

# A GENERIC PROCEDURE FOR THE ASSESSMENT OF THE EFFECT OF CONCRETE ADMIXTURES ON THE SORPTION OF RADIONUCLIDES ON CEMENT: CONCEPT AND SELECTED RESULTS

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*A screening procedure is proposed for the assessment of the effect of concrete admixtures on the sorption of radionuclides by cement. The procedure is both broad and generic, and can thus be used as input for the assessment of concrete admixtures which might be used in the future. The experimental feasibility and significance of the screening procedure are tested using selected concrete admixtures: i.e. sulfonated naphthalene-formaldehyde condensates, lignosulfonates, and a plasticiser used at PSI for waste conditioning. The effect of these on the sorption properties of Ni(II), Eu(III) and Th(IV) in cement is investigated using crushed Hardened Cement Paste (HCP), as well as cement pastes prepared in the presence of these admixtures. Strongly adverse effects on the sorption of the radionuclides tested are observed only in single cases, and under extreme conditions: i.e. at high ratios of concrete admixtures to HCP, and at low ratios of HCP to cement pore water. Under realistic conditions, both radionuclide sorption and the sorption of isosaccharinic acid (a strong complexant produced in cement-conditioned wastes containing cellulose) remain unaffected by the presence of concrete admixtures, which can be explained by the sorption of them onto the HCP. The pore-water concentrations of the concrete admixtures tested are thereby reduced to levels at which the formation of radionuclide complexes is no longer of importance. Further, the Langmuir sorption model, proposed for the sorption of concrete admixtures on HCP, suggests that the HCP surface does not become saturated, at least for those concrete admixtures tested.*

## 1 INTRODUCTION

Concrete admixtures (abbreviated to BZMs<sup>1</sup> in the following) are used for improving the workability of cement, to influence physical properties, such as compressive strength, durability or setting time, and to confer certain beneficial effects to the material [1,2,3]. In the context of the safety of cementitious repositories for low- and intermediate-level or long-lived intermediate-level radioactive waste planned in Switzerland, BZMs are of concern in the same way as other organic materials, such as cellulose or ion exchange resins. Sorption of radionuclides on the solid repository matrix is a key factor governing their possible later release from the repository [4]. Organic substances contained in the repository may positively or negatively influence this sorption. Therefore, the role of organics needs to be addressed quantitatively in overall performance assessment for the repository. The need for detailed investigations of BZMs is based on the following considerations.

- BZMs are unavoidable components of the concretes used in the construction of a cementitious, deep underground repository for radioactive waste. Although BZMs are added to the concrete batch only at the level of 1-2% (with respect to the dry weight of the cement), their total mass will be far from negligible.
- BZMs are currently used in the process of waste conditioning, with the aim of obtaining low porosity concretes. Concretes with fewer and smaller pores are more resistant to chemical attack: they have low permeability, and thus lead to lower

leaching rates of the radionuclides contained in the waste [5,6,7].

- After hydration of the concrete, BZMs are found dissolved in the pore water, as well as chemically bound to the solid [8]. With regard to their chemical structures, it can be expected that several types of BZM may form soluble complexes, with radionuclides below the alkaline conditions of cement pore water [9]. Examples of such admixtures are lignosulfonates, which are chemically related to the structures of humic substances, and gluconate, both of which are used as water reducers and/or retarders [2]. In addition, the sorption of BZMs on the cement surface may possibly alter the sorption properties of the cement in regard to radionuclides. For these reasons, it is likely that BZM may have an adverse effect on the sorption or solubility of the radionuclides.

The assessment of BZMs is complicated because of a number of special circumstances: (i) BZMs comprise a large variety of completely different chemical substances, ranging from simple carbohydrates to complex mixtures of macro-molecules; (ii) a single type of BZM is, in turn, most often composed of a variety of different compounds, the composition being in many cases ill-defined, or proprietary; and (iii) it is not known which BZM will be used in the construction of cementitious radioactive waste repositories in Switzerland — the only BZMs that can be identified at the moment are those for waste conditioning.

Considering these circumstances, it has to be realised that it is not possible to produce within a reasonable time, both a general and comprehensive assessment of the influence of BZM on the barrier performance of a repository for radioactive waste. In view of the large variety of chemical structures, the choice of a “worst-

<sup>1</sup> The abbreviation derives from the German word *Betonzusatzmittel*, no commonly used abbreviation for concrete admixtures has been found in the literature.

case proxy”, representing the chemical behaviour of the whole concept of BZMs, will be a difficult, if not impossible, task. The study of BZMs PSI has therefore focused on the development of a *screening procedure*, by which the possible adverse effects of BZMs used in the future may be evaluated. Effects of BZMs that are favourable to the performance of concrete as a safety barrier are not treated here. The experimental feasibility of this screening procedure, and the relevance of the results, have been evaluated using a few selected types of BZM as test cases. Typical representatives of superplasticisers and set modifiers have been chosen for this study, because these types of BZM will be the most important ones for the conditioning of radioactive waste, and the construction of an underground repository. The reason is their indispensable influence on the workability of the concrete, and its subsequent low porosity [10], which is a prerequisite for a concrete resistant to chemical attack and leaching [6,7].

The purpose of the present contribution is to give an overview of this *screening procedure*, and to present selected results obtained for the BZMs tested. Detailed information concerning experimental procedures, and a comprehensive compilation of the results obtained, can be found elsewhere [11].

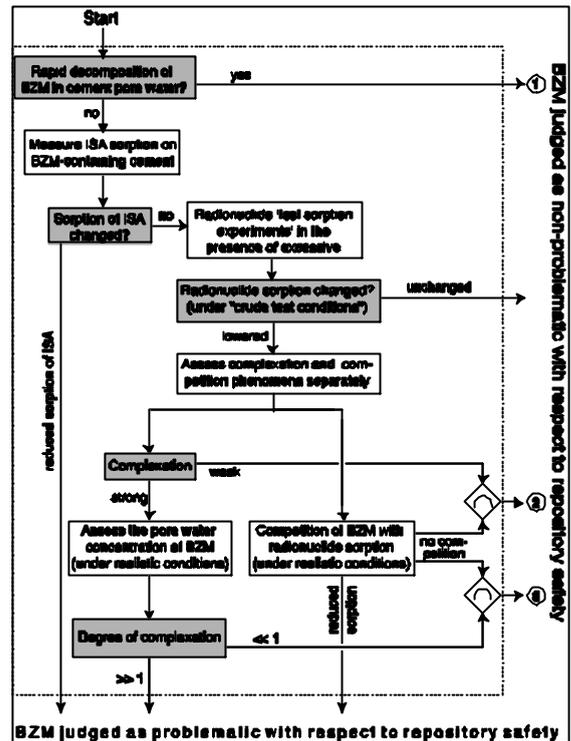
## 2 THE SCREENING PROCEDURE

The *screening procedure* involves not only the measurement of substance-specific data, it further aims at developing a deeper understanding of the dominant processes leading to a possible sorption reduction of radionuclides due to the presence of BZMs. The processes which have a central impact on the sorption and solubility of the radionuclides of interest have been identified, and are listed below.

- Interaction between radionuclides and BZMs in solution (complexation).
- Competition for surface sorption sites between BZMs and radionuclides.
- Competition for surface sorption sites between BZMs and other strong ligands sorbing on cement. A typical representative of such ligands is  $\alpha$ -isosaccharinic acid (ISA). It has been shown elsewhere [12] that the sorption of ISA on cement is a crucial process in decreasing the adverse effect of cellulose degradation products on radionuclide sorption.
- Chemical transformations of BZMs (degradation, aging, etc.). Depending on the chemical properties of the transformation products, such processes may have positive or negative effects on the sorption and solubility of radionuclides.

The *screening procedure* is designed to achieve a maximum amount of information from a reasonable experimental effort. Simple experiments are therefore proposed to test the BZMs: in a first step, under worst-case conditions. If a BZM under consideration can be shown to be innocuous under such extreme

circumstances, it may not be necessary to run through all the steps proposed, and costly experiments, such as those associated with the “squeezing out” of cement pore water, can be avoided.



**Fig. 1:** *Screening procedure* proposed to assess the effect of BZMs on radionuclide speciation. Shaded rectangles denote a decision to be made, and open rectangles an experiment to be carried out. The sign  $\cap$  denotes that both conditions must be fulfilled in order that the BZM can be judged as ‘non-problematic’. Further remarks: ① if the effects of the degradation products are not known, they have to go through the same procedure as their parent compounds; ② the sorption reduction in the ‘test sorption experiments’ is caused by the unrealistic coating of the cement surface with BZMs; and ③ BZM is a strong ligand, but the ligand concentration is too low to cause radionuclide sorption reduction under realistic conditions.

The *screening procedure* proposed comprises the following steps (c.f. Fig. 1):

1. If a given BZM decomposes rapidly under the chemical conditions prevailing in the cementitious environment, it may be regarded as non-problematic. However, the degradation products, and their effects on radionuclide sorption, have to be known, or be evaluated.
2. The sorption of  $\alpha$ -isosaccharinic acid (ISA) on hardened cement paste prepared in the presence of BZMs, (abbreviated to BZM-HCP in the following), is evaluated. Independently of the result of subsequent tests, a BZM is decided to be problematic if it causes significant desorption of ISA from the cement.

3. 'Test sorption experiments' are carried out, in which the influence of solutions of BZMs on the sorption of Ni(II), Eu(III) and Th(IV) on hardened cement paste (abbreviated as HCP in the following) is investigated under extreme conditions, i.e. at very high concentrations of the BZM, both in the liquid phase and at the cement surface. The purpose of these experiments is to make a first selection, based on whether an effect on radionuclide sorption is detected or not. If the sorption of the radionuclides is unchanged compared to their sorption on HCP measured in the absence of any BZM (and if sorption of ISA is not affected), the BZM tested may be regarded as non-problematic. This type of experiment may also be applied to detect ageing effects of BZMs. The radionuclides were chosen in order to test each representative of bi-, tri- and tetra-valent redox states.
4. If the sorption of radionuclides is reduced in the 'test sorption experiments', this does not necessarily mean that these BZMs cannot be used, since sorption reduction is assessed under very conservative experimental conditions. As a next step, it has to be decided whether the coating of the cement surface by BZMs or the complexation of radionuclides by the BZMs, causes reduction of radionuclide sorption. This question can be resolved by measuring the pore water concentrations of the BZMs, and by assessing the degree of surface coating of cement by BZMs under realistic conditions. Note that the concentrations of many of the bzms in cement pore water is strongly reduced through the sorption of the BZMs themselves to the cement [13-17].

### 3 EXPERIMENTAL

In the following, the experimental tools used for the *screening procedure* are summarised very briefly; the detailed experimental procedures can be found elsewhere [11]. Ordinary Portland cement (CPA 55 HTS, Lafarge, France) was used for preparing cylindrical cores of HCP, using a water:cement ratio of 0.7. BZM-HCP cores were prepared at the same water:cement ratio by adding 1.2–2% (dry weight of cement) of the BZMs to the cement during mixing. The cores were hydrated at various times and, if needed, crushed and sieved to sizes up to 70 µm. The artificial cement pore water (ACW-I) was a Ca(OH)<sub>2</sub>-saturated solution of 0.114 M NaOH and 0.18 M KOH (pH~13.3). The BZMs used in this study, their origins and the abbreviations used here, are summarised in Table 1.

The concentrations of the BZMs were measured by UV/VIS spectroscopy in the case of NS and LS, and by high performance anion exchange chromatography in the case of gluconate, this being an important component of PP. These measurements were accompanied by measurements of total organic carbon. Radionuclide sorption experiments were carried out using either crushed HCP or BZM-HCP as the solid phase, and ACW-I as the liquid phase. The radionuclides <sup>152</sup>Eu, <sup>234</sup>Th and <sup>63</sup>Ni were used as the test indicators. Dowex 50W-X4 was used for the ion exchange experiments as an inert solid phase, on which no sorption of BZM occurs.

Crushed HCP, prepared without BZMs, is used for the 'test sorption experiments', using <sup>152</sup>Eu, <sup>234</sup>Th and <sup>63</sup>Ni as test radionuclides, and ACW-I as the liquid phase.

**Table 1:** Overview of the BZMs used in this study.

Type	Abbrev.	Trade name	Content	Source
Sulfonated naphthalene-formaldehyde condensate	NS	Rheobuild 1000	40% <sup>a</sup>	MBT <sup>b</sup>
Sulfonated melamine-formaldehyde condensate	MS	Melment F10 Melment F 300	100% <sup>a</sup> (solid)	MBT <sup>b</sup>
SV-Polymer (Polycarboxylate)	PC	XA 3060, M 317	60% <sup>a</sup>	MBT <sup>b</sup>
Lignosulfonate (desugarised)	LS	242 Zewa EF 5	45% <sup>a</sup>	MBT <sup>b</sup>
Gluconic acid sodium salt	GL	Na-Gluconat tech.	45% <sup>a</sup>	MBT <sup>b</sup>
Sulfonated melamine-formaldehyde condensate	S1	Sikament-300	40%	Beznau Nuclear Power Plant
Sulfonated melamine-formaldehyde condensate	S2	Sikament-320	40%	Leibstadt Nuclear Power Plant
Carbohydrate	PP	PSI plasticiser	50%	PSI

<sup>a</sup> Containing the main constituents of the commercial products

<sup>b</sup> Formerly Meynadier (Zürich, Switzerland)

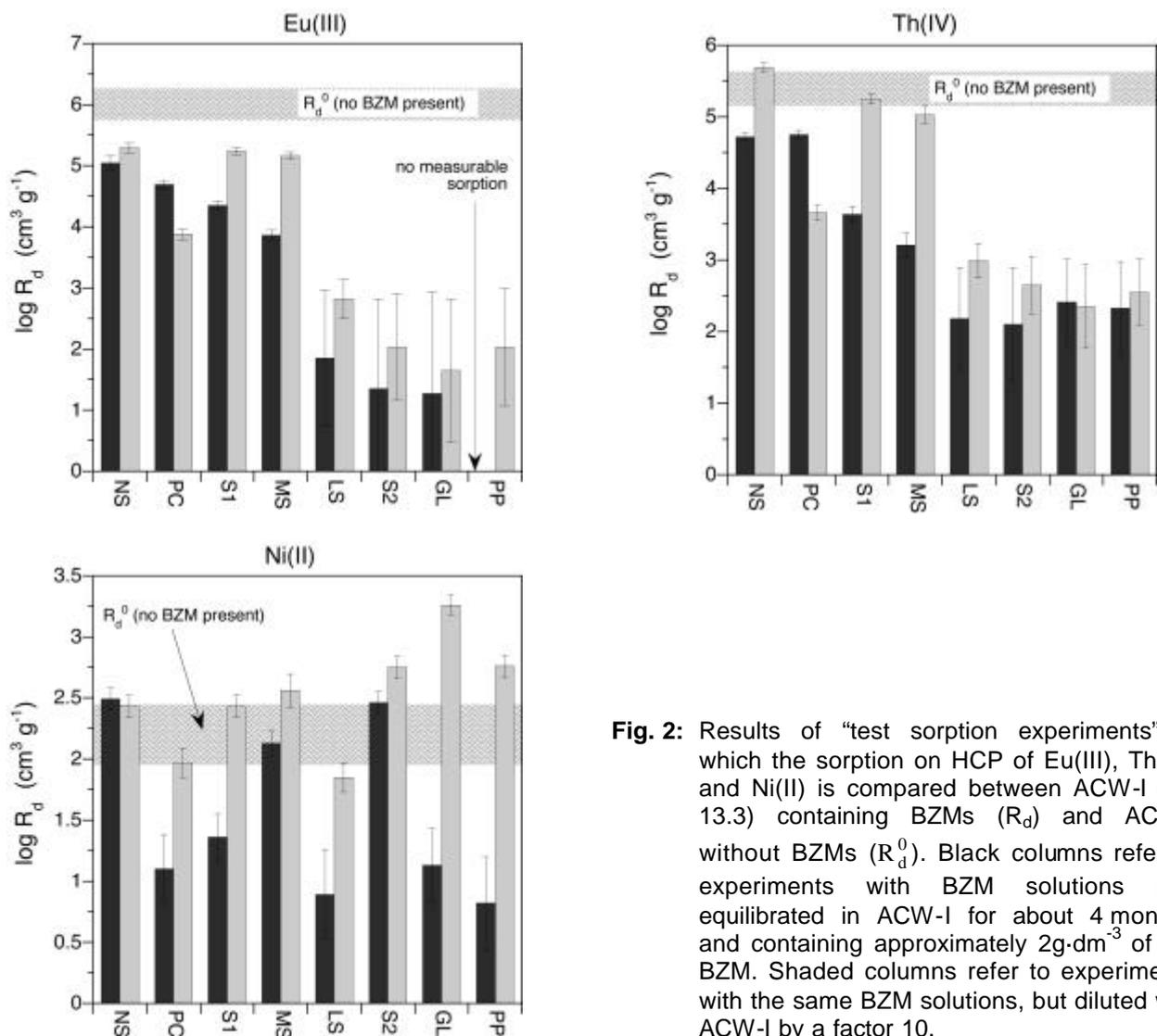
These experiments are carried out at BZM concentrations equivalent to a situation in which the total inventory of BZM would be present in the pore water, and at low solid:liquid ratios of HCP to pore water. (At realistic solid:liquid ratios, sorption reduction would not be detectable.)

Crushed BZM-HCP is used to measure the sorption of  $^{152}\text{Eu}$ ,  $^{234}\text{Th}$  and  $^{63}\text{Ni}$  on cement coated with BZMs, and to measure the sorption of ISA. Almost no desorption of BZM could be detected for such a material over several days, which is in agreement with literature data [17]. The consequence of this observation is that the saturation of the cement surface with admixtures matches that of real cement, even if the material is suspended in the pore water solution at a lower solid:liquid ratio. Pore water squeezed out of BZM-HCP cores is used to measure the pore water concentration of BZM, pH values, and concentrations of metal ions of interest (e.g. Na, K, Ca, Fe, Al). Increased solubilities for Fe or Al could be an indication of the presence of complexing agents. This type of experimental system will also be used for long-term investigations, i.e. for the detection of ageing effects.

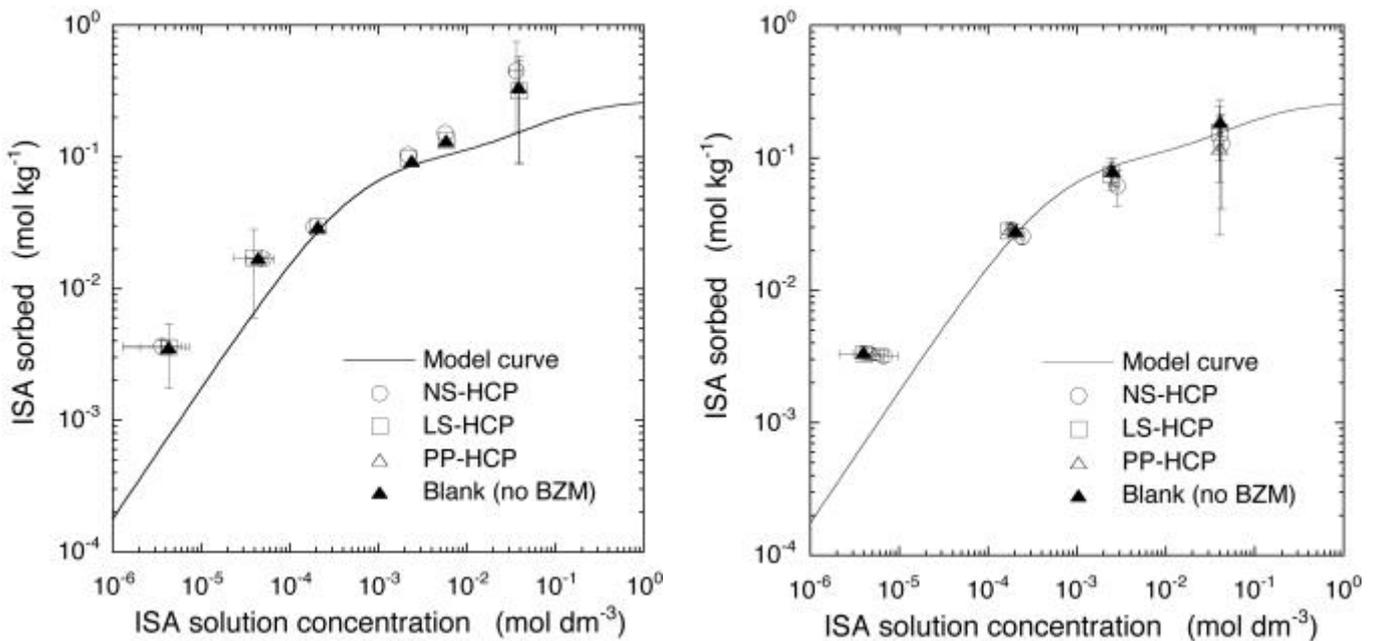
### 3 SELECTED RESULTS

Figure 2 shows the results of “test sorption experiments” using BZMs aged for about 4 months in artificial cement pore water (ACW-I). Sorption distribution coefficients ( $R_d$ ), measured in the presence of BZMs, are compared to those measured in the absence of BZMs ( $R_d^0$ ). For certain BZMs, complete desorption of radionuclides has been observed, whereas other BZMs did not have a significant effect on radionuclide sorption. Similar results were obtained for the same BZMs, pre-equilibrated in ACW-I for shorter or longer periods. No effect reflecting changes in radionuclide sorption could be traced back to possible chemical transformations of the BZMs.

Figure 3 shows that the sorption behaviour of ISA cannot be discriminated between NS-HCP, LS-HCP, PP-HCP and Blank-HCP, the latter being HCP prepared without addition of BZMs. This indicates that, at the BZM loadings currently used, the sorbed BZMs have no influence on the sorption of ISA.



**Fig. 2:** Results of “test sorption experiments” in which the sorption on HCP of Eu(III), Th(IV) and Ni(II) is compared between ACW-I (pH 13.3) containing BZMs ( $R_d$ ) and ACW-I without BZMs ( $R_d^0$ ). Black columns refer to experiments with BZM solutions pre-equilibrated in ACW-I for about 4 months, and containing approximately  $2\text{g}\cdot\text{dm}^{-3}$  of the BZM. Shaded columns refer to experiments with the same BZM solutions, but diluted with ACW-I by a factor 10.



**Fig. 3:** Sorption data for ISA on BZM-HCP at pH 13.3, measured for a contact time of 1 day. BZM-HCP samples have been hydrated for about 4 months (left-hand plot) and about 20 months (right-hand plot), respectively. The model curve (solid line) is calculated using the sorption parameters for ISA given in [18] for a two-site model.

A comparison between the left-hand and right-hand plots in Fig. 3 again shows that no aging effect can be discerned, which would indicate possible chemical transformations of the BZMs. Similar conclusions can be drawn for the influence of sorbed BZMs on the sorption of selected radionuclides, which is shown in Fig. 4. The comparison between  $R_d$  values measured for the BZM-containing material with those of the 'Blank series' shows that, at the BZM loadings currently used, the sorbed BZMs have no effect on the sorption of the radionuclides tested. The results shown in Figs. 3,4 can be understood, if the amount of the BZMs used in the preparation of the BZM-HCP is compared to the sorption capacity of the HCP for BZMs. Estimates, from a Langmuir-sorption, isotherm-based model [11], show that the HCP surface is saturated to about 10% with NS and LS, and to about 1% with gluconate (an important component of PP). Thus, there is enough capacity for either sorption of radionuclides or ISA. If the *screening procedure* is applied to NS, LS and PP based on the experimental data presented here, the following conclusions can be drawn. (An extensive discussion of the applicability and limitations of the *screening procedure* can be found elsewhere [11].) Note that some of the conclusions are not yet comprehensive, are still open to further discussions, and cannot be answered within the context of this study. The main focus of the present work aims at method development, rather than at producing reliable predictions for the three BZMs under consideration. Nonetheless, the following conclusions can be drawn.

1. No indication for a complete degradation of the BZMs to harmless products has been found in the course of this work. In the case of LS, indications for chemical transformation to compounds with weaker complexing properties have been observed [11]. Nevertheless, it would be advisable to treat these BZMs as chemically stable under the conditions of cement pore water.
2. None of the three BZMs has an influence on the sorption of ISA. In this respect, all three BZMs may be classified as unproblematic.
3. NS turned out to be unproblematic in the 'radionuclide test sorption experiments'.
4. In the case of LS and PP, the situation is more complicated. Because the results of the 'test sorption experiments' may not be applicable for a realistic situation encountered in cement (realistic solid:liquid ratios, and realistic ratios of BZM to cement), further investigations were carried out. The discussion of the effect of the concentrations of these BZMs in pore water, with respect to their formation of soluble complexes with radionuclides, is beyond the scope of the present work. A comprehensive compilation of experimental results, and conclusions drawn, can be found elsewhere [11]. Summarising, it can be stated that the pore water concentrations of LS and PP are too low to have a significant effect on the speciation of the radionuclides tested. In the case of LS, a few discrepancies remain to be understood in respect to the processes involved. Consequently, it may be advisable to treat LS in performance assessment as a strong ligand.

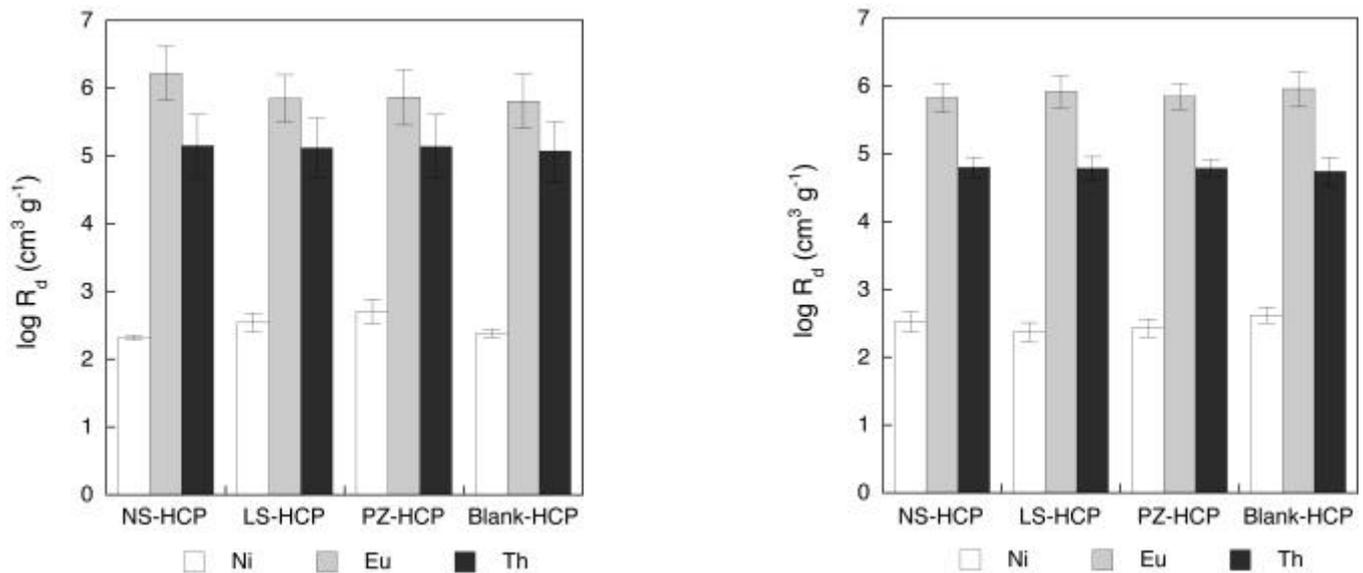
Gluconate, contained in PP, is known to be a very strong ligand at alkaline pH values. Examples for strong complexes with “hard cations” can be found, for example, in the case of Fe(III) [19], Al(III) [20], Si(IV) [21], and trivalent lanthanides [22]. Its effect on radionuclide sorption is, however, attenuated to insignificance by the very strong sorption of gluconate on cement [11]. The pore-water concentration of gluconate is too low to have an effect on radionuclide sorption.

- None of the three BZMs has an influence on the sorption behaviour of radionuclides on HCP with respect to possible competition effects for sorption sites.

It can be concluded that the proposed *screening procedure* is well suited for a broad assessment of

the effect of cement additives on the radionuclide retention potential of HCP. However, more substance-specific knowledge may be needed for a comprehensive assessment, if, for a specific case, it is not possible to break down the complexity of the system concrete–BZM–radionuclide retention in the manner proposed in this work.

The *screening procedure* focuses on possible adverse effects of BZMs, such as enhancing the solubility of radionuclides, or decreasing their sorption on cement. Other effects of the BZMs, which may be favourable with respect to radionuclide retention, such as decreasing the porosity of concrete or improving its workability, are not taken into account in the *screening procedure*. It is therefore important to balance the adverse and beneficial effects of the use of BZMs in any safety assessment.



**Fig. 4:** Sorption data for selected radionuclides on BZM-HCP at pH 13.3. BZM-HCP samples have been hydrated for ~4 months (left-hand plot) and for ~20 months (right-hand plot).

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## REFERENCES

- V. H. Dodson, “Concrete Admixtures”, Van Nostrand Reinhold, New York (1990).
- V.S. Ramachandran, “Concrete Admixtures Handbook”, 2<sup>nd</sup> edition., Noyes Publications, Park Ridge, NJ (1995).
- N. Spiratos, C. Jolicoeur, “Trends in Concrete Chemical Admixtures for the 21st Century”, in V.M. Malhotra, (Ed.), 6<sup>th</sup> CANMET/ACI Int. Conf. on Superplasticizers and Other Chemical Admixtures in Concrete, American Concrete Institute, Detroit, MI (2000).
- J. Hadermann, “The Pillars of Safety”, in I. Grenthe, I. Puigdomenech (Eds.), Modelling in Aquatic Chemistry. OECD Nuclear Energy Agency, Paris (1997).
- D.M. Roy, M. Daimon, B.E. Scheetz, D. Wolfe-Confer, K. Asaga, “Role of Admixtures in Preparing Dense Cements for Radioactive Waste Isolation”, in G.J. MacCarthy (Ed.), Scientific Basis for Nuclear Waste Management, Plenum Press, New York (1979).

- [6] M. Onofrei, M. Gray, R. Pusch, L. Börgesson, O. Karnland, B. Shenton, B. Walker, "Sealing Properties of Cement-Based Grout Materials", Stripa Project, Technical Report SKB TR 92-28, Swedish Nuclear Fuel and Waste Management Co., Stockholm (1992).
- [7] G.D. Xu, J.J. Beaudoin, "Effect of Polycarboxylate Superplasticizer on Contribution of Interfacial Transition Zone to Electrical Conductivity of Portland Cement Mortars", *ACI Mat. J.*, **97**, 418–424 (2000).
- [8] G. Spanka, G. Thielen, "Untersuchungen zum Nachweis von verflüssigenden Betonzusatzmitteln und zu deren Sorptions- und Elutionsverhalten", *Beton*, **5**, 320–327 (1995).
- [9] B.F. Greenfield, D.J. Ilett, M. Ito, R. McCrohon, T.G. Heath, C.J. Tweed, S.J. Williams, M. Yui, "The Effect of Cement Additives on Radionuclide Solubilities", *Radiochim. Acta*, **82**, 27–32 (1998).
- [10] H. Uchikawa, "Hydration of Cement and Structure Formation and Properties of Cement Paste in the Presence of Organic Admixture", *J. Res. Chichibu Onoda Cement Corporation*, **46**, 1–53 (1995).
- [11] M.A. Glaus, L.R. Van Loon, "A Generic Procedure for the Assessment of the Effect of Concrete Admixtures on the Retention Behaviour of Cement for Radionuclides: Concept and Case Studies", PSI Report 04-02, Paul Scherrer Institut, Villigen, Switzerland. Also published as Nagra Technical Report, NTB 03-09, Nagra, Wettingen, Switzerland (2004).
- [12] L.R. Van Loon, M.A. Glaus, "Experimental and Theoretical Studies on Alkaline Degradation of Cellulose and its Impact on the Sorption of Radionuclides", PSI Report 98-07, Paul Scherrer Institut, Villigen, Switzerland. Also published as Nagra Technical Report, NTB 97-04, Nagra, Wettingen, Switzerland (1998).
- [13] F.M. Ernsberger, W.G. France, "Portland Cement Dispersion by Adsorption of Calcium Lignosulfonate", *Industrial and Engineering Chemistry*, **37**, 598–600 (1945).
- [14] B. Blank, D.R. Rossington, L.A. Weinland, "Adsorption of Admixtures on Portland Cement", *J. Am. Ceramic Soc.*, **46**, 395–399 (1963).
- [15] D.R. Rossington, E.J. Runk, "Adsorption of Admixtures on Portland Cement Hydration Products", *J. Am. Ceramic Soc.*, **51**, 46–50 (1968).
- [16] M. Daimon, D.M. Roy, "Rheological Properties of Cement Mixes: I. Methods, Preliminary Experiments, and Adsorption Studies", *Cem. Concr. Res.*, **8**, 753–764 (1978).
- [17] V.S. Ramachandran, "Interaction of Calcium Lignosulfonate with Tricalcium Silicate, Hydrated Tricalcium Silicate and Calcium Hydroxide", *Cem. Concr. Res.*, **2**, 179–194 (1972).
- [18] L.R. Van Loon, M.A. Glaus, S. Stallone, A. Laube, "Sorption of Isosaccharinic Acid, a Cellulose Degradation Product, on Cement", *Environ. Sci. & Technol.*, **31**, 1243–1245 (1997).
- [19] D.T. Sawyer, "Metal-Gluconate Complexes", *Chem. Rev.*, **64**, 633–643 (1964).
- [20] R.J. Motekaitis, A.E. Martell, "Complexes of Aluminium(III) with Hydroxy Carboxylic Acids", *Inorg. Chem.*, **23**, 18–23 (1984).
- [21] S.D. Kinrade, R.J. Hamilton, A.S. Schach, C.T.G. Knight, "Aqueous Hypervalent Silicon Complexes with Aliphatic Sugar Acids", *J. Chem. Soc., Dalton Trans.*, 961–963 (2001).
- [22] S. Giroux, S. Aury, B. Henry, P. Rubini, "Complexation of Lanthanide(III) Ions with Polyhydroxy Carboxylic Acids in Aqueous Solutions", *Eur. J. Inorg. Chem.*, **5**, 1162–1168 (2002).