concentration of U(VI) and Aldrich humic acid. The metal ion concentration dependent outcome indicates the formation of polymeric products of U(VI) hydrolysis.

In summary, the method depends on non-linear isotherms with the metal ions. The large surface of the exchanger adds to further problems with the interpretation.

iii. Electrophoresis

Free liquid moving boundary electrophoresis was used for determination of the Eu(III) and Th(IV) mobility under different experimental conditions, including progressive loading of the humate ligand.

With respect to the non-hydrolyzing Eu(III), as expected, the ligand capacity of humic acid increases with increasing pH (pH 4 -> pH 6). Problems arise through sorption of europium ion and the humate complex. The analytical window is relatively narrow and the method is not sensitive close to humate ligand saturation.

With respect to Th(IV) with its strong hydrolysis in the pH range of the intercomparison study, problems encountered are sorption loss of thorium possibly accompanied by distortion of equilibrium, errors in measurement of electrophoretic mobility, and formation of mixed ternary complexes, polynuclear species, pseudocolloids and carbonate complexes. Occurrence and effect of the phenomena depends mainly on pH and concentration of thorium. In addition, the mutual effect of positively and negatively charged Th species on their mobility needs to be considered. Nevertheless, appropriate interpretation of electrophoretic data enables obtaining important information on the abundance and charge of Th humate complexes, for example on changes due to progressive ligand loading by Th(IV). Given the low solubility of Th(IV) in the pH neutral range, impurities is also a considerable problem.

In summary, the electromobility may assist in quantification and characterisation of complexes formed. Care must be given that the number of complexes of different charge is kept sufficiently small for distinction between humate and other negative complexes. The large surfaces involved makes sorption a problem. Direct deduction of complexation constants is difficult.

iv. Size exclusion chromatography

Sephadex G15 column was used in combination with UV/Vis detector for humic substances. The total europium concentration in different fractions was determined by AAS and/or OES. A large number of experimental problems are found, including the narrow humic acid metal ion loading window applicable and poor separation of humate complex and non-complexed europium ions, also influenced by charge exclusion through ionic medium and the buffer (citric acid). Furthermore, pH and degree of humate ligand loading influence sorption of humic acid. Evaluation relies on data for the generation of complexes with the buffer used.

In summary, this method is associated with considerable experimental problems and may be used only in a narrow analytical window.

v. Ultrafiltration

In the ideal case, an ultrafilter is used where the non-complexed metal ion shows no retention and no sorption, whereas the humate complex is fully retained. Ultrafilters are usually characterized by a nominal cut-off referring to full retention (> 95 %) of globular proteins of a given mass. Below that mass (size) retention decreases over a wide range with decreasing mass(size). Humate complexes can be expected over the mass range of humic acid, reaching down to few hundreds of molecular mass (known from application of recently developed mass spectroscopy methods). The effective size of the metal ion humate complexes, however, is not known. Furthermore, the effective size of hydrated metal ions is not well understood. Direct correlation to nominal cut-off is not possible due to different size to mass ratio compared to the ultrafilter reference substances (globular proteins). Thus, selection of a filter ensuring complete retention of humic acid and humate complexes is not possible. This problem may be visualised by the 86 % retention of the europium oxalate complex on an ultrafilter with a nominal cut-off of 500 (Dalton globular proteins). A carboxylic acid calibration substance for FFF and HPLC with the molecular mass of 370 is basically fully retained on a 1000 Dalton ultrafilter.

In summary, it is not possible to find an ultrafilter resulting in quantitative retention of the humate complex and quantitative permeation of the non-complexed metal ions. Sorption of the non-complexed metal ion may be significant. Build-up of concentrations in the retentate may further contribute to difficulties in analysis of the system behavior. Consequently, ultrafiltration based humate complexation data need to be interpreted with caution.

vi. Acid-base titration

High humic acid and metal ion concentrations are needed to obtain measurable effects on titration data. Slow titration is required in order to ensure equilibrium. Evaluation of data is not straightforward. The applicability of results obtained by this method is limited, particularly for environmentally relevant metal and humate concentrations.

7.1.2. Summary of progress within WP 1

A large number of experimental systems and approaches have been investigated. Most methods suffer under problems in unambiguous identification of the different species involved. Sorption on large surfaces and non-linear interactions are additional obstacles in the data evaluation process. The preferred approach is to combine methods chosen for the particular analytical window considered and the specific information required (equilibrium distribution or exchange kinetics). Furthermore, specific methods may be used for identification of particular properties, such as the charge by electro-mobility.

7.2. WP 2 (Generation and characterisation of humic material)

The generation and characterisation of humic material is divided into the types of humic material.

7.2.1. Natural humic and fulvic acid reference material

One reference batch of Aldrich humic acid was purified within the humate complexation intercomparison exercise. Basic characteristic properties show that purification was successful (cf. WP1).

Humic and fulvic acids from the Gorleben groundwater Gohy-573 has been used within the EC activities in this field since the start of the MIRAGE project (MIgration of RAdionuclides in the GEosphere). A large number of complexation data has been generated over the past many years. The original material has been used up and new batches have been prepared and characterized. These two new well characterized batches will enable continuation of generation of complexation data with humic and fulvic acids from this particular source. Large amounts of humic and fulvic acids were prepared from 6 m_3 of this Gorleben groundwater. The material was characterized by a variety of methods, such as elemental composition, including inorganic impurities, spectroscopic properties (UV/Vis and IR), functional group content (potentiometric pH titration and XPS), size distribution (AF_4), and mass distribution (TOF-SIMS and ESI-MS). The mass distribution of the humic acid has its number average molecular mass in the range 500-600 mass units, with tailing up to around 3000 mass units. The corresponding numbers for the fulvic acid are 400-500 and 2000. The proton exchange behavior has been thoroughly characterized. These results verify the typical behavior of the two new humic and fulvic acid batches.

The characterisation shows that the isolation and purification was successful. Selected properties are compared to data from the previous EC reference humic and fulvic acids from this groundwater in order to provide for comparison, especially in view of future complexation studies and the relation to results from the past almost 15 years of studies on the previous batches. The material is distributed to interested parties upon expression of interest with brief description of work to be performed.

7.2.2. Synthetic humic acids with designed properties

Synthetic humic substances can be generated with designed properties. In the present project, emphasis was on the redox properties in order to study the influence of humic acid on the behavior of redox sensitive actinide ions, and on blocking of phenolic groups for identification of their influence on the complexation process..

Variation of the starting material is done by no addition of amino acids, addition of glycine and addition of glutamic acid to synthesis of humic acid with high hydroquinone content. The redox capacity is determined by reduction of Fe(III) to Fe(II). Studies on the redox capacity show that in addition to straightforward comparison of the amount of redox sensitive groups, additional processes are involved. The redox capacity for the designed humic substances is considerably higher than for typical natural ones. At pH 9 the redox capacity of the specifically designed ones is around 35 meq/g. The corresponding number for Aldrich humic acid is about one third. Initial investigations show that phenolic groups are strongly involved in the redox processes, however, the effect is more pronounced than what would be obtained for a simple oxidation of phenolic OH groups. The capability of humic acid to reduce uranium(VI) to uranium(IV) was spectroscopically verified for pH 9.

Natural Aldrich humic acid was modified by blocking of phenolic groups. Subsequently, the interaction of this and the original Aldrich humic acid with Np(V) was studied in order to determine the role of the phenolic groups.

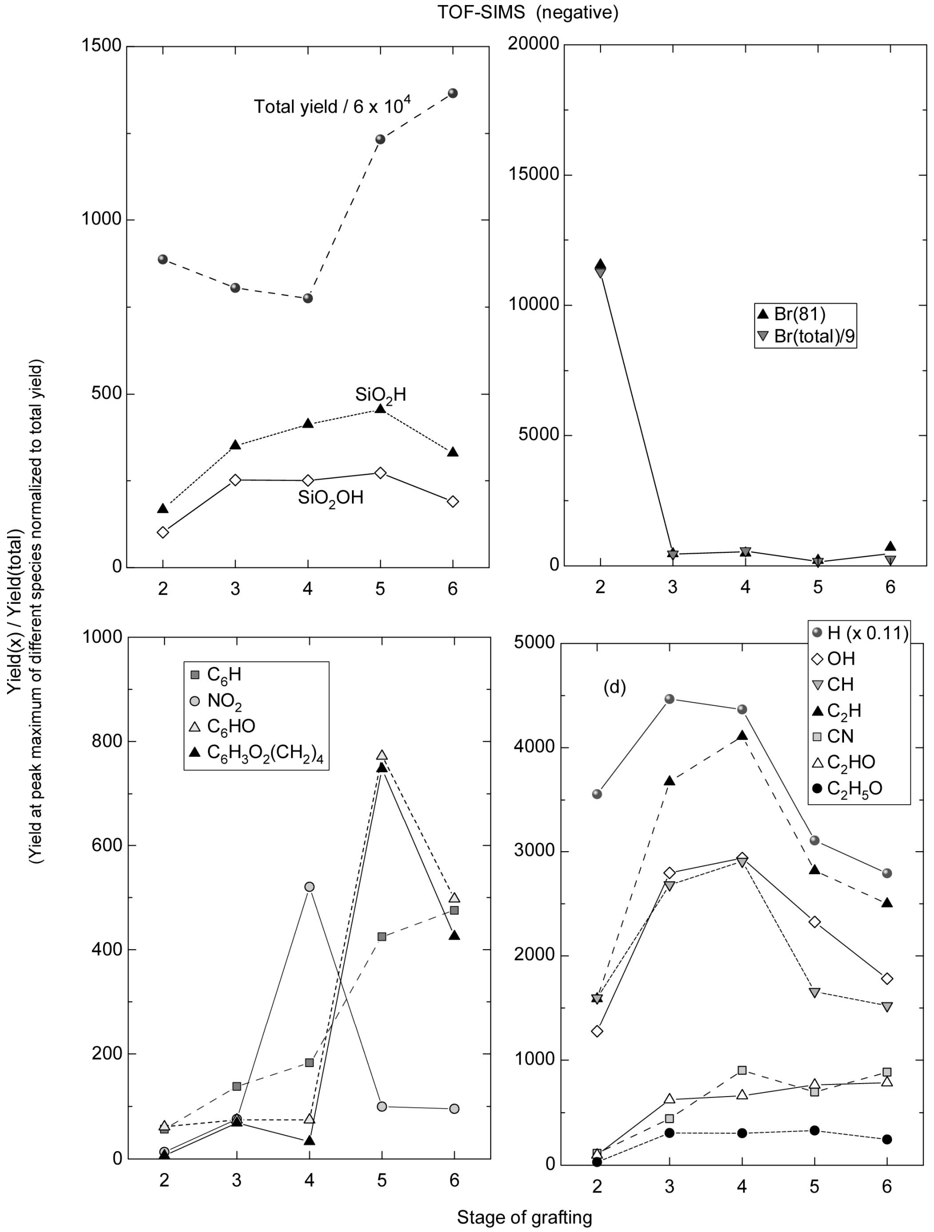

Fig. 2: TOF-SIMS characterisation of the humic wafer generation process. Analysis of different processing steps shows the appearance and disappearance of species related to progressive build-up and chemical amendment of the surface. The stages shown are: (2) bromosilane, (3) alcohol, (4) nitrobenzoyl, (5) aminobenzoyl, and (6) humic wafer (for details, see Annex 13 in FZKA 6969)

7.2.3. Humic wafers

Silica wafer surfaces are used for covalent attachment/binding of humic acid via a number of different approaches. This is done for two different reasons. Such humic acid coated silica wafer surfaces provide the possibility for studying metal ion humate coordination by a large number of surface sensitive/selective methods (for example grazing incidence x-ray spectroscopy, flat angle total reflection laser induced fluorescence spectroscopy and TOF-SIMS). Another reason for generation of such material is that interaction data can be obtained for systems where phase separation is difficult and direct speciation methods are not applicable. This is especially the case with tetravalent actinide ions. The transferability of such data from surface bound to dissolved humic acid still needs to be verified or deviations determined. In the latter case, such deviations need to be related to physico-chemical differences between surface bound and dissolved humic acid.

Three different synthesis approaches were used. Individual steps and the final product were characterized by FTIR, TOF-SIMS and AFM. Considerable problems were identified. The main problem found is that the spacer molecules do not attach as monomers to the silica surface, providing the dense homogeneous "carpet" required. Instead, the spacer molecules polymerize and large structures sorb on the surface. Such inhomogeneous distribution of large polymerized spacer material may occur, as demonstrated by a combination of AFM and TOF-SIMS. The finally used methods were shown to avoid such problems (Fig. 2).

Comparison of complexation with Am(III)/Nd(III) showed that humic wafers generated with sufficient care show comparable behavior. An important result of characterisation was that the mass distribution of humic acid on humic wafer was basically equivalent with that found for the starting humic acid. This verifies the low and narrow mass distribution of humic acid, contrary to previous assumptions (cf. below).

Reflecting the unexpected difficulties in generating and providing adequate evidence for the quality of the humic wafers, characterisation of the complexes by advanced analytical methods could not be done during the project.

7.2.4. Characterisation of humic material

Characterisation of the humic material serves different purposes, such as (i) ensuring that the material generated is adequate, (ii) providing the basis for identification of differences in, for example complexation and mobility properties, (iii) improving the overall knowledge base for this class of substances, and (iv) coupling the basic properties with adequate development of interaction processes. Contributions to all these aspects have been provided within the project.

<Mass distribution>

The mass distribution of humic and fulvic acids has become accessible in recent years by application of new mass spectroscopy approaches (MALDI-TOF, ESI-MS and TOF-SIMS) and Overhauser-NMR, showing that humic and fulvic acids. The importance of these findings, the great contribution by the present project partners and the reluctance of the concerned scientific community to accept that the humic and fulvic acid molecules have much lower mass distributions should not be underestimated. It is a key point in understanding the overall nature of these substances. A special highlight in the present project is that not only different mass spectrometry methods have been used, a plausible correlation with the size-distribution presented, but also that mass spectrometry of humic acid on humic wafers show the original mass distribution (cf. above).

<Size distribution>

One characteristic property of humic and fulvic acids are their hydrodynamic size distributions, measured by the diffusion in liquid media. Analytical methods frequently used for this purpose are size exclusion chromatography (SEC) and field flow fractionation (FFF). Evaluation is normally based on comparison with a series of standards of known molecular mass. In the past there has been a debate on the comparability of different standards and humic acid with respect to the size to mass ratio. This should also include the respective response to changes in pH and ionic strength. Finding a set of standards with similar mass to size ratio as humic acid could be an indication towards the nature of humic acid. Comparison was done of the hydrodynamic size of humic and fulvic acid on one hand, and a number of "simple" organic acids and a series of polyacrylic acid standards on the other hand. The overall outcome is that the size to mass ratio of fulvic acid is directly comparable with these simple organic molecules. The humic acid shows a more bulky behavior.

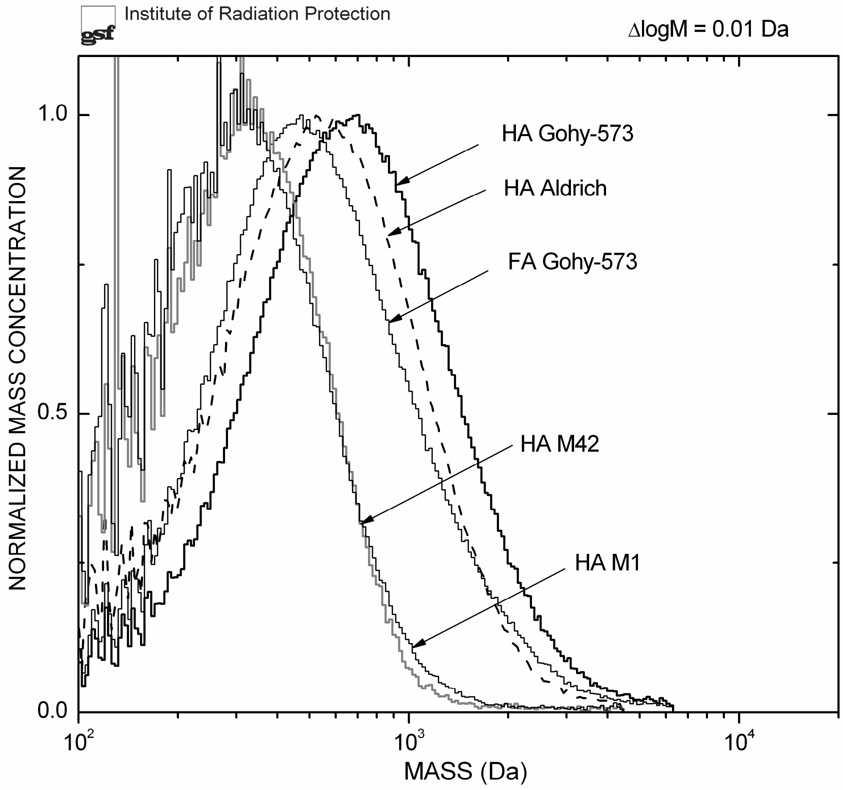

Fig. 3: Mass distribution of humic and fulvic acids from the Gorleben groundwater Gohy-573 (reference substances), Aldrich humic acid and the synthetic humic acids M1 and M42. The mass distribution is shifted to lower numbers for the Gohy fulvic acid compared to the corresponding humic acid. The mass distribution maxima of the humic and fulvic acids of natural origin fall in the range around 400-700. For details around the mass distribution of humic and fulvic acids, see Annex 8 and 12 of FZKA 6969, and Annex 4 of FZKA 7070

<Characteristic properties and humate ligand concentration>

The effective humate ligand behavior over the entire pH range up to pH slightly above 10 was evaluated by comparison of the known complexation behavior with strongly complexing tri- and hexa-valent actinide ions, as well as the protonation behavior. The result is surprisingly simple. The effective humic acid ligand concentration is equal to the number of non-protonated and non-complexed molecules. For this purpose the identical mass distribution as found by mass spectrometry was a key issue.

<Thermal stability>

The thermal stability of humic substances was investigated (Fig. 4). This is important for the generation of thermodynamic data, i.e. entropy and enthalpy. The present findings may also form the basis for basic understanding of evolution of sediment organic carbon under thermal influence and the relation to the characteristic properties, including the tendency of release of/ conversion into aquatic mobile complexing humic and fulvic acid. A combination of mass spectrometry of substances released and reflection IR-spectroscopy is used for humic acid under increase of temperature.

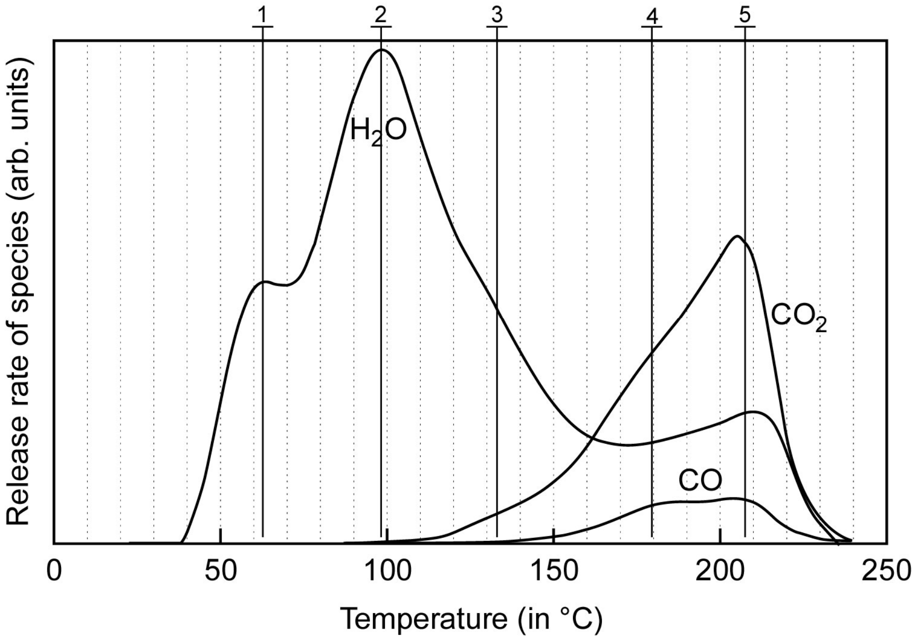

Fig. 4: Thermal stability of dried humic acid under inertgas. Release of water, carbon monoxide and dioxide are monitored by mass spectrometry (for details, see Annex 22 in FZKA 6969)

Two distinct water releases are observed at around 60 °C and around 100 °C. Just above this temperature, carbon dioxid and carbon monoxide are released showing thermal decomposition. The release of water is a combination of reversibly bound physically bound water (around 3 % of total humic acid mass), and additionally around 4 % resulting from condensation processes around carboxylic and phenolic groups. The results agree with changes in the spectroscopic properties of dissolved humic acid and thus also serve the basis for interpretation of the temperature dependency of actinide humate interaction.

7.2.5. Summary of progress within WP 2

Different types of humic material has been isolated/generated, namely new batches of natural humic and fulvic acids, synthetic humic acid with designed reducing properties, natural humic acid with blocked phenolic groups, and humic wafers by different synthesis routes, i.e. covalent binding of humic acid on functionalized silica wafer. Characterisation contributed to showing that the material is adequate, but also with information of fundamental character very much contributing to improvement in the overall system understanding. Isolation and characterisation of humic and fulvic acids from clay organic matter under high alkaline cement dissolution near-field conditions was treated under work package 8 (system definition, additional sources). Especially through the accompanying characterisation of the clay organic matter as the source for these aquatic humic and fulvic acids, characterisation workt has also contributed to the overall understanding of the nature of humic substances.

7.3. WP 3 (Radionuclide humate interaction data by designed system investigations)

Complexation data are available for a large number of types of ions. Data missing are especially on (i) ternary complexes, always formed by tetravalent actinide ions in the whole pH range of interest, the uranyl ion above pH of about 4, and trivalent actinide ions above approximately pH 7, (ii) reduction of uranium, neptunium and plutonium, especially to the tetravalent oxidation state, as the key parameter for which their humate interaction, and (iii) the possible interaction with iodine. In addition, the interaction of Np(V) was investigated with Aldrich humic acid in its original state and with after blocking of the phenolic groups. A considerable contribution to this work package is also given by the work done on critical assessment of experimental methods (cf. WP 1).

7.3.1. Ternary complexes

<Uranyl monohydroxo humate>

The complexation of the hexavalent uranyl ion with humic acid was studied. By the use of a humic acid ligand concentration prediction, discussed under work package 7, solubility enhancement over hydroxide solid phase can be rationalized by one single interaction constant. The stepwise complexation constants from different routes to the formation of the ternary hydroxo complex indicate complexation enhancement relative to expectations by comparison with other simple complexes. A suggestion is made with respect to the possibility for hydrogen bonding with the abundant neighboring oxygen functionalities. Measurements in undersaturation, however, may be desired in order to exclude the possible formation of polynuclear complexes.

<Plutonium humate interaction>

The impact of humic substances on the geochemical behavior of plutonium is related to both the interaction of different species of different oxidation states as well as the influence on the plutonium redox state. According to pH/Eh conditions of the Gorleben groundwater Gohy-532, the non-humate complexed plutonium ion is expected to be in the trivalent state. Addition of plutonium at different starting oxidation states results in the same end-state. The importance of humic substances for the redox process is seen by the rapid reduction of Pu(VI) to Pu(V) in the original groundwater compared to the much slower reduction in groundwater where the humic substances have been removed by ultrafiltration. The distribution between Pu(IV) and Pu(III) is dependent on pH and the redox potential. A complication in interpretation of the species distribution is the indication for coexistence of Pu(IV) humate complex and polymeric Pu(IV) hydroxide. The latter is identified in the groundwater samples by both XPS (satellite bands) and EXAFS (Pu-Pu bond distance). A further complication is the distinction between the impacts of physico-chemical conditions on the equilibrium distribution versus redox kinetics. A great deal of further studies will be required in order to provide a tool for reliable prediction of the chemical state of plutonium in reducing far-field relevant groundwater.

<*Tetravalent actinide ions*>

Great progress has been achieved in bringing complexation data on the humate interaction of tetravalent actinide ions together with basic input data on hydrolysis and carbonate complexation. Testing calculations with observed experimental data show that the impact of humate complexation at different pH and carbonate concentrations can be predicted with acceptable agreement for Pu(IV) and Np(IV). Problems are still there for U(IV). The overall approach and the apparent success in predicting the impact of humic substances on the species distribution of tetravalent actinide ions is a great step forward towards inclusion of the humate complexes in geochemical modeling. In order to test the plausibility of the data used and in order to provide insight in individual processes involved, individual interaction constants for the hydrolyzed tetravalent actinide ions with humic acid will be deduced and compared with expectation values.

7.3.2. Actinide reduction by humic acid

Studies have continued on the reduction of actinide ions by humic acid. Previous studies have shown that humic acid can reduce, amongst others Np(V) and U(VI). The redox impact on plutonium is discussed above. For studies of the processes involved, synthetic humic acids have been generated designed with high reducing strength and capacity. The strong reducing character of the designed synthetic humic acids is based on high phenolic OH group content. Comparison between different natural and designed humic acids shows a strong relation between the phenolic OH group content and reducing strength/capacity. Another direct evidence for phenolic OH groups being key players in the reducing character of humic acids is that chemical blocking of the phenolic OH groups results in strong decrease in the reducing character. As a number of studies reported through the HUPA project have shown, however, the phenolic OH group content is not a sole parameter capable of directly describing the overall reducing function.

7.3.3. Iodine humic acid interaction

The binding of iodine to humic acid has been studied in order to provide an answer to the question if there is a trustworthy basis for iodine retention by sediment humic substances. It was shown that the iodine under reducing conditions, i.e. present as iodide ion, does not complex with humic acid. The humic acid, however, has an influence on the reduction of iodine species and thus have an influence on the geochemical behavior. The investigations show that the influence of humic acid is different from that of simple defined phenols and that non-linear processes are involved.

Previous results showed that the iodine does bind to humic acid under specific conditions. A natural humic acid with high iodine content also shows the potential relevance for iodine humic acid binding. Humic acid bound iodine was characterized by three different advanced analytical methods. These are XPS, ESI-MS and XAFS. Both XAFS and XPS indicate dominance of covalent binding. ESI-MS, however, showed separate mass spectroscopy peaks for iodine and humic acid. To which extent the latter is a consequence of the electro spray ionization process and the other two methods show the actual binding nature still needs verification.

7.3.4. Complexation after blocking of phenolic groups

The complexation of pentavalent neptunium has been studied at pH 7 and 8. In order to obtain an insight in the complexation mechanism, Aldrich humic acid was used before and after modification by blocking "phenolic" OH groups. The stability constant remains uninfluenced of both pH and blocking of the phenolic groups. The loading capacities, however, show not only the expected decrease with decreasing pH but also with blocking of the phenolic groups. The mechanism for the decrease in the loading capacity is not yet well understood. These studies, however, are important contributions in providing information for the necessary progress in the complexation process understanding. One may consider the results in relation to the simple humate ligand description developed within the project. In that case, a number of humic acid molecules become deactivated through the chemical reaction with the phenolic groups. The rest of the molecules remain unchanged in their complexation behavior.

7.3.5. Humic wafer interaction studies

Three types of humic coated silica wafers generated by different approaches were selected for studying the possibility to use surface bound humic acid in studies on the humate complexation behavior and application of surface specific methods making use of the high local ligand concentration in a defined surface layer. One wafer type is used where the entire generation process has been thoroughly characterized by TOF-SIMS and AFM studies on the starting wafer material and all intermediate as well as the final process products. Two silica wafers coated with humic acid by other approaches were also used.

An interaction intercomparison study was made by determining the Am(III)/Nd(III) interaction with the three different wafers. It was shown, that using two different approaches give very similar sorption isotherms. As expected, a deviating behavior is found where water is used during synthesis leading to undesired and uncontrolled hydrolysis.

7.3.6. Summary of progress within WP 3

Critical data have been generated and a considerable contribution is made to the process understanding. A trustworthy evidence for the relevance in iodine binding to stationary humic acid as a reliable retention process requires further studies. Given the complexity of ternary complexes and the overlay of redox reactions, the overall process understanding with respect to the key element plutonium is still not satisfactorily.

7.4. WP 4 (Characterisation of radionuclide humate complexes)

This is a key element in the project, aiming at providing sufficient evidence for the trust in long-term predictive modeling. This section is divided into topics, namely (i) mass and size distribution of humic acid and their actinide complexes, (ii) information about the complex coordination, and (iii) the question of the origin of kinetic modes. Information on basic molecular properties and differences between humic material of different origin is also discussed. It should also be mentioned, that the studies discussed under WP1 provide information about the charge of the complexes.

7.4.1. Mass and size distribution

These studies are especially made in reflection of the possibility that complexation induced association of humic or fulvic acid molecules is responsible for the slow dissociation kinetics observed in laboratory studies.

<Mass distribution>

Mass spectrometry shows a strong impact of complexation on the mass distribution of humic acid. ESI-MS and TOF-SIMS show a decrease in overall signal with increasing Eu(III) humate loading. Thereby, the relative peak at high masses increases. To which extent ionization of europium complexed molecules with lower masses was preferentially suppressed or if the abundance of higher masses increases due to complexation induced humic acid molecule association is not fully clear. The impact is lower on fulvic acid than on humic acid. In addition, longer contact times enhance the impact on humic acid.

<Size distribution>

Size distribution measurements are conducted by AFFFF (asymmetric flow field flow fractionation) with different humic and fulvic acids at different degrees of ligand loading with Eu^{3+}, as well as impact of contact time in order to regard possible rearrangements along with progressive occupation of kinetically more stable complexation modes. In the case of fulvic acid, no impact was found on the size distribution, including different ligand loadings and contact times. For humic acid, a slight increase in size distribution and broadening of the elution peak was found. This modest effect was not observed except for upon approaching humate ligand saturation. A slight increase in the size distribution is also observed after 7 days contact time. The modest impact observed at high loading and with long contact time for humic acid may indicate complexation mediated humic-humic association, i.e. an intermolecular complex formation. The lack of such an observation in fulvic acid, however, makes conclusions difficult. In addition, if the complexation is followed by dehydration of ligand functional groups and the relatively bulky humic and fulvic acids associate in a favorable fashion, a large impact on the size distribution is not expected. The fluid medium used for AFFFF measurements is 10 mmol/L ammonium acetate without Eu^{3+}. Therefore, decomplexation at least of fast dissociation modes during measurement may also be important. Last but not least, previous investigations within the HUPA project with AFFFF fractionation into what is expected to be different size fractions followed by mass distribution of these fractions by TOF-SIMS, showed no significant correlation between the size distribution obtained by AFFFF and their humic acid mass distribution.

In summary, the AFFFF results are difficult to interpret, but may indicate generation of larger entities with complexation at high metal ion ligand loading. This is also expected because of the known flocculation of humic acid for ligand saturation with multivalent metal ions. The lack of such an observation for fulvic acid is in qualitative agreement with the lack of flocculation of fulvic acid at high metal ion ligand loading. Nevertheless, changes in size distribution could be expected also for fulvic acid reflecting observations on sharp increase in scatter light under such conditions.

7.4.2. Coordination and humate ligand behavior

X-ray absorption spectroscopy (XANES and EXAFS) has been applied to determine the local binding environment of humate bound actinides of different oxidation states (Pu(III), Th(IV), Np(IV) and Np(V). In order to obtain additional information, also humic acid with blocked phenolic groups was studied. The obtained structural parameters were compared to data on actinide hydrates, Bio-Rex 70 actinide complexes (cation exchange resin with only carboxylic groups) and crystallographic data of actinide complexes with organic ligands from the literature. The results may be interpreted as dominance of monodentate carboxylic coordination to the actinide ions. These results are of great importance for delineation of the effective humate ligand function under different physico-chemical conditions and the obviously very invariant coordination environment. It is also reflected in the invariant stability constants obtained if the effective humate ligand concentration under given physico-chemical conditions is regarded.

In general, synchrotron radiation based investigations are performed at very high substrate concentrations. The question arises to which extent data obtained under such conditions are relevant for the much more dilute conditions found in nature and used with other experimental techniques. Europium humate complexation behavior was compared from moderate to very high humic acid concentrations (2 g/L). No difference in saturation values was found for different humic acid concentrations. The results indicate that self-association of humic acid is not important for the effective humate ligand concentration and that results from synchrotron radiation spectroscopy obtained at high humic acid concentrations are applicable also in much lower concentration ranges. It furthermore supports model development according to which association is driven by charge neutralization and balancing of surface charge density versus relatively weak associative forces (cf. below, WP 7).

7.4.3. Kinetic modes

It is well documented that the actinide humic acid complexation is subject to comparably slow kinetics. The kinetics is frequently divided into two or more kinetic modes, based on fitting of complex association/dissociation data. One important question is to which extent such kinetic modes are real or merely reflect parameters that suffice for fitting the overall behavior of a gradual transition without distinct individual kinetic modes. Another question is to which extent the kinetics, and the overall interaction behavior, is significantly different between flocculated humate complex and dissolved/dispersed entities. Comparison was done of the dissociation kinetics between, on one hand low metal ion loading by scavenging of dissociated metal ions with a cation exchanger and, on the other hand isotope exchange between metal ion humic acid flocculate and non-complexed metal ions. No principle difference was seen, justifying the common approach of inclusion of humate flocculate into the amount/concentration of humate complex for the purpose of evaluating complexation constants.

EXAFS spectroscopy and time resolved laser fluorescence spectroscopy (TRLFS) was conducted on humate complexes, consisting of two different kinetic modes. The spectroscopic studies verify that these kinetic modes are different in their binding environment. The reversible exchange between the different kinetic modes was also verified by TRLFS. A shift in the fluorescence spectrum is obtained if fast dissociating metal ions are removed. Leaving the solution for five days, the original spectrum is obtained again. The magnitude in difference between the different kinetic modes is seen by a shift in emission wavelength from around 600.5 nm for the “slow” dissociation mode to around 602.8 nm for the “fast” dissociation mode. The Tb(III) oxygen distance in the “slow” dissociation mode is evaluated to be 2.33 Å. The distance of the “fast” dissociation mode is estimated to be around 2.41 Å. The results show that the kinetic modes represent differences in the coordination environment. These findings are essential for interpretation of molecular structural properties (below).

7.4.4. Complex structural properties

The structural properties are investigated especially by the energy transfer between the humic or fulvic acid and complexed metal ions, and the question if prevention of humic acid self association has an impact on dissociation kinetics.

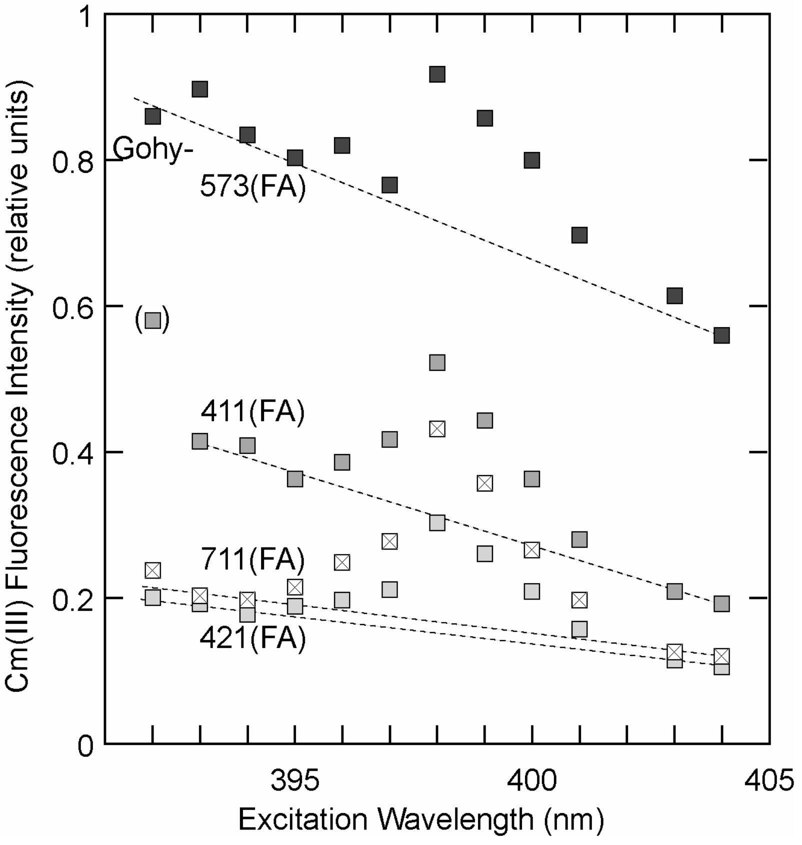

Fig. 5: Fluorescence intensity for Cm(III) complexed with different fulvic acids. The dotted lines indicate the transfer of energy from the fulvate ligand to the complexed Cm(III) ion

<Energy transfer>

The topic of energy transfer from humic/fulvic acid to complexed curium(III) was investigated by varying the excitation wavelength over the range of the direct excitation of the curium itself using four different fulvic acids from different origin and with different specific absorption and fluorescence of the fulvic acids themselves. The latter differences are also related to differences in functional entity distribution as determined by C-XANES. Conditions are chosen so as to have basically all the curium complexed by the fulvic acids. Varying the excitation wavelength over the range where there is one of the Cm(III) absorption peaks, the total Cm(III) humate complex fluorescence becomes the sum of (i) direct excitation (via absorption of the complexed curium), and (ii) curium fluorescence enhancement via energy transfer form the fulvate ligand (Fig. 5). Delineating the two contributions it is found that (i) the fluorescence contribution from direct excitation is independent of the nature of the fulvic acid used, whereas (ii) the contribution by the energy transfer is strongly dependent of the photodynamic properties of the fulvic acids.

As an immediate outcome this means that measurement of the complexation constants by TRLFS can be done irrespective of the nature of the fulvic acid by evaluation of the fluorescence contribution from the direct excitation. By this approach, the variation in total fluorescence due to different contributions from energy transfer, i.e. due to differences in the nature/ photodynamic properties of the humic/fulvic acids is removed. This approach still needs to be verified by studies on further substances, especially different humic acids. A second aspect is the desire to understand the nature of energy transfer. Present investigations indicate that the frequency of fluorescent states of the humic and fulvic acids populated for a specific excitation wavelength used is the precondition for energy transfer. These follow-up investigations will be conducted after the HUPA project, requiring networking of several institutions also from outside the HUPA consortium.

<Humic acid quench function>

The quench impact of humic and fulvic acids has been puzzling the community of involved researchers for around two decades. The fluorescence life-time of complexed curium(III) is built on four components. These are the measured emission of fluorescence light, quenching (removal of excited states by processes that diminish/drain the emission of fluorescence light) by coordinated water molecules and two components originating from the energy exchange with the humate/fulvate ligands. By measurement in both water and heavy water media, the two different life-time quench components of the humate ligand could be subtracted and the difference allocated to quenching by water. The quenching by heavy water is much lower than that of water and thus the difference can be set to be the quench influence of water.

The quench rate for water is equivalent to three to four water molecules in the inner coordination sphere. The expected total coordination number at room temperature is nine, leaving a five to six-fold coordination by humic acid functional groups. The key to this new approach in interpreting time-resolved fluorescence is that the two different life-time quench components from humic acid represent one complex and can be subtracted by comparison of water and heavy water media (Fig. 6). This is a great step forward in interpretation of time-resolved fluorescence data where the key point is showing that the two quench components of the humic acid is not related to different species and remains sufficiently constant when changing medium from water to heavy water. Use of the basic approach for other related questions, such as resolution of kinetic components and formation of ternary complexes, is under discussion for investigations beyond the HUPA project.

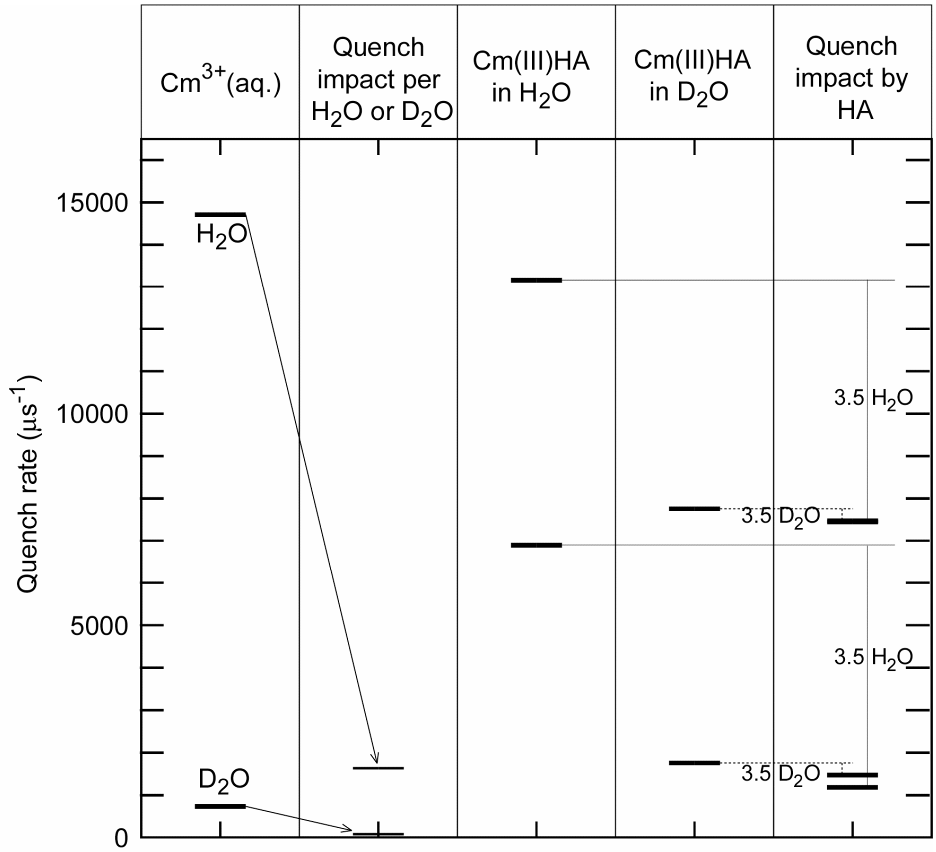

Fig. 6: Fluorescence quench rates of different species and quench contributors to Cm(III) complexed with humic acid in H_2O and D_2O medium. The quench impact of humic acid can be described by a combination of two components (very right box), increased by the contribution of H_2O or D_2O in the inner coordination sphere of the humate complexed Cm(III) (3rd and 4th boxes). The quench contribution by nine H_2O and D_2O in the inner coordination sphere is shown in the first two boxes as the measured quench rates of non-complexed aqueous Cm^{3+} ion (1st box), and normalised to one H_2O or D_2O (2nd box)

<Prevention of humic acid association>

The assumption that humic acid associates are responsible for the slow dissociation kinetics of multivalent humate complexes was investigated by addition of simple acids reported to dissociate humate associates. There was no significant impact on the dissociation kinetics by addition of reactants presumable dissociating humic acid associates. Intermolecular complexation, thus is not expected to be responsible for the gradual population of slow dissociation modes. The question remaining is to which extent intermolecular complexation by multivalent metal ions is very strong compared to the weak hydrophobic associative forces where the added simple acids are reported to lead to humic acid dissociation. A final conclusion thus is still pending.

7.4.5. Summary of progress within WP 4

There has been a great progress in the understanding of basic processes and the coordination of humic acid complexes. Despite the diversity of individual structures, the complexation properties and the associated metal ion coordination centers around a relatively narrow distribution of in principle one single type of complex. Within this distribution, differences in coordination are seen between different kinetic modes.

7.5. WP 5 (Natural chemical analogue studies)

7.5.1. Progress within experimental programme

Most information on the kinetic behavior of the metal ion humate interaction origins from designed laboratory studies where metal ions are added to more or less well defined systems. Most frequently the kinetics is studied between metal ions and purified humic acid under defined pH and electrolyte (ionic strength) conditions. A large number of studies have also been conducted in natural (ground)water, either under controlled atmosphere representing deep groundwater conditions or in contact with air. The behavior of the natural metal ion inventory and radionuclides from fall-out has also been studied aiming at determining the influence of humic substances on the bioavailability of these elements. Few studies have been conducted on the chemical behavior of chemical analogues to the actinide ions. The key question arising from comparison of the outcome of these individual studies is to which extent actinide ions in long contact with a natural system will mimic the behavior of the natural inventory of natural actinide ions, including natural chemical analogues, or if the description of their behavior can be extrapolated from laboratory studies. For this reason the chemical behavior of americium and plutonium is studied on samples from the bank of Esk Esturia, West Cumbria, UK.

The anthropogenic inventory originates mainly from releases around 30 years ago, released at 10-12 miles distance from the Sellafield plant. Actinides isotopes investigated are ^{241}Am, and ^{239}Pu and ^{240}Pu. For the laboratory studies also ^{241}Am and ^{152}Eu were used. The dissociation kinetics of these isotopes was studied. The overall results may be summarized as follows:

(i) The anthropogenic actinides are about 10 times more concentrated in the humic acid fraction than in the overall top-soil.

(ii) The differences in dissociation rates observed between anthropogenic actinides and actinide ions added in the laboratory are related to the actinide concentrations but there is no additional impact of the decades of contact time for the anthropogenic ones.

(iii) There is, however, an impact of the decades long contact time for the anthropogenic actinides, namely a higher population of the slow dissociation mode.

Application of the code K1D showed that the overall system behavior can be described by the overall kinetic approach. The extension of the code and successful adaptation to this large natural system provides confidence in this tool for the overall purpose of the project.

7.5.2. Summary of progress within WP 5

The applicability of the basic kinetic concept is demonstrated on the natural anthropogenic system with actinide contaminants in the Irish Sea. This is a key step towards trust in the capability to make predictive modeling on a real system scale over long time spans.

7.6. WP 6 (Radionuclide transport experiments)

Transport studies are conducted in order to provide data and process understanding. The coherency with data obtained from the more fundamental interaction studies is the basis for trust in application to predictive modeling. Some studies provide understanding of limitations of experimental approaches, especially in comparison with real system analysis outcome. The transport studies are restricted to few selected systems, because a large set of studies have already been conducted within the preceding HUMICS project.

7.6.1. Cobalt laboratory column experiments

The transport of cobalt with fulvic acid solution has been studied on porous sediment as well as with humic acid on intact sandstone block columns. The porous sediment system was not preconditioned prior to experiments, whereas the sandstone system had experienced considerable equilibration with solutions used. The porous sediment system was investigated by pulse addition and the sandstone system by continuous addition of solution containing humic acid and the cobalt ions, followed by flushing with humic and cobalt ion free solution. Both systems show that cobalt and humic/fulvic acid are co-eluted. No cobalt break-through was found if no humic/fulvic acid was added.

A mixture of reactions sufficiently close to equilibrium and reactions that require kinetics to be regarded describes the cobalt fulvic acid interaction. Also fulvic acid showed interaction with the sediment. This interaction is described by an equilibrium approach. No improvement in description of the elution profiles was obtained where the option for kinetics was included in the fulvic acid sediment interaction. The results show that fulvic acid sorption needs to be regarded for sediments that have not been preconditioned with humic substances and where there are humic substance concentration gradients.

For the sandstone column experiments, results were more complex. The description of the elution profiles required regard of more than one sediment surface site, i.e. the heterogeneity present in all sediments also need to be regarded for transport interpretation. In addition to elution profiles, the distribution along the column was also determined. Comparison between the two sources of information highlights a general problem in extracting/determining the relevant processes from available information. The column distribution profiles could not be well reproduced by the description deduced from analysis of the elution profiles. There are indications, that the problem is the deficient description of the cobalt ion interaction directly with the sandstone sediment. Nevertheless, the general problem remains with the extrapolation of data beyond the range of observation and beyond the type of information actually regarded/available.

In summary, the level of detail in understanding column experiments is increasing, however, under particular laboratory conditions. It is very questionable to apply the models and parameters for blind prediction to the field-scale. One may consider the need for field-scale experiments in order to provide the required confidence in predictive modeling. There is a contradiction between these laboratory experiments and natural system analysis. In the latter, the nature of stationary and mobile humic substances is so different that dissolved fulvic acid behaves like an ideal tracer. This is shown by correct groundwater dating via ^{14}C of the fulvic acid.

7.6.2. Retention dominant mineral identification approach

The influence of humic substances on the sorption of Np(V) was investigated for granite and its individual mineral components. The distribution of humic acid was also identified by the use of ^{14}C labeled synthetic humic acid. This approach has previously been successfully applied for U(VI). A slight decrease in the sorption of Np(V) is found with addition of humic acid. Through investigations with individual mineral components it was shown that Biotite seems to be the sorption dominating mineral in this system. The basic approach of determining system components that govern the species distribution and transport behavior is a key element in providing trustworthy model predictions.

7.6.3. Characterisation of Pu(III) in natural groundwater

Preliminary results on column experiments with plutonium with the Gorleben groundwater Gohy-532 had previously been obtained. Work on characterisation of plutonium in this groundwater shows, that plutonium is present in the reduced state. If the tri- or tetravalent oxidation state is predominant could not be unambiguously determined by the characterisation studies. Comparison with the transport behavior of tri- and tetravalent actinide ions revealed that plutonium shows a behavior between them. The working hypothesis is that both the reduced forms of plutonium are present, the ratio depending on the physicochemical conditions. Furthermore, the generation of polynuclear species may be important resulting in deviation from the results of other both tri- and tetravalent actinide ions. Further work will be required in order to provide the necessary knowledge and process understanding for predictive transport modeling. This includes general progress in the field of tetravalent actinide chemistry, mostly beyond the reach of the present project.

7.6.4. Uranium mining and milling rock pile material studies

Transport studies have been performed within the context of the uranium mining and milling rock pile migration case. Sorption/desorption studies were performed by batch and column experiments. Synthetic rock pile water was used reflecting the composition of analyzed rock pile water. Slow kinetics was found with about two weeks required in order to obtain steady state conditions. The natural inventory is dominated by ^{238}U whereas ^{235}U was added for the investigations. It was shown that the slow kinetics is related to the exchange between these two inventories. The impact of humic substances is moderate and direct evidence of a solubility enhancement is statistically uncertain. Separate desorption experiments under variation of physico-chemical conditions show that the desorption can be described by a comparable kinetics. Humic acid shows no significant impact on desorption rates.

The uranium distribution data with the synthetic rock pile water is interpreted by a linear sorption isotherm where the results show acceptable consistency for different volume to mass ratios during experiments. Analysis of the sediment sorption kinetics revealed that the system can be described by two processes, one which can be treated as equilibrium for the experimental conditions/time scales, and one where the kinetics of exchange with the uranium sediment inventory needs to be regarded also for field calculations. Data for the kinetics of uranyl humate interaction is already available from other sources/experiments. There is a large number of different uranyl species in solution (several carbonate and hydroxocarbonate species). It was not possible to relate the sediment sorption data to specific species in solution. The data deduced for the transport calculations thus are specific for this system composition and cannot be used for other conditions. The column experiments performed demonstrated kinetic character of uranium desorption from the rock pile material and only a moderate influence on uranium release of humic acid presence in the leachate. The obtained results provide the required basis for predictive transport calculations on the mining and milling rock pile migration case within WP 8.

7.6.5. Summary of progress within WP 6

Transport studies have been conducted providing complementary data to laboratory column experiments under near-natural conditions done during the preceding HUMICS project, providing additional information on the impact of sediments showing sorption of fulvic acid, and providing the required input data for the uranium mining and milling rock pile migration case.

7.7. WP 7 (Model development)

A great part of modeling is treated under the respective experimental studies. In this section two specific issues are discussed, namely the potential for the complexation induced association of humic acid molecules and the question of the protonation of functional groups and its relation to the effective humate ligand concentration. A final topic is the bringing together of humate interaction data for tetravalent actinide ions. The data are operational because of the need to regard individual steps within the formation of the ternary mixed complexed, formed already in the acidic range. The systematic documentation of these data is the basis for futur development of such detailed interaction process understanding.

A key modeling topic for the purpose of application to PA is given by the code K1D where mixed equilibrium and kinetics is implemented for transport calculations. This code was developed within the preceding HUMICS project. Main achievement with respect to this code in the present project was to show its applicability on the large-scale anthropogenic contaminant system (WP 5).

7.7.1. Kinetics and complexation induced humic-humic association

The dissociation kinetics of actinide humate complexes may be divided into three regions, omitting very fast kinetics that can only be investigated by fast kinetics methods, however, that has no relevance for the transport modeling. The regions of relevance are dissociation kinetics:

- in the order of hours, that can be understood based on complexation with organic ligands
- in the order of days to weeks, very difficult to interpret, and
- so slow that it cannot be adequately determined, presumably the result of inorganic mineral inclusion.

One possibility is that dissociation kinetics in the order of days to weeks could originate from screening of complexed metal ions from exchange with the solution via complexation induced humic-humic association. The great advances in the TRLFS studies indicate a number of carboxylic groups involved in the actinide complexation. This could very well be understood as complexation with two (or more) humic acid molecules for the "first metal ion to complex". If the complexation process is continued by addition of more actinide ions, either additional such individual structures may be formed or they may also associate to larger structures. Approaching saturation of the humate ligand capacity, humic acid flocculates and fulvic acid shows a strong increase in light scattering. This is also the case for protonation. Given that humic and fulvic acids have not only proton exchanging groups, but also condiderable amounts of additional oxygen containing structural elements, bridging via hydrogen bonds may occur simultaneously with complexation.

The studies presented under WP4 on the size and mass distribution of actinide and lanthanide complexes aimed at providing input to the testing of this approach. General observations to the kinetics of metal ion humate complexation may be summarized as follows:

1. All metal ions show comparable transfer rates between different kinetic modes.
2. There is one distinct fraction with a discrete, single first order desorption rate constant.
3. The rates are insensitive to total metal ion concentration and humate to metal ion ratio.
4. The distribution of metal ions between different kinetic modes varies. Metal ions with high cation charge to a larger extent occupy slow dissociation modes. This observation is independent of the metal ion concentration.
5. With increasing humic acid concentration, the amount of metal ions in the slow dissociation mode increases, the dissociation rates, however, do not change significantly.
6. In batch experiments, the distribution between slow and fast dissociation modes reaches a maximum at intermediate ionic strength. The slow dissociation rate, however, is virtually independent of ionic strength, except for I=1 M, where there is a slight decrease from around $5x10^{-7}\ s^{-1}$ to $2x10^{-7}\ s^{-1}$.
7. There is very little impact of pH on association and dissociation rates.

Observations from studies conducted under WP4 are ambiguous and do not provide direct evidence for complexation induced humic-humic association at low degree of complexation. The initial basic mechanism for humic-humic association regarded, led to qualitative agreement in the trends with some experimental observations. In other cases, the qualitative predictions are not reflected in experimental data. Furthermore, the calculated association/dissociation rates were far from realistic in absolute terms. That state of model development was hampered by the use of flat wall surface approach. The further development using a more realistic curved surface approach resulted in much better agreement with different experimental observations. The formation of associates is a kinetic process where the process also depends on the size of the entities. Diffusion-controlled association, counteracted by Coulomb repulsion, drives this process. For a specific charge density, the coulomb repulsion increases with increasing mass. The reversed reaction, namely the dissociation is also size/mass dependent. The dissociation rate increases with increasing size/mass of associates.

The overall results show qualitative agreement with experimental observations. An exact prediction still requires understanding of the shape and density (mass to effective hydrodynamic size) of individual molecules and associates. This is especially true when calculating the effective charge density. Despite the plausible relation between the slow dissociation kinetics, the expectation that if the complex dissociation is related to detachment of organic molecules centered around a complexed metal ions also requires breaking of possible bonds between the involved organic molecules, and the general agreement with the modeling development, a final evidence is still pending, especially as the experimental evidence (mass and size distribution) is not unambiguous.

It may be expected that work will continue beyond the HUPA project, aiming at providing the required process understanding. For this purpose additional fundamental understanding of basic parameters will be required and thus depends also on a general development of the field.

7.7.2. Protonation and humate ligand concentration

The effective humate ligand concentration decreases with increasing protonation. The total effective humate ligand concentration, however, is lower than the concentration of carboxylic functional groups. The decrease is also not equivalent to the increase in protonation. This means that a straight forward modeling based on the concentration of ionized groups is incorrect. It should nevertheless be noticed, that such approaches are common in the literature, resulting in the use of additional fitting parameters for consistency within small individual ranges of experimental conditions. For that reason, the known effective humate ligand concentration for tri- and hexavalent actininide ions and the protonation behavior was analyzed. The outcome is a surprisingly simple picture, where the effective humate ligand concentration is found to be the concentration of non-protonated and non-complexed molecules. A key in this development was identification and final acceptance of the mass distribution of humic and fulvic acids, very much lower than, against all experimental evidence, still frequently argued for.

Comparison of protonation and effective humate ligand concentration data in the non-hydrolyzing range of metal ions shows, that the effective ligand concentration decreases with one unit for the protonation of approximately 3.5 functional groups. Extrapolation of this ration to higher pH shows that the effective humate ligand concentration reaches its maximum slightly above pH 10. At this point the effective humate ligand concentration corresponds to an average molecular mass of about 550. This value corresponds well with the average mass of humic acid molecules as determined by TOF-SIMS. At this average mass, the proton exchanging group content is about 3.5. This leads to an overall consistent description of the humic acid ligand function. At high pH the effective humate ligand concentration is given by the number concentration of molecules. Protonation of the same number of functional groups as found per average molecule leads to the decrease in the effective humate ligand concentration by one unit. Analysis of the metal ion complexation data reveals that the effective humate ligand concentration decreases by one unit per metal ion complex. This is reflected in the metal ion complexation mediated humic entity association. A considerable problem with the approach is that comparable humate ligand concentrations are not obtained for metal ions with weaker interaction strength. For such ions lower humate concentrations are reported. The simplest approach is that all non-complexed and non-protonated humic acid molecules are reactive towards actinide ions with a high charge and complexation strengths, whereas only a fraction of these molecules react with actinide and other ions of lower charge and lower complexation strength. A final experimental evidence, however, is still pending.

7.7.3. Humate complexation data of tetravalent actinide ions

The humate interaction of tetravalent actinide ions has been brought into a consistent description with a separate database containing the required relevant data. The approach is an important basis for treatment of the tetravalent actinide ions in humate systems. It furthermore provides the basis for analysis of individual processes that can be tested for plausibility and consistency. Consequently this approach provides not only operational data for the humate interaction of tetravalent actinides, but also a basis for ongoing development of process understanding via plausibility criteria.

7.7.4. Summary of progress within WP 7

The transport code K1D where equilibrium and kinetics can be combined as required, was developed during the past HUMICS project. The applicability of the underlying approach has been verified on the large-scale anthropogenic actinide contaminant situation in the Irish Sea. The key question related to the slow actinide humate dissociation kinetics observed in laboratory experiments has been approached by modeling together with experimental results from WP4. The outcome shows that the humic-humic association may be the key to this slow dissociation, however, final evidence is still pending. The relation between the effective humate ligand concentration and protonation has been analyzed. The outcome is that the humate ligand concentration is the concentration of non-protonated and non-complexed humic acid molecules. It not only brings a consistent and plausible description of the humate ligand concentration but also provides the bridge to key developments in understanding of basic humic acid characteristics.

7.8. WP 8 (PA)

A number of elements fall within this work package. These are (i) identification of sources of aquatic humic substances, and their stability and mobility, including natural and potential additional sources from amended near-filed conditions, (ii) definition of the three migration cases used for visualisation of the overall outcome, (iii) calculations and conclusions for the three migration cases, (iv) general conclusions with respect to humic substances and PA. The first three topics are discussed below, whereas the last one is discussed under section 3.

7.8.1. Sources of aquatic humic substances

First analysis of the Gorleben aquifer system is discussed with respect to the impact of change in land-use and with respect to the mobility of fulvic acids of different origin. Thereafter, the formation of dissolved humic and fulvic acids in the high alkaline clay near-field is discussed.

<Natural aquatic systems (1): Change in land-use>

Until the year1710, part of the surface in the southeast area of the Gorleben aquifer system was a wetland. Between 1710 and 1750 this wetland was drained. Groundwater recharge from wetland has a different isotopic composition (^{18}O and ^{2}H) than recharge from non-wetland. This provides a tool for identifying groundwater from these different recharge conditions and couples the information with the historical time-marker. Part of deep groundwater is shown to originate from recharge from the previous wetland. After drainage, about 70 meters of the upper groundwater layer has been exchanged by recharge from the present non-wetland conditions. This justifies the high rates used for vertical groundwater exchange used in the formulation of the Gorleben migration case. More important, the ^{14}C content in the deep groundwater originating from wetland recharge is higher than in the overlaying non-wetland recharge groundwater. This has previously resulted in speculations on reversal of groundwater flow. The present study shows that this simply reflects the higher source term in wetland due to higher turnover of organic matter. Furthermore, calculation of the ^{14}C concentration in recharge dissolved inorganic carbon (DIC) via standard assumptions on the ^{13}C content is shown to be incorrect. The ^{13}C concentration of DIC is shifted to higher values due to microbiologically mediated methane generation in wetland. This further verifies the origin of deep groundwater from previous wetland.

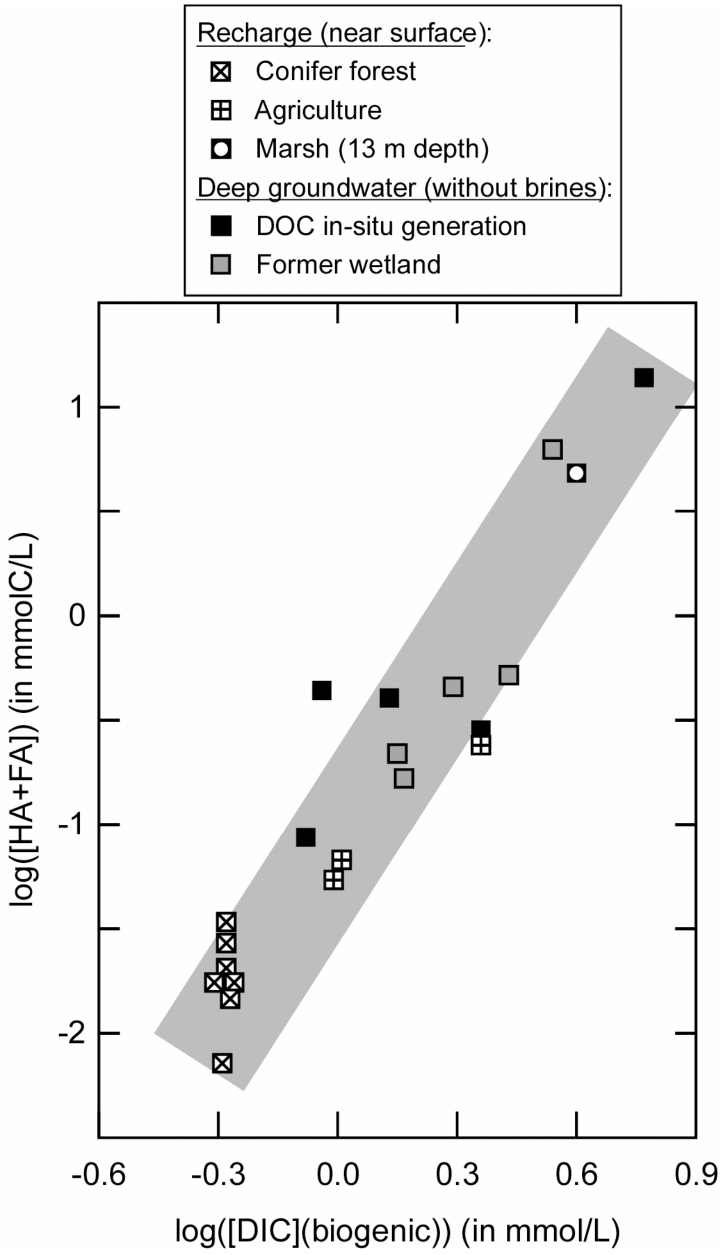

Fig. 7: Common process for the origin of humic and fulvic acids of different origin in Gorleben groundwaters, namely microbiological turnover of organic material (soil, peat and brown coal sand) under the simultaneous generation of hydrophilic humic and fulvic acids and carbon dioxide (for details, see Annex 2 in FZKA 6800)

Correlation of DIC content of biogenic origin with the humic and fulvic acid concentration shows that the aquatic humic substances in the deep groundwater originate from wetland recharge as the result of microbiological processes (Fig. 7). These humic and fulvic acids migrate like ideal tracers without retention or decomposition over several hundred years. This underlines the correctness of basic assumption applied for transport modeling under natural groundwater conditions, namely that aquatic humic and fulvic acids are stable in solution and that there is no indication for decomposition or retention by interaction with sediment surfaces. One exception is the high salinity brines (cf. below).

The key aspect of the present study is that the groundwater recharge and thus flow conditions are very sensitive to comparably marginal changes in land-use. Higher impacts can be expected from changes in vegetation via climatic changes. Consequently, specification of a very detailed groundwater flow situation over long time periods is not applicable for sandy sediment aquifers like the one in Gorleben. This supports the basic approach of using average values, as presently done, instead of trying to identify a specific flow part with well defined properties valid only for a short window in time.

<Natural aquatic systems (2): Humic substance mobility over salt gradients>

In the Gorleben aquifer system, high humic and fulvic acid concentrations are found at depths below about 50 meters. With exception for the southeastern part (cf. above) these high concentrations originate from microbiologically mediated in-situ turnover of brown-coal sand, the oxidation driven by sulfate from salt-dome dissolution (in-situ generation). At the center on top of the salt-dome, in the vicinity of the salt dome where high ionic strength brines are found, the humic acid concentrations approach zero and the fulvic acid concentrations approach values as found in the recharge waters. Analysis of fulvic acids by ^{14}C, and carbon and sulfur XANES revealed that the fulvic acids in the deep brines originate from recharge. This shows that the humic and fulvic acids found in very much higher concentrations from the in-situ generation are not mobile into the brines. Contrary to this, the recharge fulvic acids are. This shows that the mobility of humic and fulvic acids is strongly dependent of the origin. Consequently, it appears premature to draw conclusions concerning the mobility of humic and fulvic acid from additional sources, especially because there are no natural chemical analogues available (cf. below).

<Near-field clay additional source>

In various disposal concepts, cement is foreseen as a constituent of waste packages and/or as linings and part of engineered structures. Dissolution of cement leads to high pH solutions. Organic rich clay from four different depths (447 to 516 m) of the Meuse Haute Marne (MHM) site (Bure) was kept in contact with alkaline solution simulating conditions expected from cement dissolution under such near-field conditions. Original organic material in the clay consists mainly of aliphatic hydrophobic compounds basically without oxygen containing functional groups. After contact with “solid young fluid” (mimicking cement dissolution, initial pH 13.22) for around one and a half year, high concentrations of hydrophilic organic matter are found (243 to 354 mg DOC/L). Characterisation by solubility behavior, UV/Vis absorption, IR and fluorescence properties show that the dissolved hydrophilic organic matter has the characteristic features of humic and fulvic acids. Estimation of humic and fulvic acid content via UV/Vis spectroscopy results in 97.5 (±9.7) % of DOC being humic and fulvic acid. The release of humic and fulvic acid from Opalinus clay under alkaline conditions was also studied. The fulvic acids from the Opalinus clay and from different depths of the Bure clay were shows to form typical humate complexes with Cm(III) (Fig. 8).

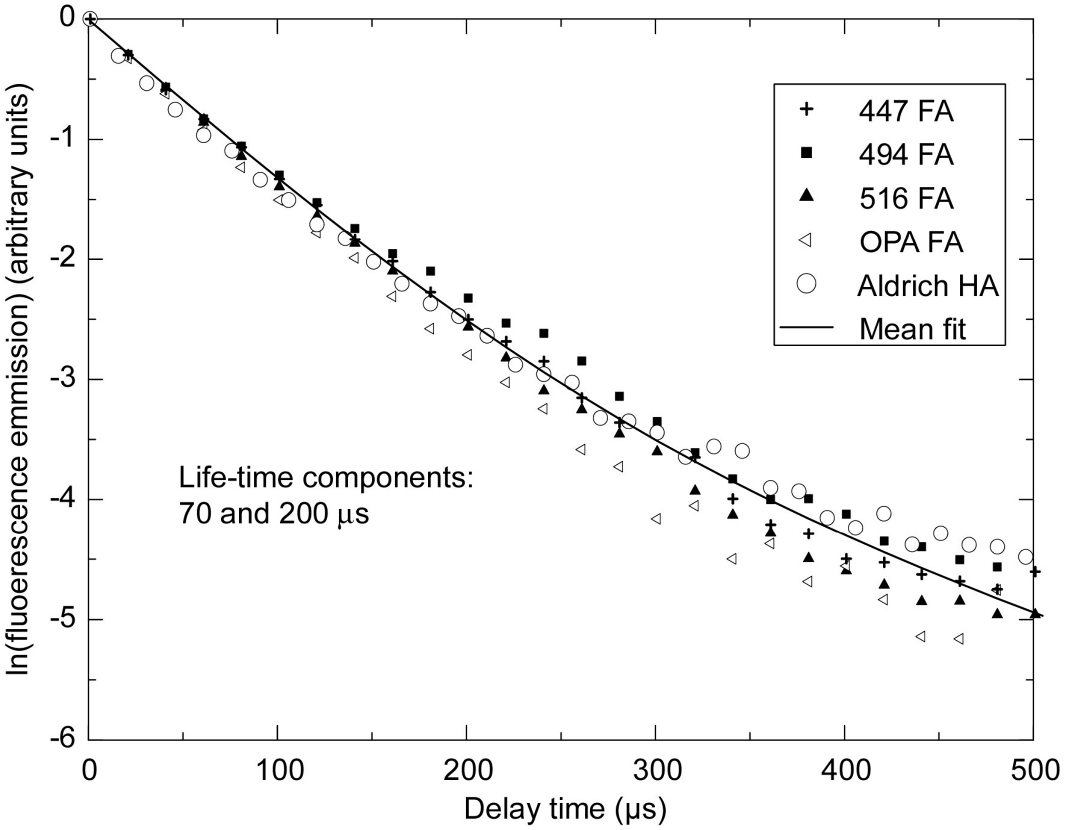

Fig. 8: Fluorescence decay of Cm(III) complexed with standard Aldrich humic acid and fulvic acids extracted from clay organic matter from the Bure and Opalinus investigation sites

Humic and fulvic acids from short term (24 hours) contact between alkaline solution and the clay and the clay source term were characterized with respect to the clay mineral origin and the solubilization process. For this purpose, spatially resolved C-XANES was used on clay samples and C-XANES on isolated aquatic humic and fulvic acids originating from the clay. It is shown that humic and fulvic acid precursors are present in clay organic matter. The fulvic acid precursors are covalently bound to mineral surfaces whereas humic acid precursors are mainly sorbed. Consequently, more humic acid dissolves than fulvic acid when clay is contacted with alkaline solution. The main difference between the clay organic humic and fulvic acid precursors and the aquatic humic and fulvic acids resulting from dissolution in alkaline solution is that the aquatic humic substances have higher concentration of carboxylic groups. This on one hand explains the selective dissolution of these acids, but it also raises the question concerning the complexation behavior of the precursors and the aquatic substances. It will need thorough future investigations in order to quantify the complexation capacity and overall behavior of clay organic matter relative to that of aquatic humic substances. The presently frequently argued for approach that the properties of aquatic humic substances can be applied to the precursor material in the clay organic matter may need revision.

7.8.2. The three migration cases

The three migration cases are (i) Gorleben; deep sandy water saturated aquifer system, (ii) Dukovany; shallow sandy water saturated aquifer system, and (iii) uranium mining and milling rock pile.

<Gorleben>

The case is defined for the central part on top of the Gorleben salt-dome. The scenario is release of radionuclides at the top of the salt dome, within the so-called ring-wall (at about 250 meters depth). The contaminated brine raises to 200 m depth by thermal motion. The migration case consists of vertical groundwater movement from this depth to the freshwater region at about 50 meters depth. The transport time for the vertical groundwater movement is set to 1,000 years.

<Dukovany>

The site is a sandy deposit with some silt and clay. The groundwater flow at the site runs from North to South with an average flow rate of $1x10^{-6}$ ms^{-1}, with a dispersion of 0.1 m over a distance of 3 m. The scenario is based upon the transport of radionuclides away from the low level waste repository at Dukovany. A leak of contamination is assumed to be constant over time. Calculations have been performed over a 300 m distance. Calculations were routinely performed on a time scale of 100 years from the onset of repository failure.

<Uranium mining and milling rock pile>

The migration case study concerns a pile of waste rock (tailings) from a mine in Schlema-Alberode, near Dresden, Germany. Before removal, the pile was about 300 m long and 30 m high. The migration case is defined by the compositions of different layers in the pile and groundwater analysis. A large number of experiments were conducted in order to generate the required data for the behavior of uranium in this environment, including the sediment sorption and uranium exchange behavior (WP 6).

7.8.3. Outcome of the three migration cases

The Gorleben and Dukovany migration cases are very similar in several aspects and the over-all outcome is presented jointly. Thereafter, the general results for the uranium mining and milling rock pile case are presented.

<Outcome of the Gorleben and Dukovany migration cases>

The outcome of the Gorleben and Dukovany migration cases may be summarized as:

(i) Equilibrium approaches are insufficient and underestimate the humic colloid mediated actinide transport.

(ii) The "quasi irreversible" transport is not relevant if not specific near-field conditions result in such inclusion of actinide ions into humic colloids.

(iii) The interaction with humic colloids will increase the mean residence time of actinides in the mobile state and thus enhance the actinide transport.

(iv) Even if there is a contribution of humic colloid sorption (not verified in isotope-geochemical real site analysis), this will only have a marginal impact.

(v) In all groundwater systems investigated, the humic colloid concentrations are found to be sufficiently high. Thus the absolute concentration of humic colloids is not critical.

(vi) There are considerable but quantifiable uncertainty ranges for the impact of humic colloid mediated actinide transport, depending on the specific conditions and uncertainty ranges of dissociation constants.

<Outcome of the uranium rock pile migration case>

The overall result of the uranium rock pile migration case is that the main factors are given by the distribution and accessibility of uranium in the pile material and that the humic colloid mediated transport enhances the initial uranium wash-out process as well as the mobility in the later phase. The significant impact of humic substances on the mobility of uranium is not in harmony with other studies. This impact originates from the predicted residence time enhancement in solution by kinetically controlled exchange on the dissolved humic substances. The relevance of this impact under real conditions still needs verification.

7.8.4. Summary of progress within WP 8

Considerable progress is made with respect to the behavior of humic colloids in natural aquatic systems. The outcome of such real system analysis reflects the actual situation in nature. This refers both to the differences in mobility of humic and fulvic acids of different origin and the strong influence of changes in vegetation, and thus also climatic changes. The potential additional source of dissolved humic and fulvic acids from alkaline solution impact in the clay near-field has been identified and thoroughly characterized. The potential mobility away from the near-field requires additional studies. Furthermore, the study has raised the question of how to treat complexation of sediment humic substances with their much lower inventory of proton exchanging groups. The three migration cases have been defined based upon thorough analysis of available data. The outcome visualises the potential for humic colloid mediated transport under these different conditions.

8. Summary of progress within the overall project

A large number of systems have been investigated, partly consisting of new humic material with designed properties. Interaction data have been added to what was known prior to the project. New advanced methods for characterisation of humic matter and complexes have been developed and applied. The anthropogenic actinide contaminant studies have been performed, the overall results brought together by various modeling approaches and the outcome visualised by the three migration cases.

The key progress has been:

- The nature of humic substances is much better understood. This especially refers to the break-through in acceptance that the mass distribution of humic and fulvic acid is as low as already argued for by project members for an extended time. The previously common confusion with respect to correct interpretation of mass and size distribution has very important consequences for the overall process understanding (cf. also below).

- The progress within complex characterisation is very important, especially correct interpretation of photodynamic processes leading towards simplification of the overall picture. Mass and size spectrometry of humic and fulvic acid as well as complexes also contributes to the overall progress in process understanding.
- The studies on redox influence are slowly providing an acceptable overall picture, especially through the use of synthetic humic acid with designed properties.
- Modeling has progressed very well, especially modeling of the basic interaction process. Taking the progress in the basic nature of humic and fulvic acid into account, the interaction process is shown to be a surprisingly simple one ligand per non-compexed/ protonated humic molecule.
- The anthropogenic actinide contaminant studies have brought trust in the capability to select data for large time and spatial scale systems. Evidence that several decades contact time does not change the nature of interaction significantly is a great step towards trust in selection of data and approaches for application to PA.
- The application of data and kinetic approaches to the three migration cases visualises the overall outcome and the trust that approaches and data can be applied for PA.

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Annex I

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