



TECHNICAL REPORT 96-04

Cementitious Near-Field Sorption Data Bases for Performance Assessment of a L/ILW Repository in a Palfris Marl Host Rock

CEM-94: UPDATE I, June 1996

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M. H. Bradbury, L. R. Van Loon
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This report was prepared on behalf of Nagra. The viewpoints presented and conclusions reached are those of the author(s) and do not necessarily represent those of Nagra.

PREFACE

The Laboratory for Waste Management at the Paul Scherrer Institut is performing work to develop and test models as well as to acquire specific data relevant to performance assessments of planned Swiss nuclear waste repositories. These investigations are undertaken in close co-operation with, and with the financial support of, the National Co-operative for the Disposal of Radioactive Waste (Nagra). The present report is issued simultaneously as a PSI-Bericht and a Nagra Technical Report.

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ABSTRACT

This report is an update on an earlier cementitious sorption data base (SDB) prepared by BRADBURY & SAROTT (1994). The aim is to review any new information or data which have become available in the intervening time and modify the existing SDB appropriately. Discussions will be confined predominantly to areas which have led to significant changes to or reappraisals of the data/values or procedures for obtaining/modifying them. From this point of view this update and the previous SDB are closely related and belong together.

The complexation of radionuclides with organic ligands resulting from the chemical degradation of cellulose, and the subsequent negative effects on sorption properties, were identified as being processes of great importance. Since 1994 significant progress has been made in this field and a major part of this work is devoted to a reassessment of the impact of "organics" on near-field sorption. In particular, the very conservative assumptions which had been made previously because of the general lack of good quality data available at that time, could be replaced by realistic parameter estimates based on new knowledge. For example, maximum likely concentrations of cellulose degradation products and cement additives in the cement pore waters could be calculated allowing the potential effects of these organics ligands on sorption to be bounded.

Sorption values for safety relevant radionuclides corresponding to the three broad stages of cement/concrete degradation during the lifetime of the repository are presented in tabulated form. The influence of the wide variety of organic ligands existing in the different waste categories, SMA-1 to SMA-4, is quantified in terms of sorption reduction factors.

In the compilation of this cement SDB update, radionuclide uptake onto the vast quantities of aggregate materials (in concretes) and corrosion products from iron/steel (from drums and reactor decommissioning) was not taken into account. A first appraisal of the potential contribution from limestone, quartz and goethite to retention in the near field is given. The aim was not so much to provide quantitative sorption data, but rather to begin the process of integrating these materials into safety assessment considerations.

Finally, some brief comments concerning the recrystallisation of calcium silicate hydrate (CSH) gels, carbonation, colloids and radionuclide incorporation into CSH phases are given.

ZUSAMMENFASSUNG

Im vorliegenden Bericht wird eine frühere Sorptions-Datenbasis (SDB) für Zement (BRADBURY & SAROTT 1994) dem neuesten Wissensstand angepasst. Neue Erkenntnisse und Daten wurden überprüft und die bestehende Datenbasis entsprechend modifiziert. Die Diskussionen in diesem Bericht konzentrieren sich vor allem auf jene Gebiete, in denen die Sorptionsdaten signifikant geändert oder neu abgeschätzt werden mussten. Ebenso wird auf Änderungen in den Verfahren, die zur Beschaffung oder Modifizierung der Sorptionsdaten benutzt werden, detailliert eingegangen. So gibt es einen engen Zusammenhang zwischen der vorliegenden, aufdatierten Version und der früheren Datenbasis.

Der Einfluss der organischen Liganden aus dem alkalischen Abbau von Zellulose auf die Sorption von Radionukliden an Zement wurde als besonders wichtig identifiziert. Seit 1994 hat man bedeutende Fortschritte in der Untersuchung dieser Prozesse gemacht; ein grosser Teil des vorliegenden Berichts betrifft daher eine Neuauswertung des Einflusses von organischen Stoffen auf die Radionuklid-Sorption im Nahfeld. Insbesondere wurden die früheren, sehr konservativen Annahmen durch realistische ersetzt. Als Beispiel sei die Berechnung der maximal möglichen Konzentration von Zellulose Abbauprodukten, sowie von Zementzusatzstoffen in den Zementporenwässern angeführt. Dies ermöglicht eine Eingrenzung der potentiellen Einflüsse dieser organischen Liganden auf die Radionuklid-Sorption.

Sorptionsdaten sicherheitsrelevanter Nuklide, die den drei Degradationsphasen des Zements/Betons zugeordnet werden, sind tabellarisch dargestellt. Dem Einfluss einer Vielfalt von organischen Liganden, die in den verschiedenen Abfallgruppen von SMA-1 bis SMA-4 vorkommen, wird in Form von Sorptionsreduktionsfaktoren Rechnung getragen.

In der vorliegenden überarbeiteten Form der Sorptions-Datenbasis für Zement wird die Radionuklidsorption auf der Fülle von Zuschlagstoffen (Aggregate im Beton) und den Stahlkorrosionsprodukten (aus den Fässern und der Reaktorstilllegung) nicht berücksichtigt, jedoch wird eine erste Bewertung des potentiellen Beitrags von Kalkstein, Quartz und Goethit zur Radionuklid-rückhaltung im Nahfeld vorgenommen. Das Ziel lag weniger auf der Ermittlung von quantitativen Sorptionsdaten, sondern vielmehr wurde hiermit ein erster

Schritt unternommen, diese Materialien in sicherheitstechnische Überlegungen miteinzubeziehen.

Abschliessend werden die Rekristallisation von Calcium-Silikat-Hydrat (CSH) Gelen, die Karbonatisierung, der Einfluss von Kolloiden und der Radionuklideinbau in CSH-Phasen kurz vorgestellt.

RESUME

Ce rapport est une mise à jour de la précédente base de données de sorption concernant le ciment (SDB) qui avait été préparée par BRADBURY & SAROTT (1994). Le but de cette remise à jour est de passer en revue toutes les nouvelles informations ou données publiées entre-temps, et de modifier en conséquence la SDB. Les discussions seront limitées d'une part aux domaines dans lesquels des changements significatifs sont intervenus, d'autre part à une réévaluation des données/valeurs ou des procédures permettant l'obtention ou la modification de ces nouvelles données. De ce point de vue, cette mise à jour et la précédente SDB sont étroitement liées et forment un ensemble unique.

Il a été montré que la complexation des radionucléides avec les ligands organiques provenant de la désintégration de la cellulose pouvait altérer de manière importante les propriétés de sorption, et qu'il s'agissait donc de processus importants. Depuis 1994, des progrès non négligeables ont été réalisés dans ce domaine et une grande part de ce travail est consacrée à une nouvelle analyse de l'impact des ligands organiques sur la sorption dans le champ proche d'un stockage. En particulier, les hypothèses très pessimistes qui avaient été adoptées à cette époque pour pallier à l'absence générale de données fiables, ont pu être remplacées par des paramètres plus réalistes estimés à partir de nouvelles recherches. Par exemple, les concentrations maximales probables des produits de désintégration de la cellulose et des additifs du ciment ont pu être calculées pour les eaux interstitielles du ciment, ce qui a permis de délimiter les effets potentiels de ces ligands organiques sur la sorption. Ce rapport rassemble sous forme de tableaux les valeurs de sorption à considérer pour les radionucléides pertinents pour la sûreté d'un stockage, et ce pour trois étapes de la dégradation du ciment. En particulier, la grande variété de ligands organiques présents dans les différentes catégories de déchets, SMA-1 à SMA-4, est prise en compte quantitativement à l'aide de facteurs de réduction de sorption.

Dans la compilation de cette mise à jour de la SDB du ciment, l'adsorption des radionucléides par d'importantes quantités d'agrégats (présents dans les bétons) et par les produits de corrosion du fer ou des aciers (issus des fûts ou des déchets provenant du démantèlement des réacteurs) n'est pas prise en compte. Cependant, ce rapport propose une première évaluation de la contribution potentielle du calcaire, du quartz et de la goéthite aux propriétés de

rétenion du champ proche. Le but n'est pas tant de fournir des données quantitatives de sorption, que d'initier le processus d'intégration de ces matériaux aux analyses de sûreté.

Enfin, ce rapport présente aussi quelques brefs commentaires concernant la recristallisation des gels de silicate de calcium hydraté (CSH), la carbonatation, les colloïdes ainsi que l'incorporation des radionucléides dans les phases CSH.

TABLE OF CONTENTS

ABSTRACT	I
ZUSAMMENFASSUNG	III
RESUME	V
TABLE OF CONTENTS	VII
LIST OF FIGURES	X
LIST OF TABLES	XI
1 INTRODUCTION	1
2 LAYOUT	2
3 SELECTED SORPTION DATA FOR UNPERTURBED CEMENT	4
Cl and I	5
Ni and Co	5
Se and Mo	6
Ag	6
Sn	7
Nb	7
Po	8
Actinides	8
4 CELLULOSE DEGRADATION: ISOSACCHARINIC ACID	9
4.1 Evidence from Radionuclide Solubility Studies	9
4.2 Evidence from Sorption Studies	10
5 CHEMICAL DEGRADATION OF CELLULOSE: MECHANISMS AND KINETICS	13
5.1 Introduction	13
5.2 The Peeling Off Reaction	15
5.3 Alkali Catalysed Cleavage of Glycosidic Bonds (Alkaline Hydrolysis)	17
5.4 Experimental Studies: Degradation Rates for Different Types of Cellulose Materials	19

6	THE SOLUBILITY OF $\text{Ca}(\text{ISA})_2$	23
7	SORPTION OF ISA ON CEMENTITIOUS MATERIALS	25
8	ESTIMATE OF THE MAXIMUM LIKELY CONCENTRATION OF ISA IN CEMENT PORE WATERS	28
9	CEMENT ADDITIVES: ESTIMATE OF THEIR MAXIMUM LIKELY CONCENTRATION IN CEMENT PORE WATERS	31
10	ASSESSMENT OF THE INFLUENCE OF CELLULOSE DEGRADATION PRODUCTS AND CEMENT ADDITIVES ON THE SORPTION ON CEMENTITIOUS MATERIALS	33
10.1	Cellulose Degradation Products: Isosaccharinic Acid	33
10.2	Cement Additives: Gluconate	36
10.3	Summary	36
	Isosaccharinic Acid (ISA)	37
	Gluconate (GLU)	38
11	OTHER ORGANIC AND INORGANIC COMPONENTS IN THE WASTE	40
11.1	Bitumen and Ion Exchange Resins	40
11.2	Low Molecular Weight Organics	40
11.3	High Molecular Weight Organics	42
11.4	Inorganic Waste Components	43
12	SORPTION SUMMARY TABLES	45
13	AGGREGATE MATERIAL AND IRON OXIDES	48
13.1	Limestone / Calcite	48
	Cs	49
	Sr and Ra	49
	Ni, Co, Pd, Pb	49
	Tc, Ag	50
	Po	50
	Trivalent Actinides: Ac, Am, Cm	50

	Tetravalent Actinides: Th, U, Np, Pu plus Zr	50
	Pa(V)	50
	Anionic Species: Cl, I, Se, Mo, Nb, Sn	50
13.2	Limestone: Concluding Remarks	51
13.3	Quartz	52
13.4	Quartz: Concluding Remarks	53
13.5	Iron Oxides	54
14	RECRYSTALLISATION OF CSH GELS AND CARBONATION	56
15	COLLOIDS	57
16	INCORPORATION OF RADIONUCLIDES INTO CSH PHASES DURING CEMENT HYDRATION	58
17	ACKNOWLEDGEMENTS	60
18	REFERENCES	61

LIST OF FIGURES

- Fig. 1: Effect of ISA and cellulose degradation products on the solubility of Pu at pH = 12. 10
- Fig. 2: Effect of ISA (closed symbols) and cellulose degradation products (open symbols) on the adsorption of Th on feldspar at pH=13.3. The degradation time varied between 1 week and 1 year (data from VAN LOON et al. 1996). 12
- Fig. 3: Schematic representation of the structure of cellulose. 13
- Fig. 4: Degradation kinetics of a cellulose material (DP=500) at 25°C in an 0.3 M OH⁻ solution, pH~13.3 (VAN LOON & GLAUS 1997). 19
- Fig. 5: Total dissolved organic carbon as a function of time for different cellulose materials degraded in simulated cement pore water (pH=13.3) at 25 °C (VAN LOON et al. 1996). 20
- Fig. 6: Evolution of the ISA concentration as a function of time for different cellulose materials degraded in simulated cement pore water (pH=13.3) at 25 °C (VAN LOON et al. 1996). 21
- Fig. 7: Adsorption isotherm for ISA on hardened HTS cement paste at pH = 13.3 for different equilibration times. 26
- Fig. 8: The sorption of Eu-152 on hardened cement paste as a function of the equilibrium concentration of ISA in ACW. 35
- Fig. 9: The sorption of Th-234 on hardened cement paste as a function of the equilibrium concentration of ISA in ACW. 35
- Fig. 10: A summary of models for the interaction of metal pollutants with cement (Figure 8-31 in COCKE & MOLLAH 1993). 59

LIST OF TABLES

Table 1: Parameters used to calculate the fraction of cellulose degraded in a repository at 25°C and $[\text{OH}^-] = 0.3 \text{ M}$.	18
Table 2: Predicted and measured extent of degradation of different cellulosic materials after ~360 days at 25°C and $[\text{OH}^-] = 0.3 \text{ M}$, pH~13.3 (VAN LOON et al. 1996).	22
Table 3: Maximum concentration of ISA in cement pore water calculated at different pH values, based on the solubility of $\text{Ca}(\text{ISA})_2$.	24
Table 4: Langmuir parameters for the sorption of ISA on HCP at pH=13.3.	27
Table 5: Estimated maximum EDTA concentrations in SMA-2 and SMA-4.	41
Table 6: Estimated polymer loadings in SMA-1 to SMA-3.	43
Table 7: Sorption data base for unperturbed cementitious material (CEM-94, Update 1, June 1997).	46
Table 8: Sorption reduction factors for safety relevant radionuclides in the presence of cellulose degradation products, cement additives and EDTA (CEM-94, Update 1, June 1997).	47

1 INTRODUCTION

The purpose of this report is to update an earlier cementitious near field sorption data base (SDB) compiled by BRADBURY & SAROTT (1994), and include advances in knowledge and understanding which have occurred over the past three years. This current report must be taken in conjunction with the previous cement SDB (BRADBURY & SAROTT 1994), which for convenience will be referred to as CEM-94 from now on. The intention here is only to reproduce those parts of that report where it is necessary for understanding, or to highlight the ideas and uncertainties which existed then with a view to bringing them up to date. In the main, the discussions will be confined to areas where new information and/or data are available which lead to (potentially) significant changes to or re-appraisals of the data/values in CEM-94 or procedures for obtaining/modifying these data values.

In the past, there has been little or no continuity between different compilations of SDB's for the same system. Generally, the production of sorption data bases has consisted of a series of separate, almost unconnected, exercises. The production of this updated SDB is intended to be a first step in the application of a new approach where the idea is to compile an initial, well documented SDB, and then produce future SDB's as updated versions, thus providing a transparent and traceable record of the development.

The general background information and discussion contained in Chapters 2 and 4 in CEM-94 are still considered to be valid, and the guiding principles given there are incorporated within this new work.

2 LAYOUT

In the following chapter the sorption values for unperturbed cement systems reported in CEM-94, Chapter 5, are briefly reviewed. Discussions are given only where new sorption values are proposed or where relevant new information supports previously chosen values. In all other cases the selected distribution ratios for the unperturbed system are the same as given in CEM-94.

One of the main topics discussed in detail in CEM-94 was the potential influence on sorption of the degradation products from the organic material present together with the radioactive waste in the cement filled drums. In particular, the organic ligands resulting from the degradation of cellulose, and those associated with cement additives, were identified as being of particular importance. However, because of the general lack of knowledge and good quality data available at the time, very conservative assumptions were made which led to strong adverse effects on many of the sorption values. This very conservative approach did however have some positive consequences. It not only emphasised the potential importance of organic degradation products with respect to their potentially negative influence on sorption, but also highlighted the large gaps in knowledge which prevented well founded and realistic assessments of their effects from being made. This led to the identification of "critical research areas" for the experimental programmes which subsequently evolved.

The most recent results and information/considerations concerning organic degradation products and cement additives are presented and discussed in Chapters 4 to 7. The new information and procedures are documented in detail so that the differences in the approaches taken here and in CEM-94, and their consequences, are clear and readily traceable. It should be noted at this point that only chemical processes are being considered. Potential effects due to the microbiological degradation of cellulosic materials is not included. This is followed in Chapters 8 and 9 by estimates of the maximum likely concentrations of cellulose degradation products and cement additives in the cement pore waters. The additional knowledge available now has enabled a more realistic assessment of the influence of organic ligands on sorption to be made, as discussed in Chapters 10 and 11.

Sorption values for safety relevant radionuclides under the different repository conditions are presented in tabulated form in Chapter 12 together with proposed element specific values for sorption reduction factors resulting from the "organics" present in the near-field. Two values are given for each element. The first set of sorption reduction factors (SRFs) are based on the maximum likely concentrations of cellulose degradation products, organic cement additives and EDTA in the different sections of the repository discussed in Chapters 8, 9 and 11. These SRFs represent "best conservative estimates" deduced from our current level of understanding and the available data. The second set of values headed SRF-10, correspond to organic ligand concentrations approximately one order of magnitude greater. Concentrations at these levels are not expected at all in the repository and as such the SRF-10s given represent extreme upper bound values.

This is followed in Chapter 13 by a first attempt at assessing the potential contribution of the aggregate materials in concretes and iron oxidation products to the retention characteristics of the near-field. Some very brief comments concerning the recrystallisation of calcium silicate hydrate (CSH) gels, carbonation, steel corrosion products and colloids are given in Chapters 14 and 15. Finally, in Chapter 16, the potential importance and consequences of radionuclide incorporation into CSH type phases is discussed.

3 SELECTED SORPTION DATA FOR UNPERTURBED CEMENT

Following the sequence of procedures used in CEM-94, the first task is to update the sorption values for "unperturbed" cement systems taking into consideration the changing conditions within the near-field resulting from the contact of the cement/concrete with the slowly moving groundwaters of the marl formation. For convenience, the temporal chemical degradation of cement was divided into three principle stages, designated regions I, II and III (see section 4.3, CEM-94).

Results and information on cement sorption published between mid 1994 and mid 1997 have not led to any fundamental changes in the SDB for "unperturbed" cement as a whole. However, in certain individual cases some additional comments on, and re-appraisal of, the sorption values given in CEM-94 are called for. The radionuclides concerned are discussed separately below. The sorption values given in CEM-94 for all other radionuclides are still considered to be valid and to represent the best values available and consequently remain unchanged. A summary of all selected sorption values for unperturbed cementitious systems is given in Table 7, Chapter 12.

Before discussing sorption values for specific elements, it is perhaps worthwhile mentioning that radionuclide uptake mechanisms at high pH are poorly understood at present. Indeed, the cation exchange and surface complexation mechanisms which are most often used to describe sorption processes occurring in the pH range 3 to 10, may not be the major processes taking place under hyperalkaline conditions. Making judgements as to how strongly or weakly a particular radionuclide may sorb on the basis of the dominant aqueous species present is even more doubtful at high pH than under normal pH conditions. As will be indicated in the following chapters, even minerals regarded as being relatively inert with respect to the sorption of radionuclides, can exhibit strong sorption at high pH. Mechanisms such as surface precipitation, surface ternary complex formation, two step sorption processes (sorption from the aqueous phase followed by surface re-arrangement reactions) and incorporation into the sorbent matrix may need to be considered in addition to the usual cation exchange and surface complexation processes in order to explain the results from "sorption" measurements. The uptake of radionuclides at high pH is a complex process,

especially in the presence of organic ligands.

Cl and I

The selected chloride sorption value of $2 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$ given in CEM-94 was taken from the work of SAROTT et al. (1992) who measured Cl^- diffusion rates through hardened HTS* cement paste discs. The proviso on this sorption value was that the chloride concentrations in the cement pore waters should not exceed 10^{-5} M , the highest concentration used in the diffusion tests. Recent laboratory experiments (BAEYENS & BRADBURY 1991, 1994) and new evaluations of in situ groundwater analyses (PEARSON & SCHOLTIS 1994) have suggested that, at the proposed location of the repository in the Palfris marl, Wellenberg, the groundwater is likely to be a NaCl-type with an ionic strength of $\sim 0.2 \text{ M}$. These high background concentrations of chloride would also be expected to be present in the cement pore waters and to influence the uptake of radioactive chloride onto the cement.

BAKER et al. (1994) have published Cl^- sorption results on OPC/lime/limestone grouts in the pH range 12 to 13.5 for initial concentrations between 5×10^{-8} and 0.5 M chloride. At the lowest concentration the measured sorption value was $\sim 4 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$ (comparable with the values of SAROTT et al. 1992) and at 0.5 M Cl^- a value of $\sim 6 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ was determined.

On the basis of these results, a reduction in the previously selected sorption value to $5 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ is proposed to take account of the higher chloride concentrations.

It is interesting to note that iodide sorption data are presented in the same work, and values between $\sim 4 \times 10^{-2}$ and $\sim 6 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ were measured in the initial concentration range 2×10^{-5} to $2 \times 10^{-9} \text{ M}$ iodide. In view of this recent information, a revision upwards of the iodide sorption to $10^{-2} \text{ m}^3 \text{ kg}^{-1}$ is justifiable and the new value still represents a conservative estimate.

Ni and Co

In CEM-94 the best estimate sorption value for Ni of $0.1 \text{ m}^3 \text{ kg}^{-1}$ proposed by PILKINGTON & STONE (1990) was accepted. However, although this value was a factor of five lower than their lowest measured value, there were still some doubts about its conservatism since considerable experimental

* Haute Teneur en Silice, a French sulphate resistant cement.

difficulties were reported by these authors.

Batch sorption experiments performed by SAROTT (1996) on hardened HTS cement paste indicated that Ni sorbed linearly over the equilibrium concentration range $\sim 4 \times 10^{-11}$ to $\sim 3 \times 10^{-9}$ M with a value of $\sim 0.2 \text{ m}^3 \text{ kg}^{-1}$. In contrast, batch desorption experiments yielded values ten times higher whereas for "through-diffusion" experiments modelling of the measured curves produced sorption values which were apparently ten times lower (JAKOB et al. 1996a). However, as the authors themselves point out, it is unlikely that a steady state diffusion condition had been reached in these tests even after times as long as 1000 days. The results from subsequent "out-diffusion" experiments (JAKOB et al. 1996b) proved impossible to reproduce on the basis of a diffusion/reversible sorption model. Although the reasons for these discrepancies are currently uncertain, the indications are that there may be more than one mechanism binding radionuclides to the surfaces which may have different release kinetics. Some of these may be so slow that they cannot be measured on laboratory time scales.

At the moment we see no compelling reason to revise the sorption value for Ni and its chemical analogue Co. The value given in CEM 94 of $0.1 \text{ m}^3 \text{ kg}^{-1}$ is therefore retained.

Se and Mo

In CEM 94 no sorption data for Se and Mo in cementitious systems were found and "nominal values of $10^{-4} \text{ m}^3 \text{ kg}^{-1}$ " were chosen. In view of the total absence of relevant sorption data, the anionic form of these radionuclides and the high pH conditions, we have reconsidered the situation and conclude that the only reasonable position to take is that both of these radionuclides do not sorb at all.

Ag

In CEM-94 a nominal sorption value for Ag of $10^{-3} \text{ m}^3 \text{ kg}^{-1}$ was selected across the whole range of cement degradation stages. While this may still be a reasonable estimate for NaHCO_3 -type groundwaters, we are of the opinion that a revised R_d value of zero for the NaCl -type groundwater ($I \sim 0.2 \text{ M}$) is more appropriate because of the strong tendency of Ag to form Ag-chloro complexes.

Sn

Under the reducing conditions existing in the repository environment (Eh ~ 300 mV), Sn is expected to be present in the tetravalent state and readily hydrolyses to the negatively charged oxocomplex, stannate (see for example POURBAIX 1974).

Measurements with SnO, SnO₂ and Sn reported by BAYLISS et al. (1989) indicated relatively high Sn solubilities of ~10⁻⁴ M in cement pore waters. In the same paper extremely high sorption values of 50-62 m³ kg⁻¹ were given where phase separation was carried out using 30,000 MWCO filters. At the relatively high initial concentrations used (~10⁻⁴ M), problems were encountered with colloid formation. In a subsequent paper (BAYLISS et al. 1991) the likely solubility determining phase was given as cassiterite (SnO₂) with a solubility limit in the range 10⁻⁹ to 10⁻⁶ M. On the basis of the above information a conservative R_d(Sn) value of 1 m³ kg⁻¹ was selected in CEM-94. Part of the reason for selecting such a conservative value was the suspicion that precipitation effects may have been playing a rôle in the sorption tests. However, some more recent data published by BAKER et al. (1994), with starting Sn concentrations of ~6x10⁻⁸ M, appear to confirm the strong sorption of Sn in cement systems. R_d(Sn) values of ~200 m³ kg⁻¹ were reported. Nevertheless, the sorption value given in CEM-94 is retained because the possibility of precipitation effects still cannot be completely ruled out on the basis of the information contained in the paper of BAKER et al. (1994).

Nb

Sorption values of ~40 m³ kg⁻¹ for Nb on OPC/lime/limestone grouts at pH=12.2 in saline solutions have been given by BAKER et al. (1994). Their data lie within the range of values, ~0.5 m³ kg⁻¹ to ~80 m³ kg⁻¹, reported by PILKINGTON & STONE (1990) but they do not appear to have encountered the sort of experimental difficulties discussed by the latter authors. The starting concentrations in the sorption tests were very low (~4.5x10⁻¹³ M) and certainly well below the solubility limit of 10⁻⁷ to 10⁻⁸ M (pH~12.2) determined in the same work.

In view of the results given by BAKER et al. (1994) at very low Nb concentrations which confirm the high sorption values given by PILKINGTON & STONE (1990), we feel justified in revising the sorption value for Nb upwards to 1 m³ kg⁻¹.

Po

Polonium is a radioactive metal which can exist in the 2+ and 4+ oxidation states and for which no relevant sorption data could be found in the literature. According to FALBE & REGITZ (1992) Po(II) oxidises easily to Po(IV) by self irradiation. Under the Eh/pH conditions envisaged for marl, Po(IV) will probably exist as the polonate anion, PoO_3^{2-} (VAN MUYLDER 1966). Although bismuth might be considered the best chemical analogue for Po (FALBE & REGITZ 1992), there is unfortunately no information on this element either. In view of the lack of sorption data, and its anionic form in solution, we set the sorption of polonium to zero.

Actinides

BAYLISS et al. (1996) have recently published R_d values for the uptake of U(IV), U(VI), Np (added as Np(IV)), Pu (redox state not given) and Am(III) on OPC/ lime/limestone aggregate concrete (the Nirex reference vault backfill) as a function of temperature up to $77 \pm 5^\circ\text{C}$ under non-saline and hypersaline (1.5 M) conditions at pH=12.5.

Increasing the salinity and temperature did not have any adverse effects on sorption, indeed in some cases (U and Pu) the sorption increased. In general the sorption values measured were high, for U the values were between 5 and $40 \text{ m}^3 \text{ kg}^{-1}$; for Np between 40 and $200 \text{ m}^3 \text{ kg}^{-1}$; for Pu between 1 and $70 \text{ m}^3 \text{ kg}^{-1}$ and Am approximately $1 \text{ m}^3 \text{ kg}^{-1}$.

Taking the above new data into consideration, the only change which might be required for actinide sorption is to revise the R_d value for Am (Cm) downwards to $1 \text{ m}^3 \text{ kg}^{-1}$. Note that there are many other Am sorption measurements which indicate much higher values, but the starting Am concentrations used by BAYLISS et al. (1996) were low, making precipitation effects less likely, and on this basis their data are preferred.

4 CELLULOSE DEGRADATION: ISOSACCHARINIC ACID

The single most important parameter determining the products formed during the alkaline degradation of cellulose is the solution composition, particularly with regard to the presence of alkaline earth cations (VAN LOON 1993, GREENFIELD et al. 1993).

In the two dominant regions of cement degradation, Regions I and II, calcium is present in the cement pore waters at levels of approximately 2 and 20 x 10⁻³ M respectively. This Ca²⁺ in the pore waters is important for the degradation of cellulose since it favours the production of isosaccharinic acid (ISA) as opposed to other potential products (BLEARS et al. 1957, MACHELL & RICHARDS 1960, COLBRAN & DAVIDSON 1961). Thus, although the hyperalkaline cellulose degradation experiments of GREENFIELD et al. (1993) and VAN LOON et al. (1996) were carried out under distinctly different conditions, both simulated cement pore waters contained significant quantities of calcium and in both cases ISA was identified as the dominant degradation product.

4.1 Evidence from Radionuclide Solubility Studies

GREENFIELD et al. (1992) reported significant increases for the solubility of Pu in particular, but for other radionuclides as well, in the presence of cellulose degradation products. In a later publication (GREENFIELD et al. 1993) it was shown that this solubility enhancement was most probably due to the ISA component in the degraded cellulose solution forming strong complexes with Pu. The ISA concentrations in the degraded cellulose solutions were determined and the Pu solubility enhancements compared with those measured in similar experiments where the solutions were made up with known concentrations of ISA. Figure 1 illustrates the correspondence of the two data sets and was compiled from the results given in GREENFIELD et al. (1992), in Figure 2 in MORETON (1993), in Table 8 in GREENFIELD et al. (1993) and in Figure 2 in GREENFIELD et al. (1995).

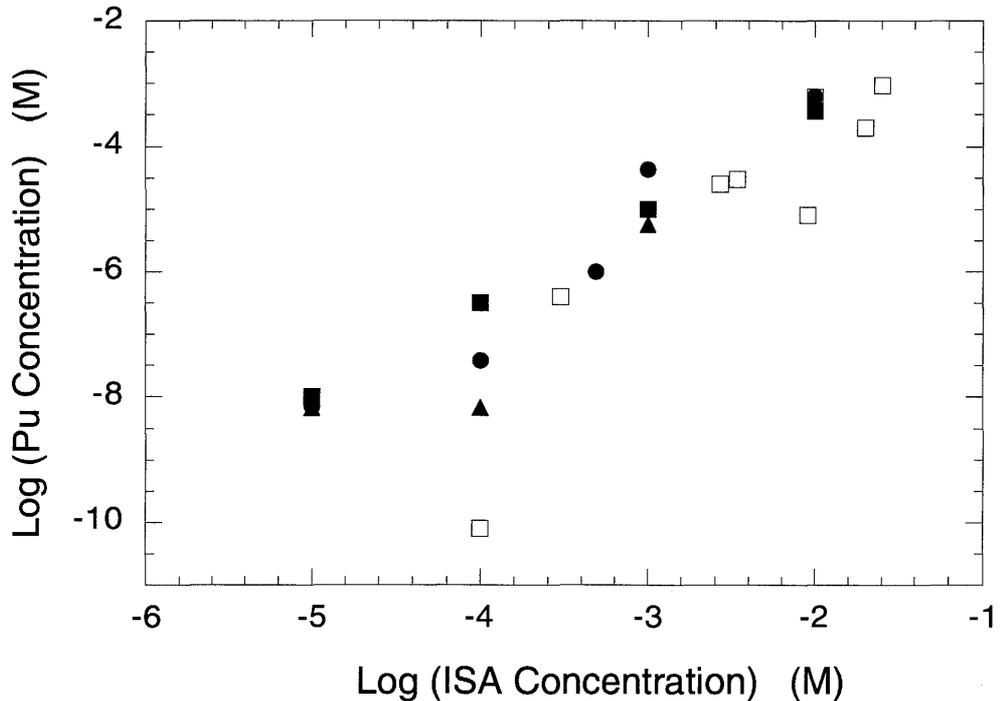


Figure 1: Effect of ISA and cellulose degradation products on the solubility of Pu at pH = 12.

Filled symbols represent experiments conducted with ISA:

(■) GREENFIELD et al. (1992); (▲) MORETON (1993)

(●) GREENFIELD et al. (1995)

Open symbols represent experiments conducted with cellulose degradation products: (□) GREENFIELD et al. (1993).

4.2 Evidence from Sorption Studies

Because of the generally low radionuclide inventories present in the planned Swiss L/ILW repository (CEM-94, Appendix C), the enhancement of radionuclide solubilities by organic degradation products is not, in general, of concern. Potentially much more important is the influence of these organic ligands on sorption. Since this is the case, a programme of work based on sorption measurements and the determination of complexation constants was initiated at the Paul Scherrer Institute, PSI.

VAN LOON et al. (1996) have performed a series of experiments in which sorption data for Th, Eu and Ni, measured in the presence of ISA, were

compared with corresponding sorption values determined in solutions containing degradation products from different cellulose source materials.

The purpose of these experiments was two fold. First, by comparing the influence of ISA with "real" cellulose degradation products from materials such as Aldrich cellulose powder, cotton, Tela tissues and recycled paper, conclusions could be drawn as to whether ISA was the main degradation product in terms of the influence on sorption. Second aim was to quantify the influence of metal complexation with ISA on sorption and to deduce conditional constants for the complexation reaction. Feldspar was chosen as the sorbing substrate since the interaction of this mineral surface with ISA was negligible. This is an important consideration if the requirement is to study the influence of aqueous complexation alone.

The sorption of Th at trace concentrations was measured on feldspar at initial ISA concentrations ranging between 10^{-5} M and 10^{-1} M in $\text{Ca}(\text{OH})_2$ saturated solutions of $(\text{Na},\text{K})\text{OH}$ at $\text{pH}=13.3$, Figure 2. The effect of various cellulose degradation product solutions in which the ISA concentrations were determined is also shown. As can be seen, ISA has an adverse influence on the sorption which can be explained, in a general way, by an aqueous complexation reaction between ISA and Th. The solutions containing cellulose degradation products also have the effect of reducing the Th sorption. If these data are normalised with respect to the ISA concentration in the solutions, then, as can be seen, the majority of the data are coincident with the ISA measurements. If metal complexation with ISA is the main cause of sorption reduction then these data should be indicative of the maximum effects to be expected.

In the case of Eu (cotton degradation products) and Ni (degradation products from paper, tissues and cotton) there appeared to be a stronger reduction in the sorption on feldspar than could be explained by ISA alone. This indicated that there may be additional organic ligands present which complex with these radionuclides more strongly than ISA. However these results cannot be directly applied to cementitious systems since the effects of organic ligands (degradation products and cement additives) on radionuclide sorption are critically dependent on the solid phase and hardened cement paste is very different from feldspar. The former sorbs ISA and GLU very strongly (and probably also their complexes with radionuclides as well) whereas the latter

does not. It also appears that the stronger the organic complexant the stronger is the uptake on cementitious surfaces i.e. GLU sorbs more strongly than ISA. Though these observations need to be investigated further it is still probably reasonable to conclude from the available evidence that ISA is the predominant product in the degradation mixtures which is responsible for the observed effects on solubility increases and sorption decreases in cementitious systems.

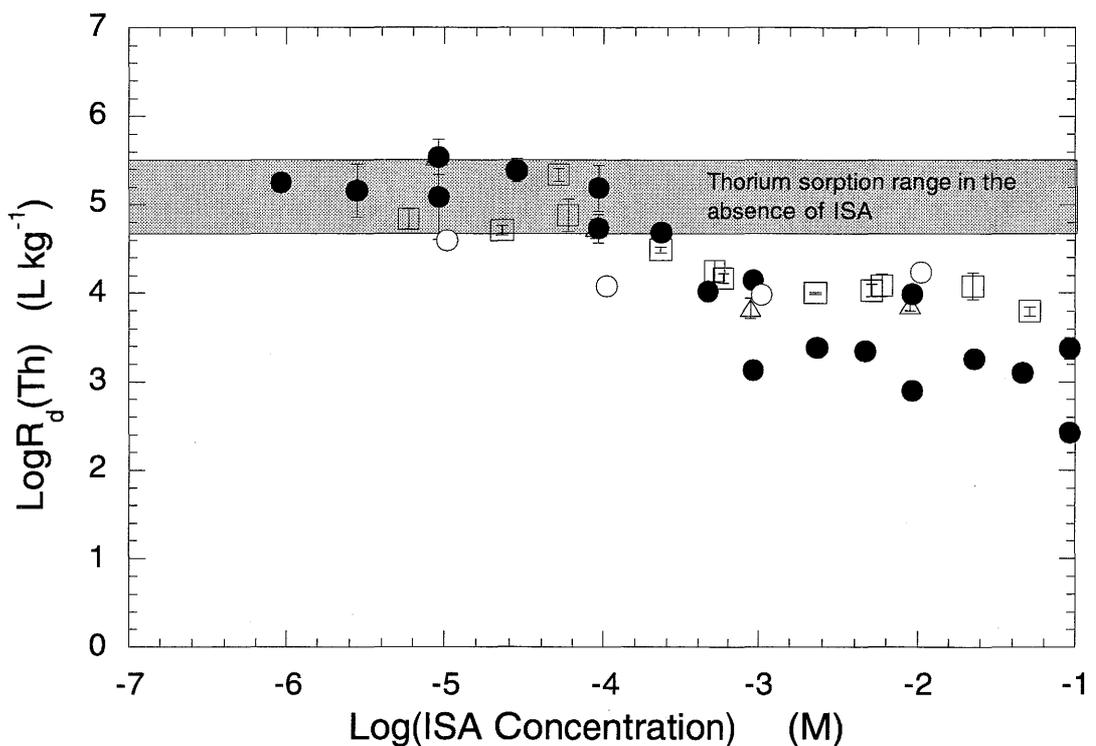


Figure 2: Effect of ISA (closed symbols) and cellulose degradation products (open symbols) on the adsorption of Th on feldspar at pH=13.3. The degradation time varied between 1 week and 1 year (data from VAN LOON et al. 1996). The overall error on the log R_d values is $\sim\pm 0.2$ log units.

ISA (●); Cellulose (□); Tela (Δ); Paper (O)

5 CHEMICAL DEGRADATION OF CELLULOSE: MECHANISMS AND KINETICS

5.1 Introduction

Cellulose is a polysaccharide of plants and is the most abundant organic compound found in nature. It is an unbranched polymer of up to 10^4 glucose units (Figure 3) joined by β -1,4 glycosidic bonds. About 50% of the organic waste present in the planned L/ILW repository will be cellulose in the form of wood, cotton and paper (NAGRA 1994).

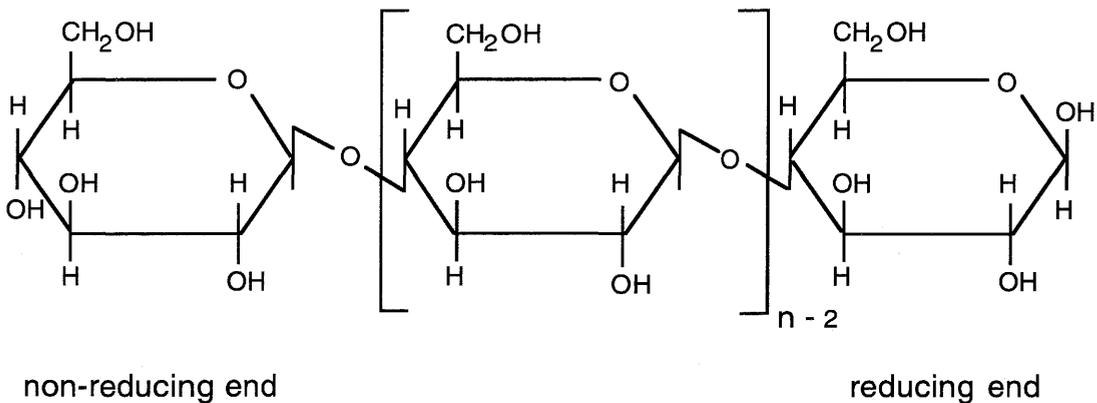
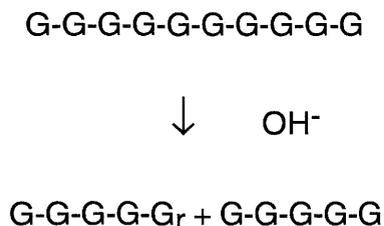


Figure 3: Schematic representation of the structure of cellulose.

The most important experimental parameters in the alkaline degradation process of cellulose are pH, temperature and solution composition. Temperature and pH influence predominantly the degradation rate (HAAS et al. 1967, LAI & ONTTO 1979, LAI 1981), but do not in themselves effect the type of degradation products formed. As mentioned in the previous chapter, the solution composition is much more important in this respect. In CEM-94 it was assumed that all the available cellulose degraded instantaneously to ISA. No account was taken of the potential influence of degradation kinetics on the maximum possible ISA levels which could be present in the cement pore waters. The intention in this chapter is to rectify this omission.

The alkaline degradation of cellulose proceeds via two main mechanisms.

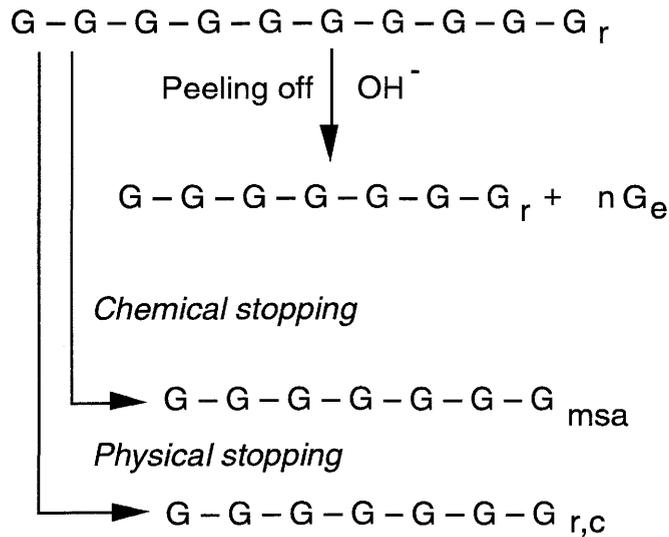
1. Alkali catalysed cleavage of glycosidic bonds in which a bond somewhere in the cellulose chain is split. This process leads to a decrease in molecular weight of cellulose and the formation of reducing end groups.



where G is a glucose monomeric unit in the cellulose chain and G_r is a reducing end group.

2. Peeling off reaction which results in the formation of soluble degradation products. The peeling off reaction is controlled by two competing processes, a *chain propagation reaction* and *stopping reactions*. In the former the cellulose molecule is progressively shortened by the elimination of glucose units to form soluble organic molecules such as isosaccharinic acid. This process may be accompanied by stopping reactions which can have a "chemical" or "physical" character. Chemical stopping reactions convert reducing end-groups into the metasaccharinic acid form while still attached to the cellulose chain, resulting in an alkali stable structure. When the reducing end-group reaches the crystalline region of the cellulose, degradation ceases due to the inability of the OH^- ions to penetrate this structure (HAAS et al. 1967). The physical stopping reaction is not an abrupt process since there is a gradual transition from the amorphous to the crystalline region rather than a distinct interface. Because of the competitive stopping reactions, the peeling off process cannot continue until all of the cellulose has been degraded.

A schematic presentation of the peeling off reaction is given below. G_{msa} is a stable end-group, G_e is a glucose unit eliminated and n are the number of glucose units eliminated. G_r is a reducing end-group in the amorphous region of the cellulose fibre and $G_{r,c}$ is a reducing end-group in the crystalline region of the cellulose fibre.



In the following only the main equations describing the kinetics of cellulose degradation are given. The processes have been described in detail in the review of VAN LOON & GLAUS (1997).

5.2 The Peeling Off Reaction

The first order rate equations for the chain propagation reaction and the chemical and physical stopping reactions (VAN LOON & GLAUS 1997) can be combined into a single rate equation describing the overall degradation of cellulose by the peeling off reactions:

$$\frac{dG_e}{dt} = k_1 \cdot (G_r)_0 \cdot e^{-k_t \cdot t} \quad (1)$$

where:

(G_e) = mole fraction of glucose units eliminated.

$(G_r)_0$ = initial mole fraction of reducing end groups at time $t=0$.

k_1 = rate constant for the chain propagation reaction.

k_t = $(k_2 + k_{cr})$, the overall rate constant for chain termination.

k_2 = the first order rate constant for the chemical stopping

k_{cr} = the first order rate constant for the physical stopping

At time $t=0$, $(G_e) = 0$ and Eqn. (1), after integration, becomes:

$$(G_e) = \frac{k_1}{k_t} \cdot (G_r)_o \cdot (1 - e^{-k_t \cdot t}) \quad (2)$$

Assuming that the glucose units are eliminated as isosaccharinic acid, i.e. there are no fragmentation reactions (BLEARS et al. 1957, WHISTLER & BeMILLER 1958, MACHELL & RICHARDS 1960, SJÖSTRÖM 1977, LAI 1991) then:

$(G_e) = (ISA)$, the mole fraction of isosaccharinic acid formed, and hence:

$$(ISA) = \frac{k_1}{k_t} \cdot (G_r)_o \cdot (1 - e^{-k_t \cdot t}) \quad (3)$$

The maximum amount of (ISA) which can be formed is then:

$$(ISA)_{\max} = \frac{k_1}{k_t} \cdot (G_r)_o \quad (4)$$

The maximum amount of ISA formed is equal to the maximum amount of glucose units peeled off, hence:

$$(\text{mole fraction of degraded cellulose})_{\max} = (G_e)_{\max} = \frac{k_1}{k_t} \cdot (G_r)_o \quad (5)$$

From equations. (4) and (5) it can be seen that $(ISA)_{\max}$ and the maximum amount of cellulose degraded depend on the initial mole fraction of reducing end-groups in the cellulose, $(G_r)_o$, and on the ratio of the rate constants of the propagation and stopping reactions. The initial mole fraction of reducing end-groups is defined as:

$$(G_r)_o = \frac{\text{moles of reducing end-groups}}{\text{moles of glucose units in the chain}} \quad (6)$$

The mole fraction of reducing end-groups depends on their average number in a cellulose molecule and on the degree of polymerisation (DP). Both these parameters have an effect on the amount of cellulose which can be degraded. In theory, one molecule of cellulose, containing n glucose units (degree of polymerisation $DP=n$), has one reducing end-group. In reality, not all cellulose

molecules will have reducing end-groups because some may have been transformed to non-reducing forms during the pulping process (PROCTER & WIEKENKAMP 1969, PROCTER & APELT 1969, BRYCE 1980, CHIANG & SARKANEN 1984). Consequently, the mole fraction of reducing end-groups in cellulose with DP=n is (VAN LOON & GLAUS 1997):

$$0 \leq (G_r)_o \leq \frac{1}{n} \quad (7)$$

The assumption of one reducing end-group per cellulose molecule implies a maximum value for the concentration of reducing end-groups $(G_r)_o$ for a cellulose molecule with DP=n and hence results in an upper bound value for the quantity of degradable cellulose. This is a very important observation and will be returned to later, see page 28.

5.3 Alkali Catalysed Cleavage of Glycosidic Bonds (Alkaline Hydrolysis)

The alkaline hydrolysis of cellulose (cleavage reactions) cannot be studied in isolation from the peeling off reaction since hydrolysis causes the formation of new reducing end-groups which then undergo peeling off reactions, see previous section.

The degradation reaction has been studied widely (see for example LAI 1981) and it has been shown that the rate of degradation can be described by the following empirical equations:

$$\ln(1/Y) = k_{obs} \cdot x_n \cdot t \quad (8)$$

where:

Y = fraction of un-reacted cellulose

x_n = average amount of glucose units removed from the cellulose chain

t = time

k_{obs} = first order rate constant

Since rate equations are now available for the fast peeling off reactions, Eqn.

(5), and the slow cleavage reaction, Eqn. (8), the overall degradation of cellulose can be expressed by the combination of these two equations:

$$(\text{cellulose remaining}) = \frac{\left(1 - \frac{k_1}{k_t} \cdot (G_r)_o \cdot (1 - e^{-k_t \cdot t})\right)}{e^{(k_{\text{obs}} \cdot x_n \cdot t)}} \quad (9)$$

Values for the parameters in Eqn. (9) have been derived by VAN LOON & GLAUS (1997) and are summarised in Table 1.

Table 1: Parameters used to calculate the fraction of cellulose degraded in a repository at 25 °C and $[\text{OH}^-] = 0.3 \text{ M}$.

Parameter	Value
$k_1 \text{ (hrs}^{-1}\text{)}$	$3.65 \cdot 10^{-2}$
$k_t \text{ (hrs}^{-1}\text{)}$	$6.9 \cdot 10^{-4}$
$k_{\text{obs}} \cdot x_n \text{ (hrs}^{-1}\text{)}$	$5.25 \cdot 10^{-11}$
$(G_r)_o$	0.002

As mentioned previously, the importance of the peeling off reaction in the short term degradation of cellulose depends on the value of $(G_r)_o$, i.e. on the initial mole fraction of reducing end-groups in the cellulose, or, since $(G_r)_o = 1/\text{DP}$, on the degree of polymerisation, DP, of the particular form of cellulose under consideration. Figure 4 illustrates the temporal degradation of a cellulose material having a degree of polymerisation value of 500 at 25°C in a solution with an OH^- concentration of 0.3 M (pH~13.3).

As can be seen, there is an initial fast degradation phase, followed by a further very slow process. In the first degradation phase, the peeling off reaction is the dominant mechanism and is therefore the rate determining process. In the second phase, the slow cleavage reaction is rate determining. Consequently, there is a fast ingrowth of ISA into the cement pore water which reaches a plateau value within a few years.

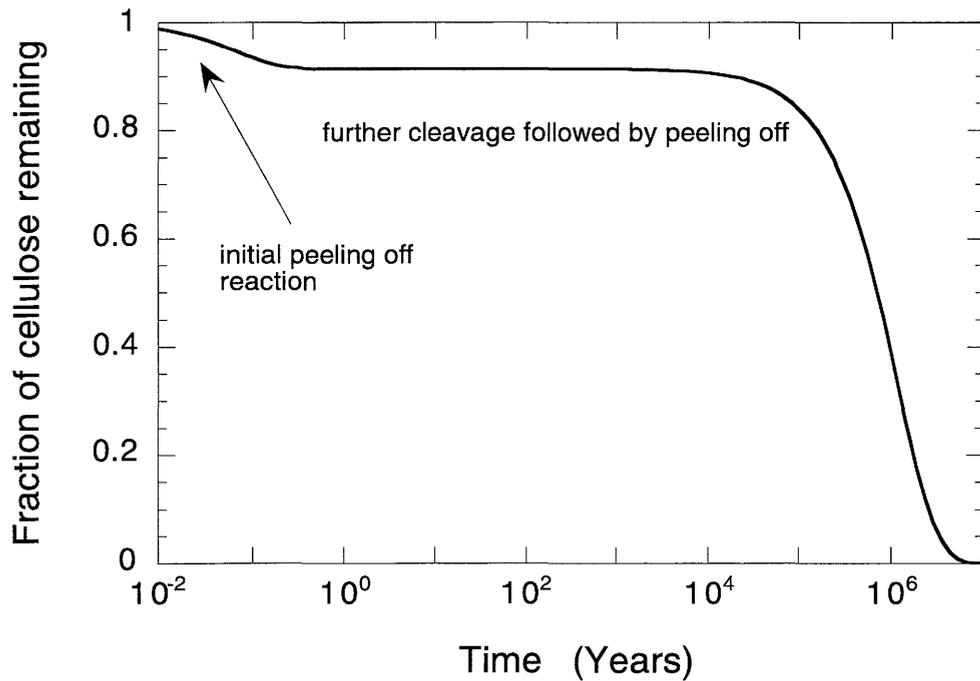


Figure 4: Degradation kinetics of a cellulose material (DP=500) at 25°C in an 0.3 M OH⁻ solution, pH~13.3. (VAN LOON & GLAUS 1997).

5.4 Experimental Studies: Degradation Rates for Different Types of Cellulose Materials

It is apparent from the foregoing section that the concentration of ISA produced by the alkaline degradation of cellulose in the cementitious near field will rapidly reach a plateau value dependent predominantly upon the degree of polymerisation of the particular types of cellulose present.

Some typical ranges of values for the degree of polymerisation for different cellulose containing materials, taken from MOROHOSHI (1991) for cotton and wood, and from GASCHE (1996) for paper, are given below.

Cotton fibres	degree of polymerisation	3000 to 14000
Wood cellulose	degree of polymerisation	3000 to 9000
Paper	degree of polymerisation	700 to 2000

An experimental programme on cellulose degradation has been started at PSI

in support of the modelling studies. Different kinds of cellulose (cellulose powder supplied by Aldrich (20 μm particle size), cotton, Tela tissues and recycled paper) were degraded as described in section 4.2. The data are presented in Figure 5 for the different cellulosic materials in terms of the levels of total dissolved organic carbon (DOC) in solution which is a measure of the amount of cellulose degraded.

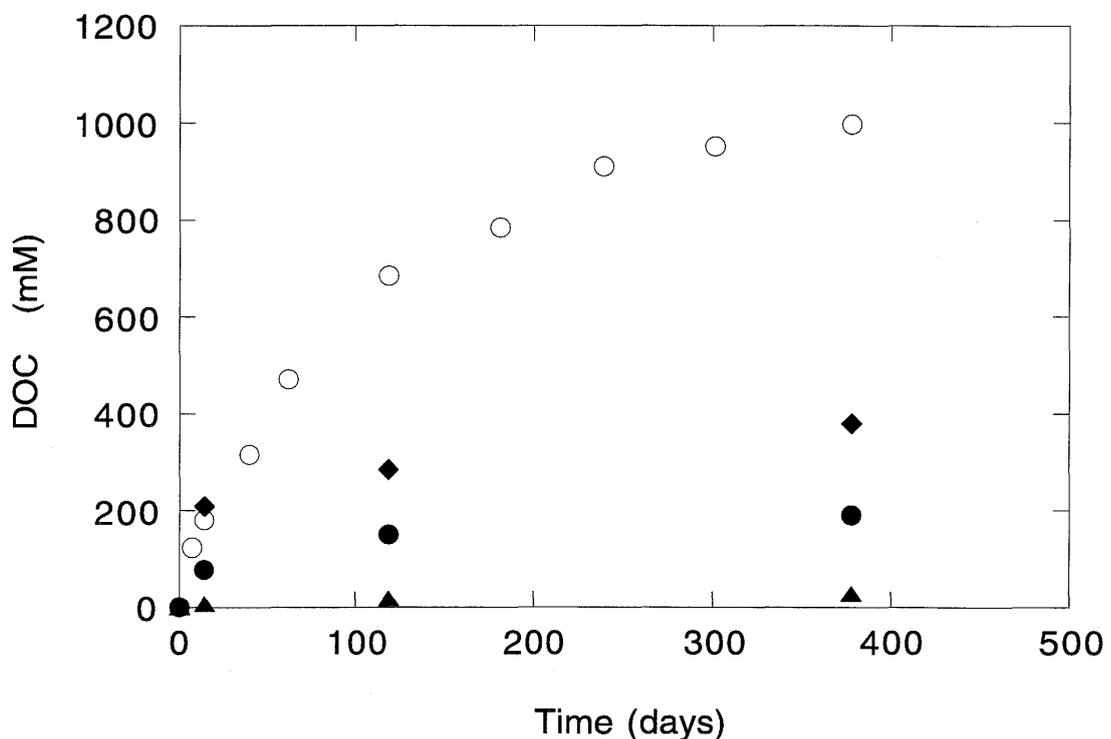


Figure 5: Total dissolved organic carbon as a function of time for different cellulose materials degraded in simulated cement porewater (pH=13.3) at 25 °C (VAN LOON et al. 1996).

(O): Aldrich cellulose

(▲): cotton; (●): Tela tissues; (◆): recycling paper

Figure 6 is complementary to Figure 5, and illustrates the concentrations of ISA in the solutions. The kinetics of evolution of the ISA concentrations are similar to those of the total dissolved organic carbon concentrations. It should be noted here that the above determinations of ISA are for the alpha isomer only. Determinations for the beta form are underway and the preliminary indications are that the concentrations of the two isomers are similar (VAN LOON et al. 1996).

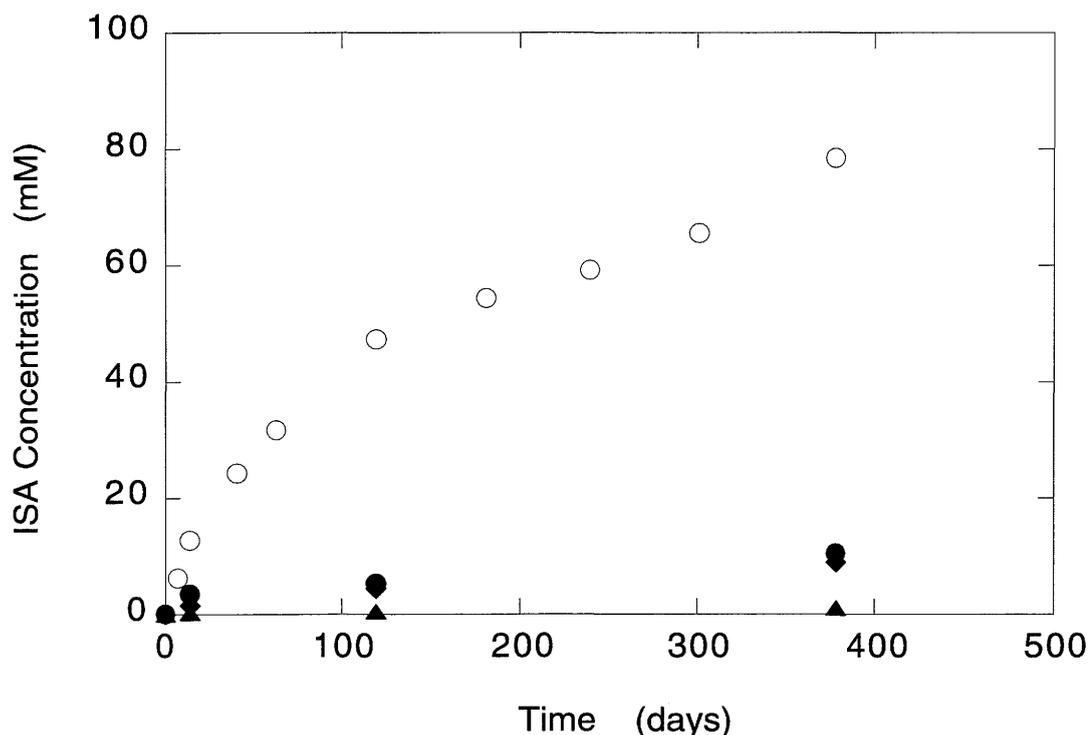


Figure 6: Evolution of the ISA concentration as a function of time for different cellulose materials degraded in simulated cement porewater (pH=13.3) at 25 °C (VAN LOON et al. 1996).

(O): Aldrich cellulose

(▲): cotton; (●): Tela tissues; (◆): recycling paper

After a period of approximately one year, the following percentages, with respect to mass, of each cellulose containing solid had degraded; ~27 % for the cellulose powder, ~10 % for the recycled paper, ~5 % for the Tela tissues and 0.7 % for the cotton.

A comparison between the measured and predicted quantities of degraded cellulosic material is presented in Table 2. The predicted quantities were calculated using equation (5). Two values are given for the predicted degraded percentages for each material; those in bold type are based on kinetic parameters measured by VAN LOON et al. (1996), $k_1/k_t = 32$, whereas those in parenthesis are deduced from literature data, $k_1/k_t = 53$, given in VAN LOON & GLAUS (1997). The data deduced from the literature give higher predicted values for the amount of cellulose degraded.

Table 2: Predicted and measured extent of degradation of different cellulosic materials after ~360 days at 25 °C and $[\text{OH}^-] = 0.3 \text{ M}$, $\text{pH} \sim 13.3$ (VAN LOON et al. 1996).

Cellulose	DP	* $(G_r)_o$	% Degraded #(Predicted)	% Degraded (Measured)
Aldrich cellulose	117	$8.6 \cdot 10^{-3}$	27 (45)	27
Tela tissues	1110	$9.0 \cdot 10^{-4}$	2.7 (4.8)	5.1
Cotton	1800	$5.6 \cdot 10^{-4}$	1.7 (2.9)	0.7
Recycling paper	290	$3.5 \cdot 10^{-3}$	11 (18)	10

* $(G_r)_o = 1/\text{DP}$

using equation (5) with $k_1/k_t = 32$ or $(k_1/k_t = 53)$

The current results indicate that steady state conditions corresponding to the complete reaction of all the initially present reducing end groups by the peeling off process have not been achieved for any of the cellulosic materials under test. It is foreseen to follow the progress of the degradation process over the next two years at least.

6 THE SOLUBILITY OF $\text{Ca}(\text{ISA})_2$

Another means by which the maximum concentration of ISA in the pore waters of a cementitious material could be limited is through solubility constraints. It is known from the literature that ISA forms sparingly soluble salts with Ca^{2+} (WHISTLER & BeMILLER 1963) and hence the Ca^{2+} concentration in a cement pore water could set an upper limit on ISA concentrations. However, the solubility product of $\text{Ca}(\text{ISA})_2$ is not known. This was considered to be a sufficiently important gap in our knowledge to warrant its determination and the necessary measurements were therefore carried out (VAN LOON & GLAUS 1995).

Briefly, the dissolution of $\text{Ca}(\text{ISA})_2$ is simply be described by:



for which the solubility product ($K_{s,0}$) is defined as:

$$K_{s,0} = a_{\text{Ca}} \cdot (a_{\text{ISA}})^2 \quad (11)$$

with:

a_{Ca} = activity of Ca^{2+} in solution

a_{ISA} = activity of ISA^- in solution

A mean value for $\log K_{s,0}$ was determined to be -6.22 ± 0.03 at $I=0$ and $T = 21 \text{ }^\circ\text{C}$.

This solubility product can be used to calculate the maximum concentration of ISA which may be present in cement pore waters. Two examples are given below which correspond to the pore water compositions in degradation Regions I and II (See CEM-94, section 4.3).

Immediately apparent from the values given in Table 3 is, that the equilibrium concentrations of ISA calculated according to the solubility limits of $\text{Ca}(\text{ISA})_2$ in the two cases are high. As will be shown later in Chapter 8, processes other than the solubility of $\text{Ca}(\text{ISA})_2$ are more likely to bound the upper value for ISA concentrations.

Table 3: Maximum concentration of ISA in cement pore water calculated at different pH values, based on the solubility of $\text{Ca}(\text{ISA})_2$.

pH	Ionic Strength M	$[\text{Ca}^{2+}]$ $\times 10^{-3}$ M	$[\text{ISA}]_{\text{max}}$ $\times 10^{-3}$ M
13.3 (Region I)	0.3	2	43
12.5 (Region II)	0.08	20	11

7 SORPTION OF ISA ON CEMENTITIOUS MATERIALS

To our knowledge there are no reports available in the open literature describing direct measurements on the sorption behaviour of ISA on cementitious materials. The only published estimates of ISA sorption values are those presented in CEM-94 section 6.2.2. These estimates were deduced from measurements performed on OPC/BFS blended cements (GREENFIELD et al. 1992) and it was by no means certain that a similar behaviour on cement types relevant to Swiss repository designs would occur. Since in CEM-94 the reduction in ISA concentrations in the cement pore water via sorption played an important rôle in determining the influence of this organic degradation product on radionuclide sorption, and because of the importance placed on system understanding in our research programmes, priorities were set to characterise the uptake of relevant organic ligands on cement. Consequently, the sorption kinetics and sorption isotherms for the uptake of ISA on crushed hardened cement paste (HCP) were determined over an initial concentration range from 10^{-5} to 10^{-2} M.

The monitoring of ISA (by ion chromatography) and measurements of total dissolved organic carbon gave some initial information on the processes taking place. For example, in the case of ISA sorption alone, both the ISA and the DOC would have to decrease proportionally. If ISA had undergone degradation, then the ISA concentration would have been expected to decrease and the DOC concentration to remain constant, as long as any new degradation products did not sorb. (More details of the methodology are described in VAN LOON et al. 1996). The consistency of the chromatographic (ISA) measurements and the corresponding DOC data clearly indicated that on the time scales of these experiments sorption processes were occurring rather than any further degradation of the organic molecules.

Preliminary data for the sorption of ISA on hardened HTS cement paste are shown in Figure 7.

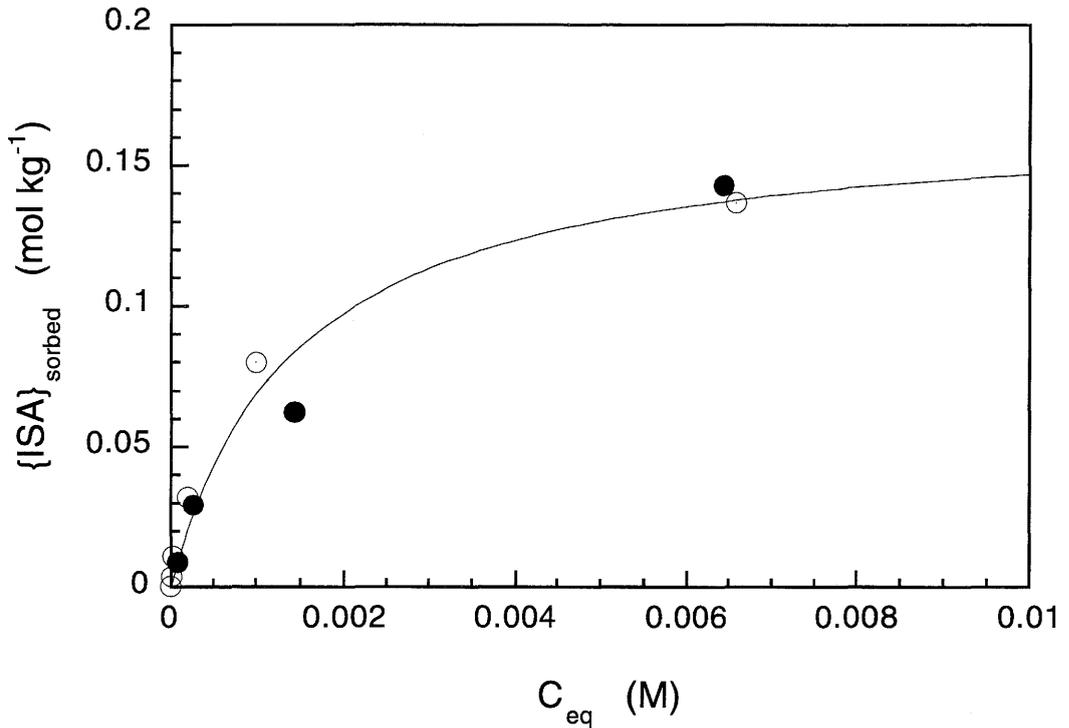


Figure 7: Adsorption isotherm for ISA on hardened HTS cement paste at pH = 13.3 for different equilibration times. Equilibration times: 1 day (●); 7 days (○).

The adsorption of ISA takes place rapidly under the experimental conditions used and appears to be complete after a time of approximately one day. The sorption of ISA can be described by a Langmuir type of isotherm:

$$\{ISA\}_{sorbed} = \frac{K_{isa} \cdot \{ISA\}_{max} \cdot C_{eq}}{1 + K_{isa} \cdot C_{eq}} \quad (12)$$

where:

$\{ISA\}_{sorbed}$ = the quantity ISA sorbed on hardened cement paste (mol kg⁻¹)

$\{ISA\}_{max}$ = the maximum sorption capacity of ISA on hardened cement paste (mol kg⁻¹)

K_{isa} = the sorption-affinity parameter (L mol⁻¹)

C_{eq} = the aqueous equilibrium concentration of ISA (M)

The Langmuir isotherm parameters extracted from the experimental data are summarised in Table 4.

Table 4: Langmuir parameters for the sorption of ISA on HCP at pH=13.3.

Langmuir Parameter	Value
K_{isa} (L mol ⁻¹)	~690
Sorption Capacity (mol kg ⁻¹)	~1.7x10 ⁻¹

These measurements indicate that the sorption capacity of hardened HTS cement paste for ISA is ~0.2 mol kg⁻¹ which can be compared with the estimate of 0.3 mol kg⁻¹ given in CEM-94, section 6.2.2.

The preliminary conclusion from this study, which is still continuing, is that ISA can sorb to a significant extent on cementitious materials. Consequently, organic ligand sorption effects must be taken into account in any considerations of their influence on radionuclide sorption values, whether this is in laboratory experiments or in the repository near-field.

8 ESTIMATE OF THE MAXIMUM LIKELY CONCENTRATION OF ISA IN CEMENT PORE WATERS

The simple calculation given below is intended to yield a conservative estimate of the maximum concentration of ISA likely to be present in the cement pore waters during the first $\sim 5 \times 10^4$ years when the average pH lies above 12.5 i.e. during Region I. After this time period the cellulose still continues to degrade, by a cleavage plus peeling off mechanism, but at a much slower rate, which, according to Figure 4, corresponds to a value less than 1 wt% per 5×10^4 years. Even this estimated rate is probably very conservative since the values in Figure 4 were calculated for a constant pH of ~ 13.3 . During the long time scales considered, the pH will fall to below 10, and the pH is one of the main parameters determining the kinetics of degradation, section 5.1.

Consider a representative 1 m^3 volume of the repository with an average porosity, P , containing Z kg of hardened cement paste and I kg of organic material. Assume conservatively that the whole of this organic material is cellulose in the form of paper, and that a fraction, F , proportional to the initial mole fraction of reducing end groups present, degrades to ISA, MW=180 (see equations 5 and 6).

The above assumption regarding the type of organic material is conservative for two reasons. First, the organic matter present in a repository is not just cellulose but contains "high" molecular weight organic polymers such as polythene, neoprene etc. PLUS "low" molecular weight organic compounds such as NTA, EDTA etc. PLUS ion exchange resins. At the very maximum, only about 50% of the total can be regarded as being of cellulosic origin (NAGRA 1994) and it is well documented that the degradation products from cellulose have a far greater influence on radionuclide solubilities and sorption than any other organic material source so far investigated (ALLARD & PERSSON 1985, ALLARD et al. 1987, PILKINGTON & STONE 1990, EWART et al. 1991, VAN LOON & KOPAJTIC 1991, HUMMEL 1992, BROWNSWORD et al. 1992, GREENFIELD et al. 1992, VAN LOON et al. 1992, HUMMEL 1993, VAN LOON & HUMMEL 1995).

The second reason is that all the cellulose containing material is assumed to be in the form of paper. Paper has a generally lower degree of polymerisation

than the other cellulose forms (see section 5.4) which implies, according to equations 5 and 6, that a larger fraction of the available cellulose will degrade by the rapid peeling off mechanism i.e. the quantities of ISA released will be greater.

The number of mols of ISA present in the pore waters of the representative 1 m³ repository volume after degradation of all the cellulose which can do so rapidly, is given by the following relation:

$$\frac{I \cdot F \cdot 10^3}{180} \quad \text{mols of ISA} \quad (13)$$

According to Eqn. 12, Chapter 7, the amount of ISA sorbed (mol kg⁻¹) can be described in terms of a Langmuir isotherm and expressed as:

$$\{ISA\}_{\text{sorbed}} = \frac{K_{\text{isa}} \cdot \{ISA\}_{\text{max}} \cdot C_{\text{eq}}}{1 + K_{\text{isa}} \cdot C_{\text{eq}}} \quad \text{mols of ISA kg}^{-1} \quad (14)$$

For an equilibrium concentration of ISA of C_{eq}, the number of mols present in solution after sorption in the pore volume within the 1 m³ representative repository volume is:

$$1 \cdot P \cdot C_{\text{eq}} \cdot 10^3 \quad \text{mols of ISA} \quad (15)$$

A mass balance can now be made in the representative volume to find C_{eq} by equating the number of moles present in the pore water plus the number of moles sorbed with the number of moles of ISA produced, thus:

$$1 \cdot P \cdot C_{\text{eq}} \cdot 10^3 + Z \cdot \frac{K_{\text{isa}} \cdot \{ISA\}_{\text{max}} \cdot C_{\text{eq}}}{1 + K_{\text{isa}} \cdot C_{\text{eq}}} = \frac{I \cdot F \cdot 10^3}{180} \quad (16)$$

The maximum likely equilibrium concentration of ISA in the cement porewater is then given by substituting the following measured values, or conservative estimates, into Eqn. 16.

P = 0.1

Average pore volume fraction in the SMA-4 region of the repository (SUTER 1996a).

$Z = 580 \text{ kg m}^{-3}$	Mass of hardened cement paste (SUTER 1996a).
$I = 60 \text{ kg m}^{-3}$	Average organic matter loading in the SMA-4 region of the repository (SUTER 1996a).
$F = 0.05$	Fraction of organic matter converted to ISA by the rapid peeling off reaction (an average DP value for paper of 1000 was taken).
$K_{\text{isa}} = 690 \text{ L mol}^{-1}$	Langmuir sorption affinity parameter (Table 4).
$\{ISA\}_{\text{max}} = 0.17 \text{ mol kg}^{-1}$	Sorption capacity of hardened cement paste for ISA (Table 4)
Molecular weight ISA = 180	

The result of the above calculation, $\sim 3 \times 10^{-4} \text{ M ISA}$, represents the best (conservative) estimate for the maximum likely ISA equilibrium concentration in the cement pore water. Considering that ~ 16 moles of ISA are potentially available per cubic metre in that part of the repository where the organic loading is highest (SMA-4), the amount finally present at equilibrium in the pore water is quite small. The reason for this is simply that the quantities of cement available are very effective with respect to the uptake of ISA. It should also be remembered that as the ISA migrates from the SMA-4 region through the rest of the repository, it will be retarded and its concentration significantly reduced by further sorption.

9 CEMENT ADDITIVES: ESTIMATE OF THEIR MAXIMUM LIKELY CONCENTRATION IN CEMENT PORE WATERS

There are a large number of different types of organic based compounds added to cement in order to influence its properties. Often the composition of these cement additives is only approximately known. Typical examples of the main organic components of additives are Ca-naphthalene sulphonate, Na-gluconate, melamine sulphonate, lignin sulphonate. Of these different organic ligand types, Na-gluconate was reported by EWART et al. (1991) to have the most significant influence on Pu solubilities.

If we take Na-gluconate (GLU) as being a representative example of the "additives" present in the cementitious materials in the 1 m³ representative volume of the repository, a similar mass balance calculation can be carried out to estimate the equilibrium GLU concentration in the cement pore water. Additives (A) are normally present at the 1 wt. % level with respect to the cement content. This is equivalent to approximately 31 moles of GLU in the representative 1 m³ of repository. Hence the likely concentration of GLU can be estimated using,

$$1 \cdot P \cdot C_{\text{eq}} \cdot 10^3 + Z \cdot \frac{K_{\text{glu}} \cdot \{\text{GLU}\}_{\text{max}} \cdot C_{\text{eq}}}{1 + K_{\text{glu}} \cdot C_{\text{eq}}} = \frac{A \cdot 10^3}{196} \quad (17)$$

and the parameters,

P = 0.1	Average pore volume fraction (SUTER 1996a).
Z = 580 kg m ⁻³	Mass of hardened cement paste (SUTER 1996a).
A = 6 kg m ⁻³	Maximum likely organic additive loading.
K _{glu} = 3360 L mol ⁻¹	Langmuir sorption affinity parameter for GLU (VAN LOON 1996, Pers. Comm.).
{GLU} _{max} = 0.57 mol kg ⁻¹	Sorption capacity of hardened cement paste for GLU (VAN LOON 1996, Pers. Comm.).
Molecular weight GLU = 196	

The calculated equilibrium concentration of GLU in the cement pore water is ~3x10⁻⁵ M.

The high uptake of gluconate by the cement indicated by the Langmuir parameters should not be too surprising since in many cases additives are used to increase the workability of cement or retard the hydration process which implies modifications to the surface properties of the cement particles. These additives are chosen for their effectiveness, which presumably arises from their high affinities for the cement surface.

10 ASSESSMENT OF THE INFLUENCE OF CELLULOSE DEGRADATION PRODUCTS AND CEMENT ADDITIVES ON THE SORPTION ON CEMENTITIOUS MATERIALS

The aim here is to attempt an assessment of the influence of cellulose degradation products (ISA) and cement additives (represented by GLU) on the uptake of radionuclides by the cementitious near-field barriers. The information given in Chapters 4 to 9 will be used together with the results from experimental studies described below. However, it should be recognised that systematic studies carried out under well defined conditions on the sorption of key radionuclides (as a function of concentration) on cementitious materials in the presence of cement additives and degradation products at levels expected under repository conditions are rare. Also, our understanding of the processes taking place is incomplete and needs to be improved in order to be able to draw quantitatively defensible conclusions concerning the effects of "organics" on near-field sorption. Despite the paucity of relevant data, it is still possible to bound the likely effects of ISA and cement additives and give conservative estimates for sorption reduction factors within the appropriate organic ligand concentration regions.

10.1 Cellulose degradation products: isosaccharinic acid

In CEM-94 evidence was presented indicating that the influence of cellulose degradation products on the sorption characteristics of transition metals and heavy metals was considerably less than on tri- and tetravalent radionuclides. There are even results indicating that the sorption of the former may be enhanced in the presence of ISA (EWART et al. 1991). This general observation has been confirmed in some recent work carried out by WIELAND et al. (1997,1998). These authors measured the sorption of several radionuclides on cement suspended in an artificial cement pore water (ACW), and were unable to detect any effects on the sorption of Cs, Sr and Ni on HCP for equilibrium ISA concentrations up to $\sim 10^{-2}$ M and equilibration times in excess of 50 days. The measurements made on the uptake of Eu and Th on HCP are discussed in detail below.

Eu exhibited a very high affinity for HCP surfaces with distribution ratios of $>10^3$ m³ kg⁻¹. Equilibrium concentrations of ISA up to 10^{-4} M produced no

reductions in these sorption values and even raising the levels to 10^{-3} M caused only a minor reduction. In order to observe significant effects on sorption, ISA concentrations of 10^{-1} M were required. At these exceedingly high levels sorption was reduced by about a factor of 100. (See Figure 8.)

The uptake of Th onto HCP was as strong as Eu and sorption values $>10^3$ m^3 kg^{-1} were measured. At ISA concentrations $\leq 10^{-4}$ M no influence on sorption was detected, Figure 9. However, in the equilibrium ISA concentration range $>10^{-4}$ to 10^{-2} M sorption values fell by over four decades. A similar sharp fall in sorption was observed for Eu at ISA concentrations $> 10^{-2}$ M.

It is worth remarking that the sorption values for tri- and tetra-valent metals measured by WIELAND et al. (1997) are orders of magnitude greater than those given in the cement SDB, Table 7, which indicates just how conservative the selected values are for these groups of elements.

The sorption data given in Figures 8 and 9 may be contrasted with those given previously in Figure 2 for Th on feldspar, where a reduction in sorption of only a factor of 10 was observed in the ISA concentration range between 10^{-4} and 10^{-2} M. In section 4.2 we indicated that these data probably represent the maximum effects of ISA complexation on Th sorption whereas WIELAND et al (1997) are measuring considerably greater effects.

One hypothesis proposed to explain this apparent inconsistency is that we are not dealing here with a metal-ISA complexation effect but rather that the ISA, at these high concentrations, is competing with the metal for the same sorption sites i.e. a site competition phenomena. The competitive effect of ISA on Eu sorption on HCP is less effective than in the case of Th since higher concentrations are required before it becomes effective. Further, these results would imply that the binding of tri-valent actinide to the sorption sites on HCP is stronger than tetra-valent actinides and that sorption is occurring on the same site types. This hypothesis will be checked during the course of 1997.

Finally, SAROTT (1996) measured the sorption of Am at $\text{pH}=13.3$ and trace concentrations ($<10^{-12}$ M) in short time tests (a few days) on hardened HTS cement paste in the absence and presence of ISA (10^{-3} M). The sorption in all cases was so high that only a lower bound sorption value of $\sim 10^3$ m^3 kg^{-1} could be given. No adverse effect on sorption due to the presence of ISA could be measured.

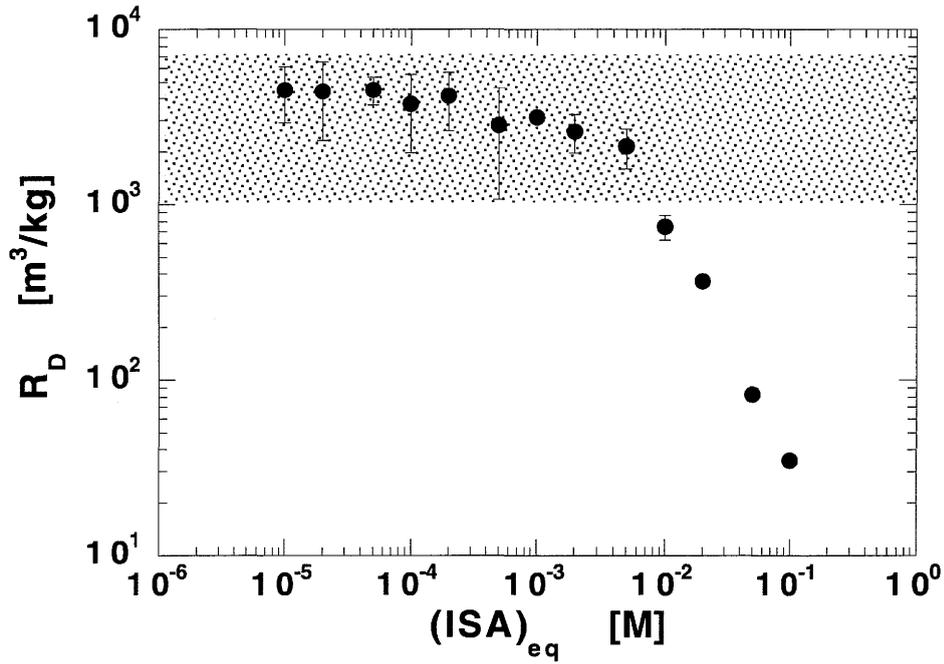


Figure 8: The sorption of Eu-152 on hardened cement paste as a function of the equilibrium concentration of ISA in ACW. (S:L=10 mg L⁻¹, [TOT-Eu] = 1.24E-10 M. Equilibration time=14 days.)

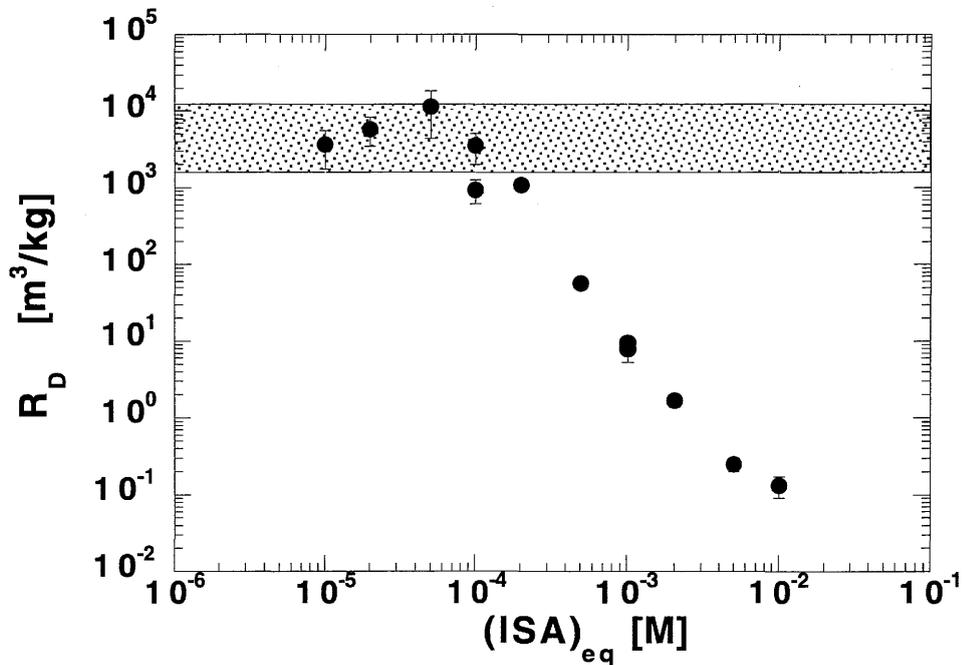


Figure 9: The sorption of Th-234 on hardened cement paste as a function of the equilibrium concentration of ISA in ACW. (S:L=10 mg L⁻¹, [TOT-Th] = 1.0E-10 M, Equilibration time=14 days.)

10.2 Cement additives: gluconate

Where data exist at all, on the influence of cement additives on sorption in a near-field environment, the measurements have almost exclusively been carried out using gluconate (GLU). NORDEN & ALLARD (1994) determined the sorption of Eu on cement at initial GLU concentrations "greater than 10^{-4} M". A decrease in Eu sorption of approximately three orders of magnitude was measured, from an R_d of $\sim 10^2$ m³ kg⁻¹ to an R_d of $\sim 10^1$ m³ kg⁻¹. However, within ~ 200 days the sorption values had fully recovered to their original values.

TITS et al. (1998a) studied the uptake of Cs, Sr, Ni, Eu and Th on amorphous CSH phases at pH ~ 13.3 in the absence and presence of GLU. These authors concluded that there were no adverse effects on sorption for starting concentrations of GLU up to 10^{-4} M.

GLAUS et al. (1995) made up a series of solutions containing 5 g of different commercially available additives in 100 ml of (K,Na)OH saturated with portlandite. (The additives used were Sikament 300™, Sikament 320™, and six others where the main organic components were Pozzoloth, Ca-naphthalin sulphonate, Na-gluconate, melamine sulphonate, SV-polymer and lignin sulphonate.) Samples of these solutions were taken after different times (up to 4 months), filtered (0.45 μ m), labelled with ¹⁵²Eu and used in sorption experiments on feldspar. The initial results indicate that even at these very high levels of 5 g of additive in 100 ml solution, which, in the case of GLU, would be equivalent to a maximum concentration of ~ 0.25 M, the effects on the uptake of Eu were not large, with maximum long term reductions in sorption of approximately one order of magnitude.

10.3 Summary

New information is slowly coming together which indicates that organic ligands present in the near field of a L/IL radioactive waste repository do not have anywhere as severe an influence on sorption as indicated in CEM-94. Particularly important in this respect is cellulose containing material. Although this was already suspected to be the case during the compilation of CEM-94, the difference now is that a weaker organic ligand effect on sorption compared

to that on radionuclide solubilities can be considerably better explained and justified.

One of the most important new developments is that it is now possible to give good estimates of the maximum amount of cellulose, depending on its form, which is likely to degrade in the short term (first few years). Furthermore, from section 5.3, it can be stated that in the first 10^4 to 5×10^4 years in the lifetime of the repository, little significant additional quantities of cellulose are likely to degrade. Only on time scales greater than $\sim 10^5$ years are increases of degradation product concentrations in solution from the cleavage reactions to be expected.

An equally important factor limiting the quantities of organic degradation products in solution is their relatively high sorption on HCP phases. Although the sorption of ISA on cement was postulated in CEM-94, and values deduced indirectly from the open literature data, it was by no means a proven fact, especially for cement/concrete blends of relevance to the Swiss case. It has now been unambiguously demonstrated that ISA and GLU do sorb to a significant extent on cementitious materials.

The combination of the two processes led to estimates for the concentrations of ISA and GLU in cement porewaters of 3×10^{-4} M and 3×10^{-5} M respectively. The concentration of ISA may be regarded as a maximum estimate since it was calculated for the SMA-4 region of the planned repository (see NAGRA 1994) where the solid organic matter loading is at its highest (~ 10 wt %).

Isosaccharinic acid

The available experimental evidence indicates that radionuclides in the alkali and alkali earth groups do not have any significant interaction with ISA and consequently their sorption characteristics remain unaffected by the presence of this organic ligand.

Although transition and heavy metals do form complexes with ISA, experimental measurements in the range of (maximum) ISA concentrations anticipated in the near-field have shown that the effects on sorption are negligible and indeed, increases in sorption have been recorded. Realistically, no reductions in sorption values for these classes of radionuclides would be expected from the degradation products of cellulose throughout the whole repository. Even if ISA concentrations were an order of magnitude higher, still

no influence would be expected on the basis of our current understanding. In the case of Ni for example, ISA concentrations of $>10^{-2}$ M would be required before any effects were seen.

There is however an unresolved question surrounding other highly soluble organic ligands present in paper and wood. (The quantities available depend on the origin/history of these materials.) Preliminary tests with Ni indicate that such organics can reduce the sorption of transition metals in particular. More work is required here, especially with respect to the concentration dependence, estimates of the maximum quantities likely to be available in a repository and their long term stability at high pH. Because of the uncertainty associated with this class of organics we tentatively assign a sorption reduction factor of 10 to transition and heavy metals (Co, Ni, Pd and Pb) in columns SFR and 100 in SRF-10, even though this effect has nothing to do with cellulose degradation products.

The sorption of tri- and tetra-valent radionuclides onto HCP do not appear to be adversely influenced by the presence of ISA at concentrations corresponding to the maximum estimated levels for SMA-4. In the repository regions SMA-1 to SMA-3, where ISA concentrations are unlikely to reach levels anywhere near these estimates, no reduction of sorption due to ISA is expected under realistically conceivable circumstances.

In region SMA-4, where ISA concentrations might conceivably be an order of magnitude higher than the estimated value, the sorption of the trivalent actinides would still most probably remain unaffected. For tetravalent actinides sorption reduction factors as high as 100 could occur, and this value is given in column SRF-10.

The sorption reduction factors resulting from the presence of cellulose degradation products given in Table 8 are based on our current understanding of the system which we know is incomplete. The research programmes are continuing with the aim of elucidating and quantifying the major processes further.

Gluconate

If it is assumed that GLU can be taken as being representative of organic cement additives, then the single most important bound on their influence on radionuclide sorption arises from the very strong uptake by HCP surfaces

which reduces aqueous concentrations to very low levels. The measurements of GLAUS et al. (1995) and TITS et al. (1997, 1998a, 1998b) on tri- and tetravalent radionuclides (Eu and Am/Th respectively) at considerably greater concentrations of GLU than are expected to be present in the repository indicate that sorption reduction factors of 10 for such radionuclides would represent a very conservative estimate.

NORDEN & ALLARD (1994), even though measuring initial reductions in Eu sorption of ~1000, observed a recovery with time to the original value. EWART et al. (1991) report that the sorption of Pu in leachates from cement mixtures containing 0.5-1% additives are not adversely influenced.

If the equilibrium "additive" concentrations are near to those estimated in Chapter 9, then WIELAND et al. (1997), Figures 8 and 9, show that no influence on the sorption of tri- and tetravalent radionuclides would be anticipated. Even for GLU concentrations an order of magnitude higher, ($\sim 3 \times 10^{-4}$ M), there is still no distinct effect on trivalent radionuclides, whereas for tetravalent radionuclides a sorption reduction factor of ~10 is proposed. For all other radionuclides, additives are not expected to influence sorption to any significant degree.

One additional factor which could have an important influence on the effect of degradation products and cement additives on sorption is the long term instability of such ligands at high pH. NORDEN & ALLARD (1994) tentatively suggest the degradation of GLU as one of the possible explanations for the recovery of Eu sorption values as a function of time. On the other hand, GREENFIELD et al. (1995) suggest that further degradation of ISA requires the presence of oxygen and/or microbes and VAN LOON et al. (1996) showed that ISA was stable under alkaline conditions for at least one year.

Although all the available evidence points towards a weak influence of organic cement additives on the sorption of those radionuclides for which the effects might be expected to be the largest, it must be recognised that the experimental basis is relatively weak, and that "additives" are present wherever cement/concrete is used.

11 OTHER ORGANIC AND INORGANIC COMPONENTS IN THE WASTE

There are many different types of organic ligands present in a low and intermediate level radioactive waste repository. They range from decontamination agents such as EDTA, DTPA etc. to the degradation products from polymers, bitumen (predominantly oxalic acid), cation exchange resins (also predominantly oxalic acid), anion exchange resins (amines), cellulose (isosaccharinic acid) through to cement additives such as Na-gluconate.

It was concluded in CEM 94 that, in comparison with cellulose degradation products and organic cement additives, the other "organics" did not have any significant adverse influences on radionuclide sorption under near field conditions (see Chapter 7 in CEM-94). The same was also true for the inorganic waste components. (see Chapter 8 in CEM-94). The reason for this lays in the overwhelming effect of the cellulose degradation products and additives on radionuclide uptake estimated on the basis of the existent data, which were then available.

The new information available, described and discussed above, suggests a much weaker influence. In the light of this it is necessary to look again at the other organic and inorganic materials in the repository.

11.1 Bitumen and Ion Exchange Resins

In CEM-94 it was concluded that the degradation products from these two classes of solids did not have any significant influence on the sorption of radionuclides on cementitious materials. In the intervening time no additional information has become available which would alter this conclusion.

11.2 Low Molecular Weight Organics

This category includes organic ligands such as NTA, EDTA, DTPA; oxalic, citric and tartaric acids; alkyl sulphonic acids and substituted phenols. Of these, EDTA is the most abundant and one of the strongest complexing decontamination agents present. Speciation calculations under representative

repository conditions indicated that the only safety relevant radionuclide likely to be influenced was Ni. This was only the case when the free concentration of EDTA was well in excess of 10^{-3} M (see Tables 10 and 11 in CEM 94).

According to ALDER & McGINNES (1994), decontamination agents, all taken here to be EDTA, are only present in regions SMA-2 and SMA-4 of the repository. The inventories are given in Table 5. From the average pore volumes in each of these regions (SUTER 1996b) the corresponding concentrations of Na-EDTA can be calculated assuming that the Na-EDTA is non sorbing and that it all goes into solution. As can be seen from Table 5, the concentrations are potentially high. In SMA-4 the effect is marginal, but at the EDTA levels estimated for region SMA-2 significant complexation of Ni (and chemically analogous metals) may occur (see Table 11, CEM-94). Since no data on the sorption of Ni on cement at high pH in the presence of EDTA could be found, a sorption reduction factor of 50 is taken for Ni and chemical analogues in region SMA-2. Pb forms weaker complexes with EDTA and a sorption reduction factor of 5 is selected.

Note that in Table 8, where the origin of the sorption reduction factor is EDTA, the values given in columns SRF and SRF-10 are the same. The reason for this is the assumption made above of taking the whole decontamination agent inventory to be EDTA.

Table 5: Estimated maximum EDTA concentrations in SMA-2 and SMA-4.

	SMA-1	SMA-2	SMA-3	SMA-4
Averaged Pore Volume (m ³)	6131	1958	2134	5401
Decontamination agents (All taken as EDTA) (kg)	NP	2.7 E4	NP	8.9 E3
EDTA Concentration (M)	-	~4.6 E-2	-	~5.5 E-3

NP: Not Present

11.3 High Molecular Weight Organics

Practically all of the work on the influence of the alkaline degradation products from "high molecular weight organics" on the solubilities and sorption of actinides under the near-field conditions in a cementitious repository has been carried out at AEA Technology and is consequently the only source of such data.

In the tests described by GREENFIELD et al. (1994), degradation was generally carried out anaerobically at 80 °C in the presence of water and crushed cement with a ~10% loading of organic material for times up to 500 days. In addition, alpha irradiation tests under alkaline conditions (pH 11.8 to 12.4) were performed for times up to 8 years which resulted in nominal doses of $\sim 5.5 \times 10^8$ Gy.

The findings of these extensive investigations may be briefly summarised by noting that for degradation under alkaline conditions alone, increases in Pu solubilities by (at most) a factor of 10 (for PVC) were observed. (Other polymer materials exhibited a much weaker effect and for comparison, cellulosic solids, discussed earlier, caused solubility increases by factors of up to 10^7 .) Thus the effect of high molecular weight organics appears to be orders of magnitude less than cellulosic materials. At first sight this appears re-assuring but as GREENFIELD et al. (1994) point out "*.....the failure to observe any significant effectsmay be due to slow rates of degradation*". It is worth mentioning in this context that the experimental conditions are estimated to be equivalent to 50 to 100 years under repository conditions, so the degradation kinetics must be really slow if the lack of an effect is attributed to this reason.

The alpha irradiation tests were meant to address the kinetics issue, though there is no guarantee that the degradation products are the same. Again the results presented for a very wide range of organic materials¹ indicate effects on Pu solubilities which are many orders of magnitude less than cellulosic compounds. (The doses delivered in these tests are orders of magnitude higher than any expected in a Swiss L/IL waste repository.)

Most of the work described by GREENFIELD et al. (1994) was carried out at 10% loadings and it is instructive to estimate what "polymer loadings" are

¹ Polythene, neoprene, white hyperlon, polystyrene, polypropylene, polymethylpentene, polycarbonate, latex, nylon, polytetrafluorethylene, polymethylmethacrylate, polyvinylchloride.

expected in the repository regions SMA-1 to SMA-3. This is done in Table 6. Note that SMA-4 has already been dealt with in Chapter 8 since all the organic material there was assumed conservatively to be cellulosic. The polymer inventory data was taken from ALDER & McGUINNES (1994), and data on the quantities of hardened cement paste in the different repository regions was provided by SUTER (1996b). In all cases the polymer loadings in SMA-1 to SMA-3 are considerably less than the 10% value used in the experiments. In the case of region SMA-1 the loading is a factor of ~30 less.

Table 6: Estimated polymer loadings in SMA-1 to SMA-3.

	SMA-1	SMA-2	SMA-3
Hardened Cement Paste (kg)	63.8 E6	20.4 E6	22.2 E6
"Polymers" (kg)	2.1 E5	3.0 E5	7.4 E5
Polymer loading (%)	0.3%	1.5%	3%

On the basis of the above information and discussions we would conclude that the balance of evidence indicates that no adverse effects of "high molecular weight organics" over and above those estimated for cellulosic materials and cement additives for all parts of the repository are to be expected. However, it has to be said that we could not find any direct measurements of the influence of the degradation products from polymer materials on the sorption of key safety relevant radionuclides on cementitious materials.

11.4 Inorganic Waste Components

Radioactive waste contains inorganic salts, and these will dissolve to a greater or lesser extent giving rise to ligands such as CO_3 , NO_3 , SO_4 , S, PO_4 , CN, $\text{B}(\text{OH})_4$, F, I, Cl, Br in solution. Speciation calculations for cement pore waters at pH values in excess of 12.5, and the application of a data evaluation methodology similar to that described in HUMMEL (1993), led to the conclusion that only cyanide complexes of Ni, Ag and Pb are likely to be of any significance (see Chapter 8, CEM 94) under repository conditions.

The only source of cyanide in the repository is "Prussian Blue" (iron cyanide) in region SMA-4 at an inventory of approximately 4000 kg total. (McGUINNES pers. comm. 1996). Under ambient conditions this decontaminant agent is a chemically inert, sparingly soluble, non-toxic solid. However, at high pH all forms of Prussian Blue are readily soluble (MEEUSSEN et al. 1992a) and any complexed radionuclide will be released into solution together with the hexacyanoferrate anion, $[\text{Fe}(\text{CN})_6]^{4-}$. Although this anion is expected to be very mobile, because of its high negative charge, it forms only weak complexes with metal cations which makes it irrelevant from a performance assessment point of view.

Kinetic measurements (MEEUSSEN et al. 1992b) have indicated that at pH values in excess of 8 the hexacyanoferrate anion is indefinitely stable provided light is excluded. UV irradiation, and even diffuse daylight, cause the rapid (in the order of days) photo decomposition of $[\text{Fe}(\text{CN})_6]^{4-}$ with the release of free cyanide which forms very strong complexes with Ni, Ag and Pd cations.

The influence of Prussian Blue depends critically on the stability of $[\text{Fe}(\text{CN})_6]^{4-}$ under repository conditions. Whether the gamma radiation fields present will have a similar effect to UV light, or whether the higher gamma energies lead to radiolysis products other than CN which have less complexing strength, is currently not known. Under these circumstances it would seem prudent to carry out some specific scoping stability tests on Prussian Blue if the more detailed review planned by HUMMEL (1997) confirms the uncertainties mentioned above.

12 **SORPTION SUMMARY TABLES**

Based on the information and discussions given in sections 5.2.1 to 5.2.14 in CEM-94, and Chapter 3 in this report, an updated summary of distribution ratios for safety relevant radionuclides as a function of cement degradation (sections 4.3 and 5.1, CEM-94) and redox (section 4.2, CEM-94) for an "UNPERTURBED" repository is presented in Table 7.

In Table 8, an element by element listing of sorption reduction factors appropriate to each of the four waste categories is given. These estimates are based on the information and discussions given in Chapters 4 to 11. Two values are given for each element. The first set of sorption reduction factors (SRFs) are based on the maximum likely concentrations of cellulose degradation products, organic cement additives and EDTA in the different sections of the repository discussed in Chapters 8, 9 and 11. These SRFs represent "best conservative estimates". The second set of values headed SRF-10, correspond to organic ligand concentrations approximately one order of magnitude greater. Concentrations at these levels are not expected at all in the repository and as such the SRF-10s given represent upper bound values.

In SMA-4 the cellulose degradation products will determine the sorption reduction factors whereas for SMA-1, SMA-2 and SMA-3, organic cement additives are probably more important due to the lower cellulose loadings in these waste categories. The values given for Ni, Co, Pd, and Pb in SMA-2 are determined by EDTA.

Table 7: Sorption data base for unperturbed cementitious material (CEM-94, Update 1, June 1997).

Element	State of Cement Degradation					
	#Region I		#Region II		#Region III	
	Oxid.	Red.	Oxid.	Red.	Oxid.	Red.
H (HTO)	0	0	0	0	0	0
CO ₃ ²⁻	see section 5.2.7 CEM-94					
Cl	5·10 ⁻³	5·10 ⁻³	5·10 ⁻³	5·10 ⁻³	5·10 ⁻⁴	5·10 ⁻⁴
K	0	0	10 ⁻⁴	10 ⁻⁴	10 ⁻⁴	10 ⁻⁴
Co	10 ⁻¹	10 ⁻¹	10 ⁻¹	10 ⁻¹	10 ⁻²	10 ⁻²
Ni	10 ⁻¹	10 ⁻¹	10 ⁻¹	10 ⁻¹	10 ⁻²	10 ⁻²
Se	0	0	0	0	0	0
Sr	10 ⁻³	10 ⁻³	10 ⁻³	10 ⁻³	10 ⁻³	10 ⁻³
Zr	5	5	5	5	1	1
Nb	1	1	1	1	10 ⁻¹	10 ⁻¹
Mo	0	0	0	0	0	0
Tc	10 ⁻³	1	10 ⁻³	1	0	10 ⁻¹
Pd	10 ⁻¹	10 ⁻¹	10 ⁻¹	10 ⁻¹	10 ⁻²	10 ⁻²
Ag(NaCl)	0	0	0	0	0	0
Ag(NaHCO ₃)	10 ⁻³	10 ⁻³	10 ⁻³	10 ⁻³	10 ⁻³	10 ⁻³
Sn	1	1	1	1	10 ⁻¹	10 ⁻¹
I	10 ⁻²	10 ⁻²	10 ⁻²	10 ⁻²	10 ⁻³	10 ⁻³
Cs	2·10 ⁻³	2·10 ⁻³	2·10 ⁻²	2·10 ⁻²	2·10 ⁻²	2·10 ⁻²
Pb	5·10 ⁻¹	5·10 ⁻¹	5·10 ⁻¹	5·10 ⁻¹	5·10 ⁻²	5·10 ⁻²
Po	0	0	0	0	0	0
Ra	5·10 ⁻²	5·10 ⁻²	5·10 ⁻²	5·10 ⁻²	5·10 ⁻²	5·10 ⁻²
Ac	1	1	1	1	2·10 ⁻¹	2·10 ⁻¹
Th	5	5	5	5	1	1
Pa	5	5	5	5	10 ⁻¹	1
U	2	5	2	5	10 ⁻¹	1
Np	5	5	5	5	10 ⁻¹	1
Pu	5	5	5	5	1	1
Am	1	1	1	1	2·10 ⁻¹	2·10 ⁻¹
Cm	1	1	1	1	2·10 ⁻¹	2·10 ⁻¹

#: Definitions of regions I, II and III are given in CEM-94, section 4.3.

Elements are listed according to increasing atomic number. All distribution ratios are in units of m³ kg⁻¹. Data selection procedures are described in CEM-94, Chapter 5, and here in Chapter 3.

Table 8: Sorption reduction factors for safety relevant radionuclides in the presence of cellulose degradation products, cement additives and EDTA (CEM-94, Update 1, June 1997).

Element	*Sorption Reduction Factors							
	SMA-1		SMA-2		SMA-3		SMA-4	
	SRF	SRF-10	SRF	SRF-10	SRF	SRF-10	SRF	SRF-10
H(HTO)	1	1	1	1	1	1	1	1
Cl	1	1	1	1	1	1	1	1
Co	1	1	<u>50</u>	<u>50</u>	1	1	<10>	<100>
Ni	1	1	<u>50</u>	<u>50</u>	1	1	<10>	<100>
Se	1	1	1	1	1	1	1	1
Sr	1	1	1	1	1	1	1	1
Zr	1	10	1	10	1	10	1	100
Nb	1	1	1	1	1	1	1	10
Mo	1	1	1	1	1	1	1	1
Tc	1	1	1	1	1	1	1	10
Pd	1	1	<u>50</u>	<u>50</u>	1	1	<10>	<100>
Ag	1	1	1	1	1	1	1	1
Sn	1	1	1	1	1	1	1	10
I	1	1	1	1	1	1	1	1
Cs	1	1	1	1	1	1	1	1
Pb	1	1	<u>5</u>	<u>5</u>	1	1	<10>	<100>
Po	1	1	1	1	1	1	1	1
Ra	1	1	1	1	1	1	1	1
Ac	1	1	1	1	1	1	1	1
Th	1	10	1	10	1	10	1	100
Pa	1	10	1	10	1	10	1	100
U	1	10	1	10	1	10	1	100
Np	1	10	1	10	1	10	1	100
Pu	1	10	1	10	1	10	1	100
Am	1	1	1	1	1	1	1	1
Cm	1	1	1	1	1	1	1	1

*The reduction factors are assumed to be valid for both reducing and oxidising conditions and at all stages of the cement degradation.

The sorption of ^{14}C in the form of $^{14}\text{CO}_3$ is not influenced by organic ligands.

Origin of the sorption reduction factors: Values given in **bold type** arise from the influence of cellulose degradation products, those given in **bold italics** from cement additives, those given in **bold type underlined** from EDTA, and those given as **<bold type>** from the unknown and readily soluble organic ligand in wood and paper, see section 10.3.

13 AGGREGATE MATERIAL AND IRON OXIDES

Performance assessment studies of the near-field have focused on the retention characteristics of hardened cement paste. However, there are a number of other materials present, in massive quantities, whose sorption properties do not appear in any sorption data base and for which no credit has been taken in earlier safety studies. Their contribution has been largely ignored without making any serious attempts to assess their significance. The potentially most important of such materials are the vast quantities of limestone and quartz aggregates in the cementitious liners, backfill and containers; and the large amounts of iron and steel (approximately sixty thousand tonnes) from drums and reactor decommissioning, which will corrode to iron oxides during the lifetime of the repository.

As will become apparent, there is a general lack of sorption measurements made under the relevant conditions for the above mentioned materials. Therefore, the aim here is not so much to provide quantitative data but rather to start the process of assessing the relevance of these materials and thereby begin the process of integrating them into the safety assessment of the near field.

13.1 Limestone / Calcite

Limestone aggregate is a possible component in near-field concrete blends and might also be considered as an alternative to the quartz grains in the "monokorn" back fill. The major component of limestone is calcite and the following discussions will centre on studies carried out on this mineral.

Calcite is stable in the hyperalkaline environment of the near-field due to its low solubility at high pH, the presence of portlandite and the calcite saturated groundwaters in the host rock. Once emplaced within the repository it is likely to remain there indefinitely.

The general sorption properties of calcite have been discussed by BRADBURY & BAEYENS (1997a) and what is known of its sorption properties at high pH described and assessed in BRADBURY & BAEYENS (1997b). The findings can be summarised as follows. Laboratory sorption data usually apply to crushed materials and therefore they often need to be modified to account

for the reduced sorption areas available in the intact material in situ. This so called lab-to-field transfer factor for calcite has an estimated value of ~20 (see BRADBURY & BAEYENS 1997a, Chapter 8) i.e. laboratory sorption data have to be reduced by a factor of 20 to provide the values appropriate in situ sorption values.

Cs

Based on the investigations of TITS et al. (1998b) for Cs concentrations in the range 10^{-6} to 10^{-10} M, Cs is considered to be non sorbing at high pH values.

Sr and Ra

Although there are clear indications in the work of ZACHARA et al.(1991) that Sr sorption increases with increasing pH (a value of $\sim 0.05 \text{ m}^3 \text{ kg}^{-1}$ was measured at the highest pH of ~ 9.5), TITS et al. (1998b) were not able to detect any evidence of sorption at pH=13.3. We must therefore assume that Sr (and Ra as its chemical analogue) is not taken up by calcite under near field conditions.

Ni, Co, Pd, Pb

ZACHARA et al. (1991) measured the sorption of the transition metals Ni, Mn, Zn, Co and Cd as a function of pH up to ~ 9.5 . The trend in the data was of either increasing sorption with pH or constant high sorption at pH values in the range of 8-9.5. The exception was Co, which showed a down turn in sorption above a pH of ~ 8.5 , possibly due to the formation of negatively charged carbonato complexes.

Relatively low sorption values of $\sim 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ have been measured by TITS et al. (1998a) for Ni on CaCO_3 at a pH of 13.3. These data could be compatible with those from ZACHARA et al. (1991) if other transition metals behave similarly to Co, but at a higher pH. Hyperalkaline conditions could then lead to a significant reduction in sorption through the formation of negatively charged hydroxy or carbonato complexes for example. However, whatever the reason is for the low Ni sorption, we must take the distribution ratio of TITS et al. (1998b) and, by chemical analogy, give the same value to the other metals in this grouping. If the lab-to-field transfer factor of ~ 20 is applied then this yields a calculated value of $\sim 5 \times 10^{-5} \text{ m}^3 \text{ kg}^{-1}$, i.e. effectively zero sorption.

Tc, Ag

No sorption data could be found for Tc and Ag on calcite. Under these circumstances R_d is set to zero for both radionuclides.

Po

No sorption data for Po on calcite could be found. The R_d value for Po was set to zero.

Trivalent Actinides: Ac, Am, Cm

Although the uptake mechanism of Am on CaCO_3 is uncertain, CaCO_3 appears to be extremely efficient at removing this trivalent actinide from solution.

BEALL & ALLARD (1981) give R_d values for Am on calcite and dolomite (pH 7 to 9) in the range 10 to 50 $\text{m}^3 \text{kg}^{-1}$. The trend in the data was one of increasing sorption with increasing pH. TITS et al. (1997) measured the sorption of Am on synthetic CaCO_3 in the pH range 11 to 13.3. No pH dependency was observed and sorption values were in all cases higher than 100 $\text{m}^3 \text{kg}^{-1}$. Similar results were also measured for the trivalent lanthanide, Eu. Taking into account the lab-to-field conversion factor of 20, these data still indicate sorption values in excess of 5 $\text{m}^3 \text{kg}^{-1}$.

Tetravalent actinides: Th, U, Np, Pu plus Zr

The only data available for the sorption of tetravalent actinides on calcite at elevated pH are those for Th on CaCO_3 (TITS et al. 1998b). Again the sorption values at trace Th concentrations ($\sim 10^{-11}$ M) at pH \sim 13.3 are high, $>10 \text{ m}^3 \text{kg}^{-1}$, which would represent an in situ value for massive calcite of $\sim 1 \text{ m}^3 \text{kg}^{-1}$.

Pa(V)

For Pa(V) we follow the practice described in BRADBURY & BAEYENS (1997b) and take Np(V) as chemical analogue. The same sorption value of 0.1 $\text{m}^3 \text{kg}^{-1}$ for Pa(V) is selected.

Anionic Species: Cl, I, Se, Mo, Nb, Sn

In common with many other mineral systems, the tendency is for anions to sorb less on CaCO_3 as the pH increases (see for example the work of COWAN et al. (1990) for Se). Given also the fact that we could not find any sorption values

for the anions I, Cl, Se, Mo, Nb and Sn on calcite under the appropriate conditions, there is no choice but to assume that they are non-sorbing. Note that Sn is included in this grouping because it is taken to be present as the stannate anion, SnO_3^{2-} .

13.2 Limestone: Concluding Remarks

Most of the sorption measurements on calcite systems have been performed at pH values below 10. A number of different nuclide uptake mechanisms have been suggested (BRADBURY & BAEYENS 1997a in Chapter 6) but at the moment there is no general consensus. Indeed, it appears likely that the removal process from solution may be nuclide and conditions dependent. For this reason "extrapolating mechanisms" to hyperalkaline environments is probably not justifiable given our present state of understanding. Despite the lack of data and mechanistic understanding it is still possible to make some general comments regarding the potential contribution of calcite to the retention of radionuclides in the near-field, $\text{pH} > 12.5$.

1. Alkaline metals most probably do not sorb on calcite
2. Likewise, alkaline earth metals (including Ra) are not sorbed.
3. Transition metals are only taken up to a very limited extent by calcite, so that under in situ conditions the sorption is negligible.
4. Anions such as Cl and I, and the metals Se, Mo, Nb and Sn, predominantly present as anionic oxy species are unlikely to sorb on calcite.
5. The uptake of trivalent lanthanides and actinides on calcite appears to be very strong so that even taking into account a lab-to-field transfer factor of 20, distribution ratios of the order of $5 \text{ m}^3 \text{ kg}^{-1}$ are to be expected.
6. If other tetravalent actinides behave similarly to Th, then in situ sorption values around $1 \text{ m}^3 \text{ kg}^{-1}$ are to be anticipated.
7. Chemical analogy with Np(V) led to a selected sorption value for Pa(V) of $0.1 \text{ m}^3 \text{ kg}^{-1}$. (See BRADBURY & BAEYENS 1997b).

Note: A sorption data base for calcite at pH values greater than 11 is given in BRADBURY & BAEYENS (1997b). This data set would be the most

appropriate one available, in case that the contribution of calcite (within the repository) to the overall retention in the near field need to be considered.

A final point worth mentioning here is that the sorption data from laboratory experiments on pure calcite at high pH may not be entirely appropriate for real calcite systems under the same conditions. Natural calcite is seldom pure and often contains quartz, or there may be another source of silica somewhere in the system. Under hyperalkaline conditions this combination may lead to the formation of amorphous calcium silicate hydrates or similar phases. CSH phases sorb most safety relevant radionuclides strongly. In addition to sorption, the formation of secondary phases in the near-field may lead to the removal of radionuclides through processes such as incorporation into the freshly precipitated phases and co-precipitation. Such removal mechanisms and the sorption on new CSH phases have the potential of being significantly more important than any radionuclide uptake processes on calcite itself, particularly with respect to alkaline, alkaline earth and transition metals. Thus, what may be important here is not the physical presence of calcite (or quartz) per se but rather continuous and high enough aqueous concentrations of Ca and silica species to cause the precipitation kinetics of secondary minerals to be rapid.

13.3 Quartz

The proposed "monokorn" backfill material contains mm sized grains comprising mainly of quartz which are surrounded and held together by layers of hardened cement paste. In contrast to calcite, quartz is very soluble at the pH values expected in the near field for at least the first few hundred thousand years after closure. As long as the surface coating of hardened cement paste remains intact, and the quartz grains are shielded from the hyperalkaline solutions, no adverse effects would be anticipated. However, damage to or local degradation of the protecting cement layer could result in rapid dissolution of the exposed quartz surfaces and large quantities of silica being released into solution. EIKENBERG (1990) has addressed the question of silica solubility at high pH. The solubility of quartz can reach values in excess of 0.1 mol Si per litre at pH values >12.5 where low molecular weight polynuclear species and (Na,K)-Si-complexes are likely to dominate the

aqueous speciation. Whether and to what extent Si colloids form is not addressed in EIKENBERG (1990).

Quartz can only make a contribution to sorption when its surfaces become accessible to radionuclides i.e. when the layer of hardened cement paste is no longer present. As mentioned above, once this occurs at pH values above 12.5 relatively rapid dissolution follows (SCHWARTZENTRUBER et al. 1987, KNAUS & WOLERY 1987). Whether it is possible to talk of sorption when quartz surfaces are in such a dynamic state of change is an open question.

There is little information available on radionuclide uptake on quartz at elevated pH. ALLARD et al (1983) found that the "sorption" of Th(IV) and Pa(V) was high ($\sim 5 \text{ m}^3 \text{ kg}^{-1}$) and remained relatively constant from pH 10 to 13. The sorption of Am(III) was moderate at pH=10 ($\sim 0.5 \text{ m}^3 \text{ kg}^{-1}$) reducing to $\sim 0.1 \text{ m}^3 \text{ kg}^{-1}$ at pH~13. U(VI) was generally weak over the above pH range, $< 0.01 \text{ m}^3 \text{ kg}^{-1}$.

The accessible porosity in quartz is low. If a lab-to-field transfer factor similar to that for calcite is assumed (~ 20), then a relatively small contribution from quartz to the overall sorption of trivalent actinides may be expected $R_d(\text{Ac-III}) \sim 0.01 \text{ m}^3 \text{ kg}^{-1}$. Tetravalent actinides sorb more strongly with a likely R_d of $\sim 0.1 \text{ m}^3 \text{ kg}^{-1}$.

No other sorption data on quartz in the appropriate pH range could be found for other safety relevant radionuclides.

13.4 Quartz: Concluding Remarks

The general lack of sorption measurements at pH>10 makes it difficult to assess the contribution quartz might make to the overall retention of radionuclides in the near-field. It is doubtful whether sorption mechanisms and models developed for lower pH ranges are appropriate at pHs of interest here particularly because of the abrupt and strong increase in quartz solubility at pH>10 which leads to rapid changes in the state of the surface. More information is clearly necessary to quantify the rôle played by this aggregate material. However, from the little data which is available it is to be expected that the sorption of alkaline/alkaline earth metals is either very weak or zero, transition metals probably sorb only weakly and anionic species not at all. The

uptake of trivalent actinides is probably weak and only the tetravalent actinides are likely to exhibit significant sorption.

The possibility of the formation of Si-colloids and their potential impact on radionuclide transport through the repository remains an open question. If there is a problem then it is only likely to be relevant for tetra-valent actinides judging by the sorption properties of quartz.

Finally, the same might be said of quartz as was said above for calcite, i.e. what may be important here is not the physical presence of quartz per se but rather the aqueous phase reactions between Si-species and Ca to form calcium-silicate-hydrate phases as secondary minerals. Radionuclide sorption onto and incorporation into CSH phases is likely to be more significant generally than any direct uptake by quartz.

13.5 Iron Oxides

The planned L/IL waste repository at Wellenberg is estimated to contain approximately 6×10^7 kg of iron/steel mainly from drums and the decommissioning of nuclear power plants. Under the pH, E_h and temperature conditions existing in a re-saturated repository the most likely steel corrosion product is goethite, $\alpha\text{-FeOOH}$. Goethite most probably forms via a relatively rapid transformation of an amorphous ferrihydrite phase. However, the stability of the latter is sensitive to local water chemistry conditions, e.g. see SCHWERTMANN & MURAD (1983).

Iron oxide phases could be influential in controlling the concentration of radionuclides in the cement pore water fluid via a number of processes such as surface sorption, incorporation into the oxide lattice, co-precipitation and surface precipitation. These processes are not necessarily distinct from one another but may be coupled. For example, sorption may be a necessary precursor to the substitution of a lattice Fe^{3+} cation by a radionuclide. Or, in a system where iron oxides are precipitating, sorbed radionuclides may be trapped within the oxide by further precipitation.

The potential of iron oxide phases to retard radionuclide migration under near and far field conditions was reviewed and assessed by GILLESPIE in 1992. In most respects this work is still "state of the art" and only the most important

points or additional points will be mentioned here. Where further details or additional references are required the original report is recommended.

Activation products in the steels and crud are the primary source of the radioisotopes of Ni, Mo, Nb and Co in the repository. The only conceivable way in which these radionuclides can be released from the steels is via corrosion. The corollary to this is that the maximum possible release rate may be strongly coupled to the corrosion rate. The formation of Fe-oxides could play a particularly important rôle in retarding the transport of these radionuclides through the near field because they are locally present at all places where corrosion is occurring. The implication is that incorporation into the goethite structure by isomorphous substitution of the central octahedral Fe³⁺ cation may be a very effective removal mechanism. Numerous authors have experimentally demonstrated this process to occur, see for example the studies of GERTH (1990) and CORNELL (1991) on the incorporation of Co, Ni, Cu, Zn, Cd and Mn, Ni, Co respectively. It has also been shown that Al (e.g. SCHULZ 1984) Cr (SCHWERTMANN et al. 1989), Ge (BERNSTEIN & WAYCHUNAS 1987), and Ti (FITZPATRICK et al. 1978) can isomorphously substitute Fe³⁺.

In contrast to GILLESPIE (1992), it appears to us that incorporation of Ni and Co, especially, into the forming Fe-oxides may possibly be more important than sorption onto them or indeed sorption onto cementitious phases. The same could also be true for Nb and Mo, though we were unable to find any direct experimental evidence to support this.

We can say little about the sorption potential of goethite for safety relevant radionuclides under hyperalkaline conditions since we could not find any relevant data. Such measurements are obviously needed if an assessment of the contribution of Fe-oxides to near-field radionuclide retention is considered to be important. Also in this context, iron corrosion products may be potential sources of colloids in the near field, which is a further reason why the sorption characteristics of Fe-oxides may have implications for repository safety.

1 4 RECRYSTALLISATION OF CSH GELS AND CARBONATION

Chapters 9 to 11 in CEM-94 covered the topics of recrystallisation of CSH gel, carbonation, and steel corrosion products respectively. Since mid 1994 no additional information has become available which would require any significant revision to what was written then. The one exception to this concerns carbonation. The gradual conversion of portlandite to calcite predicted from the cement degradation model was stated to have negative consequences for radionuclide sorption in the near-field. However, the measurements of TITS et al. (1997, 1998b), indicate that the uptake of actinides on calcite at high pH is very strong. Further, there is the possibility of radionuclides being removed from solution via coprecipitation with calcite (CURTI, 1997).

15 COLLOIDS

Even though no really new information on the question of colloids in cementitious materials has emerged since mid 1994 (see GARDINER & SWANTON 1994), this topic is listed separately in this update of CEM-94 because of its potential importance. Colloids have been viewed as being "potentially important" since the early eighties and in the second half of the nineties they are still classed as being "potentially important", which reflects the general lack of progress made in this area.

The procedure described in CEM-94, Chapter 12, for bounding estimates of the potential influence of near field colloids on radionuclide transport still appears to be a reasonable one and no real improvement on this approach has evolved since. Essential data such as colloid size distributions, types and masses of materials present as colloids and their sorption characteristics are still missing. A programme of work was started at PSI towards the end of 1994 with the aim of quantifying these parameters for the specific cementitious materials in the Swiss repository concept. Also important in this context are questions such as generation mechanisms, colloid stability and, in particular, the reversibility of radionuclide uptake. Whether sorption is reversible or not is one of the crucial unknowns at the present time.

Finally, since the alkaline degradation of organic materials present in the waste will be taking place in the repository, the consequences of the presence of soluble organic ligands on all aspects of colloid behaviour must be taken into consideration. The influence of these degradation products may not only be confined to effects arising from their aqueous phase complexation characteristics, but may be much broader. If, as is strongly suspected, they can sorb onto or form a surface layer on existing colloids, then colloid size, stability, generation mechanisms and surface sorption characteristics may all be affected. This is an area where little or nothing is known. Organic ligand-colloid interaction is part of the PSI experimental programme mentioned above.

1 6 INCORPORATION OF RADIONUCLIDES INTO CSH PHASES DURING CEMENT HYDRATION

The generally good retention characteristics in a cement based repository have mainly been attributed to the sorption of radionuclides onto hardened cement paste, quantified in innumerable batch sorption type tests. However, the effectiveness of the near field barriers to the migration of radionuclides may not be predominantly just a question of sorption, but rather may have strong connections with what is happening during the cement paste hydration process. If the radionuclides are present in the cement pore waters during hydration, which may last many tens of years, then there is the possibility of them being incorporated into the structure of the minerals being formed. Indeed, even after the cement has hardened and surface sorption reactions are the major "short term" removal mechanisms, these may only be precursor reactions to further processes involving the chemical incorporation of the radionuclides into one or more of the hardened cement paste phases. Despite the fact that "chemical incorporation" is sometimes mentioned in connection with potential radionuclide removal mechanisms, the bulk of the research effort has been directed to sorption measurements in batch type tests on hardened cement paste and cured concretes. There is an increasing body of evidence, arising predominantly from outside the radioactive waste community, which is suggesting that chemical incorporation reactions, either during hydration or as a subsequent reaction to surface sorption, is an important removal mechanism for many metal ions. Although most of the published results are for transition and heavy metals, with nothing on trivalent metals and actinides, it is reasonable to believe that these too will take part in chemical incorporation processes. Some examples of the sort of data available on this topic are given below. These examples are only meant to illustrate a point, and the list is certainly not meant to be a comprehensive one.

In an interesting overview paper, COCKE & MOLLAH (1993) summarise the uptake processes for Hg, Pb, Cd, Zn, Cr and Ba on hardened cement paste in the form of a diagram which is reproduced below, Figure 10.

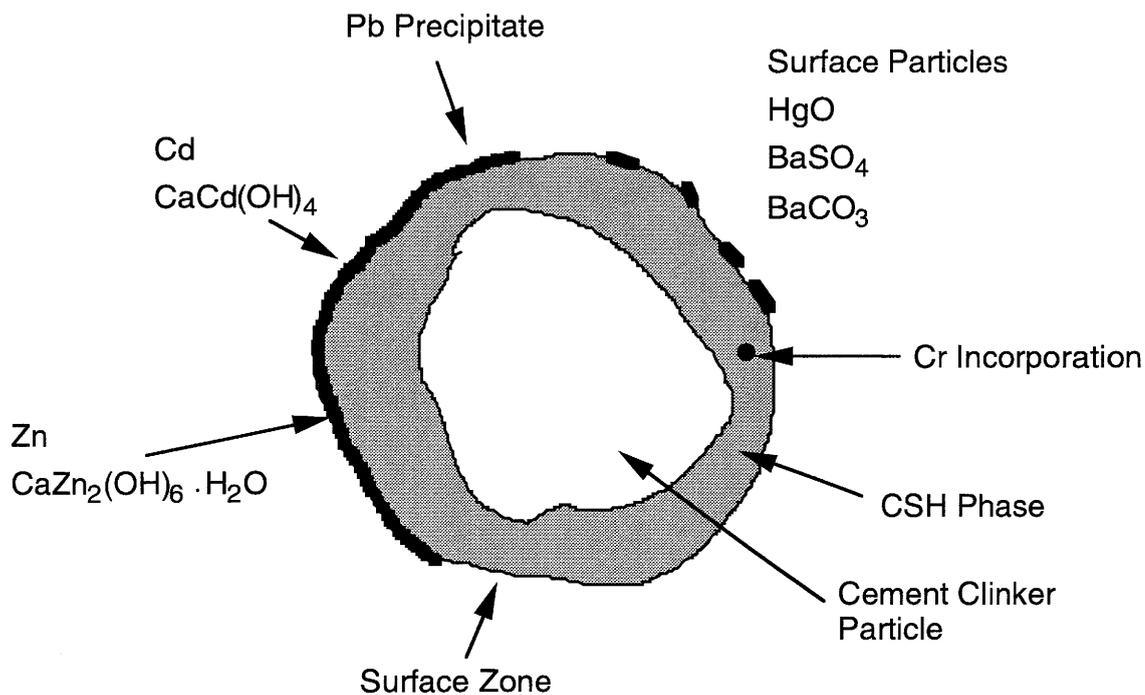


Figure 10: A summary of models for the interaction of metal pollutants with cement (Figure 8-31 in COCKE & MOLLAH 1993).

BAUMBAUER (1992) in his paper talks of "Speicherminerale" (storage minerals) i.e. minerals which are capable of incorporating heavy metals and certain anions into their structures during their formation. As examples he gives the incorporation of Cl and Fe, Cr, Mn, Co, Ni, Zn, Pb, As, Cd in ettringite and/or monosulphate phases (Note: the uptake of anions such as Cl⁻ and I may be predominantly by chemical incorporation and not sorption, and consequently require long reaction times. Batch sorption tests are normally only carried out for short times).

Other interesting work in this area can be found in COCKE (1990), COCKE et al. (1992), KOMARNENI & ROY (1981, 1985), KOMARNENI et al. (1982, 1986), KOMARNENI et al. (1988), LABHSETWAR & SHRIVASTAVA (1988, 1989), LAMEILLE et al. (1987), KINDNESS et al. (1994), TITS (1994).

The extent to which "chemical fixation" is an important mechanism, and for which radionuclides, is still an open question. Also, the consequences for, and the influence on, performance assessment studies have yet to be assessed.

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