INTERACTION OF REE, ZR AND U WITH HUMIC COLLOIDS – AN A4F-ICP-MS STUDY

T. Ngo Manh, M. Bouby [*], H. Geckeis [*]

Department of Chemistry, Ho Chi Minh City University of Technology,
268 Ly Thuong Kiet, District 10, Ho Chi Minh City, Viet Nam.
[*] Institut für Nukleare Entsorgung, Forschungszentrum Karlsruhe,
P.O. Box 3640, D-76021 Karlsruhe, Germany.

BẢN TÓM TẮT

Bản báo cáo trình bày sự phân bổ kích thước của keo humic (Aldrich) trong môi trường nước (15 mg/l, pH ~ 8) sau tương tác với ion kim loại các nguyên tố đất hiếm, Zr(IV) và U(VI) ở mức nồng độ vết (~ 2-4x10^{-8} mol/l), trong thời gian 3 năm. Mẫu được phân tích bởi thiết bị phân đoạn dòng trường thủy lưu bất đối xứng, nối với đầu dò UV/VIS và ICP-MS. Keo polystyren được sử dụng làm chuẩn kích thước. Peak của sự phân bổ kích thước keo humic lại được tìm thấy trong khoảng ~ 2 nm, giống như các kết quả thu được trước đây. Đối với keo humic chứa REE, Zr, peak này dịch chuyển tới ~ 2,5 nm. Keo chứa U có đỉnh peak ở khoảng 2,3 nm. Sự hiện diện của ion Ca^{2+} với nồng độ 2 mg/l đã kích thích sự tăng trưởng cỡ hạt keo humic chứa các ion kim loại nghiên cứu. Tuy vậy, ngay cả sau thời gian 3 năm "già hóa" mẫu, kích thước này vẫn nhỏ hơn hẳn kích thước keo chứa các ion kim loại tương ứng trong mẫu nước ngầm tự nhiên (Gorleben, CHLB Đức), chúng ở vào khoảng từ 20 – 100 nm.

ABSTRACT

The size distribution of purified humic acid (15 mg/l; Aldrich) interacted with REE(III), Zr(IV) and U(VI) at trace concentration (~2-4 x10^{-8} mol/l), pH ~ 8 after "ageing" for three years is reported. Analysis is done by Asymmetric Flow Field-Flow Fractionation (A4F) coupled to an UV/VIS absorption detector and ICP-MS. Size calibration is made by reference polystyrene colloids. The maximum of the Aldrich humic acid size distribution again is found as in the earlier study at around 2 nm. The size distribution maximum of colloids containing REE and Zr is shifted towards ~ 2.5 nm. Colloidal U–species exhibit an average size at around 2.3 nm. Addition of Ca^{2+} ions at a concentration of 2 mg/l again induces an increase of the average size for the humic acid and the colloid borne metal ions. But even after three years ageing time, they still remain significantly smaller than those colloids containing the naturally abundant polyvalent metal ions (Th, REE and a part of the U) found in a natural groundwater (Gorleben site, Germany). The latter species are found in a size range from 20 to 100 nm.

Keyword: humic colloids, metal-humate complexation, aquatic colloid size, fff

1. INTRODUCTION

Colloids are ubiquitous in all natural aquifer systems. Due to interactions of heavy metal ions with aquatic colloids, their "solubility" could be enhanced and their migration in the environments facilitated [1-3]. Therefore, sustainable developments of waste depositories require informations about in the local groundwater system. An usual way is to investigate colloid-metal ions interactions in simplified model solutions under laboratory conditions, and then transfer the results obtained to natural systems [4-6]. However, this procedure is highly questionable due to many differences between the diverse natural conditions and the simplified laboratory ones. In our previous work [7], The size distributions of REE, U, and Th ions spiked to purified humic colloids was found totally different from naturally occurred in a groundwater system, and dependent on the „ageing" of samples during

170 days. This paper reports the results obtained from another laboratory samples after 3 years „ageing" time.

2. Materials and method

Humic acid (Aldrich) was purified and characterized according to the procedures described elsewhere [8]. All other chemicals were of analytical grade or suprapure, and were used as purchased. Solutions of purified Aldrich humic acid (15 mg/L), buffered with 1 mmol/L Tris (2-amino-2-(hydroxymethyl)-1,3-propandiole) at pH=8.0 (Merck), ionic strength 0.1 mol/L NaClO$_4$ (Johnson & Matthey, Germany) were spiked with standard solutions (Alfa) of REE(III), Zr(IV) or U(VI) to final concentrations of 2 - 4·10^{-8} mol/L under anaerobic conditions. Similar samples with additional standard solution of Ca(II) to conc. 5.10^{-5} mol/L were prepared too. All samples were sealed, stored for 3 years under anaerobic conditions with weekly shaking.

Analysis was performed using an asymmetric flow field flow fractionator HRFFF 10000 AF4 (Postnova Analytik, Munich, Germany). The accumulation wall of the channel was covered by an ultrafiltration membrane from regenerated cellulose with a 5 kDalton pore size (Postnova Analytics). The PTFE spacer delimits the channel thickness to a height of 0.5 mm. The channel flow rate was maintained at 0.5 ml/min, while the crossflow was kept at 1.5 ml/min for 10 minutes and then programmed to decrease exponentially during the next 10 minutes to zero. From the AF4 channel, the effluent was directed on-line to an UV/VIS detector to determine humic and fulvic acids at λ=225 nm. Then, it was on-line mixed with a 5% ultrapure nitric acid solution containing 50 μg/l Rh as an internal standard before feeding to an ICP-mass spectrometry Elan 6000 (Perkin-Elmer) to determine trace metal ions.

3. Results and discussion

Principles and applications of F4 techniques could be found in several papers, e.g. [9-11]. The main advantages of F4 come from the reduced extent of interactions between the sample and the channel components, compared to e.g. the gel permeation chromatography. The symmetrical F4, however, suffers in some cases on corrosion products of the ceramic frits. With the asymmetrical F4, such undesirable effects diminished, for the crossflow is not circulated back into the channel [12].

3.1 "Laboratory" systems

All the fractograms obtained from analyses of Aldrich humic acid samples are shown in Fg.1a-1d. In each figure, the corresponding signals obtained from 3 samples: 1/ Purified HA, 2/ purified HA with REE(III), U(VI), or Zr(IV), and 3/ purified HA spiked with Ca(II) and REE(III), U(VI), or Zr(IV) are compared. One can see that the spiked REE(III), Zr(IV) and U(VI) are completely attached to humic colloid fractions. They are distributed into humic fractions of slightly higher sizes, compared to that of Aldrich humic acid itself. In samples spiked only with REE(III), Zr(IV), or (VI), the size distributions of spiked metal ions as well as of Humic acid remain practically unchanged, compared to those of the original purified sample. Clearly shifts towards higher size fractions are observed only from samples with Ca^{2+} added. It is in accordance with literature data where Ca^{2+} cations were observed to cause colloid agglomeration [7]. However, the colloid agglomerations due to the presence of Ca^{2+} cations in our samples is not significant, even after 3 years aging. All peak maxima are shifted only about 0.2 nm towards higher size fractions, compared to those of samples without Ca^{2+}.

In our previous work, similar "laboratory system" of purified Aldrich humic acid were spiked with Eu(III) and U(VI), respectively, for shorter time periods to maximal 170 days [7,12]. Due to limitations of the symmetrical F4 used for analysis, only signals of the size distributions of humic acid and the spiked metal ions were obtained and compared. For both the metal ions spiked as well as for the humic acid, small but evidentially ageing time dependent shifts of peak maxima were registered. This work intended to determine the extent of metal-humate complexe agglomeration after longer ageing time. The results obtained show that, the time factor alone cannot cause significant agglomeration of metal-humate complexes as in multi-component natural aquifer systems. With ageing time, the size distributions of spiked REE(III), Zr(IV), and U(VI) tend to those of their traces in even "purified" humic acid.
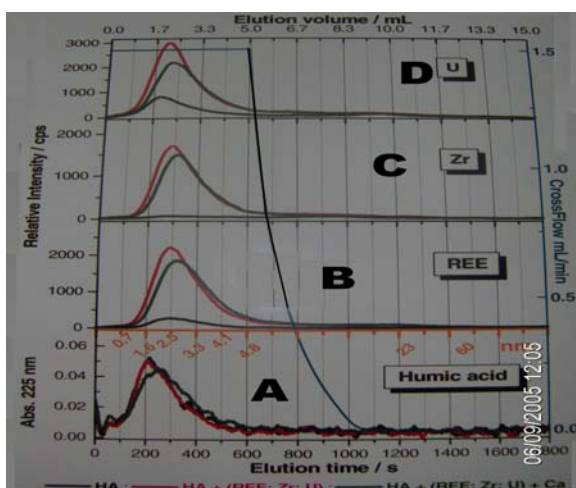
Fig. 1a-1d: Size distribution of purified humic acid (Aldrich) and spiked metal ions in "laboratory" systems.

3.2 "Natural" system

Samples of a natural, humics and fulvics rich groundwater from Gorleben (Germany) were re-analysed by the AF4 equipment. The results are shown in Fig. 2a-2d. While the groundwater samples were analysed as obtained, each figure shows only a fractogram of the natural abundant components of interest. The natural contents of REE(III), Th(IV) in this groundwater are preferentially attached to colloid fractions of sizes higher than 20nm, while humic colloids themselves remain to a great extent in lower size fractions under about 5 nm. This finding is in accordance with our previous work where the same samples were analysed by the symmetrical F4 [7]. However, previous results show that the size distributions of REE(III) and Th(IV) do not correlate with that of Ca^{2+}. Therefore, explanation why the size distributions of the metal ion of interest in natural and laboratory systems differ from each other could only be suggested, but not experimentally confirmed.

The size distribution of Al(III) couldn't be obtained due to the corrosion of the channel frits. In the present work, the AF4 advantageously yields the size distribution of Al(III) too. Though Al(III), similarly as humics and fulvics in this groundwater, is to a great extent distributed in colloid fractions of lower sizes, it is also present in colloid fractions of

higher sizes corresponding to those of REE(III) and U(VI). This finding suggests the presence of inorganic colloids in this groundwater, onto them small REE(III) and U(VI)-humate colloids are preferentially attached. Being agglomerated together with such inorganic colloids, the heavy metal-humate complexes in natural aquifer systems become kinetically irreversible, and their migration in the environment enhanced [1-3].

4. Conclusions

Aquatic colloids enhance the extent of water pollution by heavy metal ions and their migration in the environment. In order to maintain this problem, experiments in-situ, or at least under similar conditions as the natural ones should be performed. As experiments in-situ are not easy to conducted, the results obtained under laboratory conditions should be considered with great care. The developement and/or application of innovative analytical tools, such as the AF4 used in this work, is highly desired.
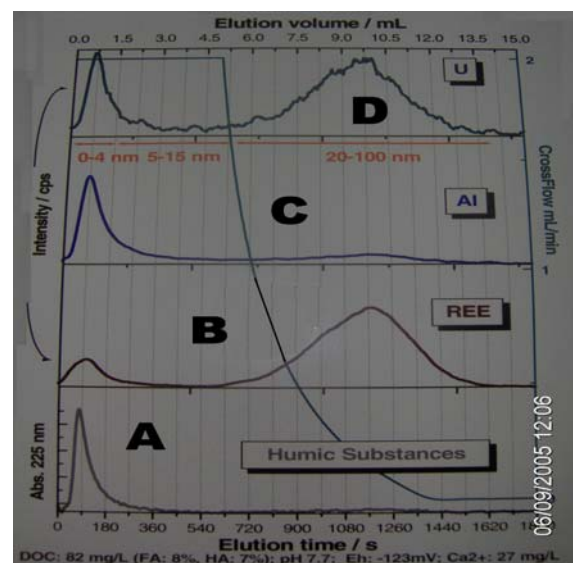

Fig. 2a-2d: Size distribution of humics and spiked metal ions in groundwater Gohy 2227

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