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How speciation studies can support the development of chemical and radiochemical methods for the characterization of radioactive wastes

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The French National Radioactive Waste Management Agency (ANDRA) requires chemical and radiochemical characterizations of radioactive wastes to guarantee the safety of the disposal facilities[1,2]. Laboratories dedicated to the analysis of nuclear wastes, such as LASE laboratory (located at CEA Saclay in France), must have accurate chemical and radiochemical protocols valid for all the various matrices encountered (sludges, muds, metals or concretes). Since the decommissioning and dismantling of nuclear sites are in growth, it is of prime interest for laboratories to develop robust and selective methods[3,4] while taking into account of European REACH regulation. The aim of this work is to demonstrate how speciation studies can help in the optimization of chemical and radiochemical characterizations of nuclear wastes.

Among the chemical measurements to be performed[1], the determination of complexing agents, such as polyhydroxycarboxylic acids, is required since those molecules favour the migration of radionuclides and toxic metals in the environment and represent a risk for the safety of waste repositories. EDTA and DPTA (respectively ethylenediaminetetraacetic acid and diethylenetriaminepentaacetic acid) are the two chelating compounds that have to be identified in priority. Due to their use in decontamination processes, they are present in effluents such as sludges resulting from the distillation of radioactive liquid effluents. Owing to the complexity of the sludge composition, the technique of HPLC-ESI-MS (High-Performance Liquid Chromatography-ElectroSpray Ionisation tandem Mass Spectrometry) has been selected for the quantification of the target compounds[3] using ion-pair chromatography for the separation step and metal-complexes with EDTA and DTPA for the MS-detection step. The speciation modelling revealed that the target compounds are present in solution as several complexes with metals (see Figure 1) and that a sample treatment has to be applied prior to HPLC-ESI-MS analysis. The presentation will show how speciation studies gave a support for the choice of the appropriate conditions for EDTA and DTPA quantification. As an example, this approach can be extended to other chelating agents such as NTA and TTHA (respectively nitrilotriacetic acid and triethylenetetramine-N,N,N',N",N"',N"'-hexaacetic acid).

In regards to the radiochemical characterizations, ANDRA imposes a detailed inventory for 143 radionuclides stored in the repository site devoted to the Low and Intermediate Level short-lived Waste[2]. Among this long list, Fe-55 has to be determined since it is a major contributor to the radioactivity of nuclear wastes in the first years of storage. The LASE laboratory has adapted the NF M60-322 standard for the measurement of this radionuclide[5]. The radiochemical method relies on an anion exchange chromatography step in HCl medium, followed by an ammonium hydroxide precipitation step and finally a solvent extraction step based on cupferron and chloroform. The protocol is highly selective towards the elimination of interfering analytes (such as Co-60 and Ni-63) but it must evolve because of the restriction use of chloroform and harmful reagents through the European REACH regulation. The presentation will demonstrate how speciation modelling contributed to the evolution of the radiochemical Fe-55 procedure. In particular, it was inferred that cobalt can co-precipitate with iron in ammonia medium depending on the cobalt concentration in the sample (see Figure 2). Consequently, a supplementary separation step has to be implemented to remove entirely cobalt. The extraction solvent step was finally replaced by an extraction chromatography step using TRU® resin to achieve a highly selective method. This approach can be extended to the characterization of other key radionuclides such as Sr-90 in nuclear wastes.

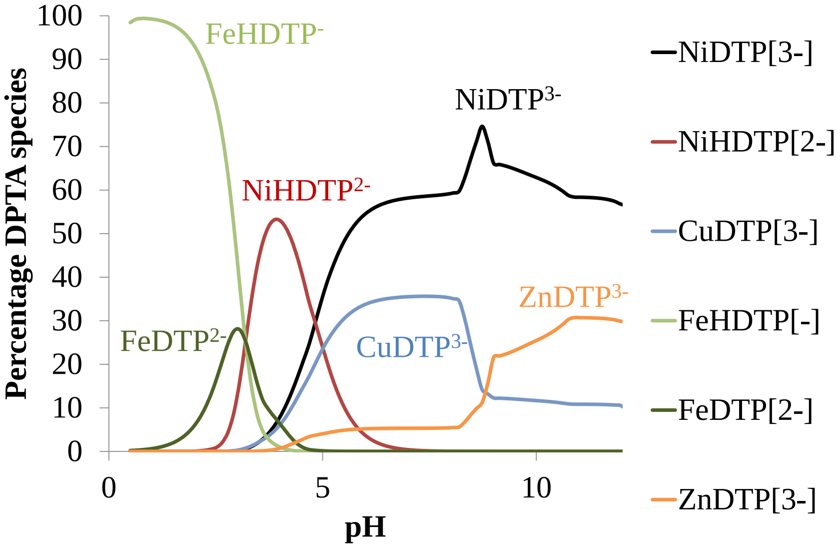

Figure 1: Speciation diagram of DTPA in a radioactive sludge.

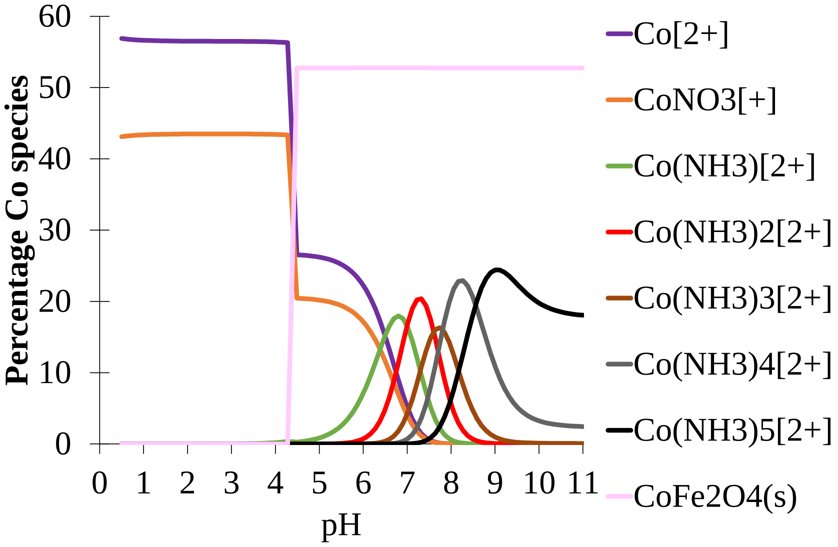

Figure 2: Speciation diagram of Co in an activated steel sample after acid digestion and addition of ammonium hydroxide.

References

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