

Radionuclide Migration in the Environment – the Role of Aquatic Colloids

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For the safety assessment of nuclear waste repositories, the risk of radionuclide migration into the environment has to be evaluated on time scales of the order of 100 000 years. Container materials cannot be expected to withstand corrosion for these time periods and finally, radionuclide retention in the surrounding geological formation becomes an integral component of a multibarrier safety system. However, in recent years plutonium was found to migrate fast over km-distances in the aquifer near a Nevada nuclear detonation site [1] and this unexpected effect was attributed to colloid mediated transport. Aquatic colloids of organic or inorganic composition originating from mobilization of preformed colloid-sized materials or in situ precipitation of supersaturated mineral phases are omnipresent in natural groundwaters [2]. Obeying Pareto's power law, particle number density increases strongly as the size decreases ($\propto D^{-5}$) and natural ground waters may contain up to 10^{15} particles per liter below 50 nm. They may form pseudocolloids by uptake of actinide ions and due to their large number may act as a very efficient carrier in the groundwater [3]. But even a groundwater poor in natural colloids does not circumvent this problem entirely, because the tetravalent actinides are known to form stable eigencolloids by aggregation of the hydrolyzed species [4]. Destabilizing conditions lead to the formation of large aggregates and finally to immobile precipitates. If, however, only very small (< 100 nm) colloids are formed, they remain suspended and migration is strongly enhanced [5]. Detailed knowledge on formation mechanisms and stability of the colloidal phase is hence of cardinal importance and the investigation of long term stability as a function of colloid concentration and geochemical parameters is a prerequisite for the assessment of actinide migration.

Conventional detection methods, e.g., photon correlation spectroscopy (PCS), are not capable of characterizing size distribution and number density for small

species (< 50 nm). Other methods, like scanning (SEM) or tunneling (TEM) electron microscopy or field flow fractionation (FFF), perturb the initial state of aquatic colloids in the characterization procedure. Atomic force microscopy (AFM) is a non-discomposing method but requires a relatively concentrated colloid suspension, which means that a condensation of sample is necessary for the colloid characterization.

For this means, the laser induced breakdown detection (LIBD) was developed, tailored to the in-situ detection of very small colloids (≥ 5 nm) down to very low concentrations (10^5 cm⁻³) [6,7]: A pulsed laser is focused tightly into a quartz cell containing the sample (Fig.1). In the focal region, free charge carriers are created due to multi photon ionization and inverse bremsstrahlung - a dielectric breakdown occurs. Further heating leads to the formation of a hot expanding plasma which is detected via its (acoustic) shock wave [8] or optical emission [9]. The pulse energy density (threshold) necessary to induce a breakdown event is lower for solid matter as compared to pure water. By a suitable choice of pulse energy, breakdown events can be selectively initiated by particles in the focal volume and from the characteristic photon-fluence dependence (s-curves), particle size distributions and concentrations are deduced.

Applications are of great variety: groundwaters are characterized with respect to colloid content in-situ in underground laboratories in Grimsel (CH) and Äspö (S) [10]. In order to understand formation and growth processes of actinide colloids, aggregation is observed time resolved for model colloids ZrO₂ [11] as well as for Pu(IV) species. Trace detection of colloids in oversaturated solutions can be used to very precisely determine thermodynamic solubility data [12]. Recently, the method was refined to probe element-composition and valence state of the colloids by a resonance enhanced excitation scheme.

Literature:

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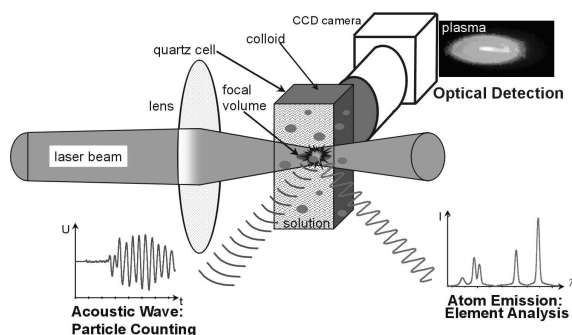


Figure 1: LIBD detection setup. Details see text.