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Sorption Databases for the Cementitious Near-Field of a L/ILW Repository for Performance Assessment

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Note:

This work was essentially completed in the summer of 1992 and hence only the published sorption data available to the authors up to this time have been taken into account in the writing of this report.

ABSTRACT

Approximately 95 weight per cent of the material in the L/ILW repository for short-lived low- and intermediate-level wastes consists of concrete; the remaining approx. 5% consists of steel (4%) and high molecular weight organic waste components (1%). Radionuclide sorption onto concrete represents one of the most important retardation mechanisms in the disposal caverns. This report compiles the sorption properties of hydrated cement, the most important sorbing material present in concrete, in the form of data sets for safety relevant nuclides under repository conditions; these data can then be used directly in performance assessment.

In the disposal caverns, the cement is affected by a range of different processes which can influence the sorption of radionuclides. External processes include the leaching of the cement by inflowing groundwater, while internal processes include dissolution of repository components in the cement pore water; these components can react with radionuclides and thus alter their sorption behaviour or they can react with the cement and alter its leaching properties.

Processes which affect sorption onto cement in the disposal caverns are documented in different data sets in this report. Degradation (leaching) of cement is described in three characteristic degradation steps and the redox state of the cement is accounted for by assuming two extremes (oxidising and reducing). The effects of complexants are presented for 10 material groups. Half of these groups consist of different high molecular weight organic compounds which are present in high concentrations in the waste and decompose to low molecular weight compounds in the caverns. Besides these 5 groups, 5 low molecular weight compounds are considered; these are either present in large volumes or have a large complexation capacity with respect to nuclides.

In this report, the distribution coefficients for radionuclides on cement are based to a large extent on values measured under repository-relevant conditions; this is true for cement without complexants in particular. The selection of the distribution coefficients is justified on the basis of the original studies carried out, thus ensuring transparent derivation of the data. Where data are lacking, the assumptions made are clearly documented. In the case of safety relevant nuclides for which there are no published values at present, the distribution coefficients were selected on the basis of chemical analogy with other elements.

PREFACE

Within the framework of its Waste Management Programme, the Paul Scherrer Institute is performing work to increase the understanding of the sorption behaviour of nuclear waste relevant radionuclides on cement. These investigations are performed in close cooperation with, and with the financial support of, NAGRA. The present report is issued simultaneously as a PSI Bericht and a NAGRA NTB.

ZUSAMMENFASSUNG

Das Endlager SMA für kurzlebige schwach- und mittelaktive Abfälle besteht zu ca. 95 Gewichtsprozent aus Beton, zu ca. 4% aus Stahl und zu ca. 1% aus hochmolekularen organischen Abfallkomponenten. Die Sorption der Radionuklide an Beton ist einer der wichtigsten Retardationsmechanismen in den Endlagerkavernen. Im vorliegenden Bericht werden die Sorptionseigenschaften von Zementstein, dem wichtigsten Sorptionsmaterial in Beton, für sicherheitsrelevante Radionuklide unter Endlagerbedingungen in Datensätzen zusammmengestellt, die direkt in Sicherheitsbeurteilungen verwendet werden können.

In den Endlagerkavernen wirken verschiedene Prozesse auf Zementstein ein, welche die Sorption von Radionukliden beeinflussen. Von aussen ist dies die Auslaugung von Zementstein durch das durchströmende Grundwasser. Von innen ist dies die Auflösung von Endlagerkomponenten in das Zementporenwasser, welche einerseits mit Radionukliden reagieren und dadurch ihre Sorption verändern können, andererseits mit Zementstein reagieren und dadurch seine Auslaugung verändern können.

Prozesse, welche die Sorption an Zementstein in den Endlagerkavernen beeinflussen, wurden im vorliegenden Bericht durch verschiedene Datensätze berücksichtigt. Die Degradation (Auslaugung) von Zementstein wurde mit drei charakteristischen Degradationsschritten erfasst. Der Redoxzustand von Zementstein wurde durch zwei Extreme (oxidierend und reduzierend) berücksichtigt. Die Auswirkungen von Komplexbildnern wurden im Rahmen von 10 Stoffgruppen wiedergegeben. Diese Stoffgruppen bestehen zur Hälfte aus verschiedenen hochmolekularen organischen Verbindungen, die in den Abfällen in grossen Mengen vorkommen und in den Endlagerkavernen zu niedermolekularen Verbindungen abgebaut werden. Neben diesen 5 Stoffgruppen wurden 5 niedermolekulare Verbindungen berücksichtigt, die in grossen Mengen vorkommen oder ein grosses Komplexbildungsvermögen gegenüber Radionukliden aufweisen.

Die Verteilungskoeffizienten von Radionukliden an Zementstein, die im vorliegenden Bericht enthalten sind, beruhen zu einem wichtigen Teil auf Messwerten unter endlagerrelevanten Bedingungen. Dies gilt vor allem für Zementstein ohne Komplexbildner. Die Auswahl der Verteilungskoeffizienten wird, ausge-

hend von den Originalarbeiten, begründet und gewährleistet so eine nachvollziehbare Herleitung der Daten. Insbesondere wurden bei lückenhafter Datenlage getroffene Annahmen explizit aufgeführt. Bei sicherheitsrelevanten Radionukliden, für welche gegenwärtig keine publizierten Messwerte vorliegen, wurden die Verteilungskoeffizienten durch chemische Analogie mit anderen Elementen ausgewählt.

RESUME

Le dépôt final pour déchets de faible et moyenne activité à vie courte (DFMA) contient en poids environ 95% de béton, env. 4% d'acier et env. 1% de déchets constitués de composés organiques de poids moléculaires élevés. La sorption de radionucléides par le béton représente l'un des plus importants mécanismes de retardation dans les cavernes de stockage final. Les caractéristiques de sorption de la pierre de ciment, sous conditions prévalant dans un dépôt final, c.-à-d. du matériau de sorption majeur des radionucléides significatifs pour la sécurité dans le béton, sont présentées dans ce rapport sous forme d'ensembles de données qui peuvent être utilisés directement dans les analyses de sûreté.

Divers phénomènes influençant la sorption des radionucléides dans les cavernes de stockage final affectent la pierre de ciment. De l'extérieur ce sera la lixiviation de la pierre de ciment par la circulation d'eau souterraine. De l'intérieur cela sera la dissolution, dans l'eau intersticielle du ciment, de composants de déchets qui d'une part réagissent avec certains radionucléides et de ce fait peuvent modifier leurs caractéristiques de sorption et d'autre part réagissent avec la pierre de ciment et peuvent par conséquent modifier sa dissolution.

Dans le présent rapport il a été tenu compte des processus qui influencent la sorption sur la pierre de ciment dans les cavernes de stockage sous forme de divers ensembles de données. La dégradation (lixiviation) de la pierre de ciment a été appréhendée par trois étapes de désintégration caractéristiques. L'état redox de la pierre de ciment a été considéré par ses deux extrêmes (oxydant et réducteur). L'effet d'agents complexants a été représenté dans le cadre de 10 groupes de substances. Ces groupes sont constitués pour moitié de divers composés organiques de poids moléculaires élevés qui apparaissent en grandes quantités dans les déchets et qui se désintègrent en composés de faibles poids moléculaires dans les cavernes de stockage final. A côté de ces 5 groupes de substances on a retenu 5 composés de faibles poids moléculaires que l'on trouve en grandes quantités ou qui présentent une forte aptitude à former des complexes avec les radionucléides.

Les coefficients de distribution des radionucléides dans la pierre de ciment contenus dans le présent rapport se basent pour une grande partie sur des résultats de mesures faites sous conditions représentatives du stockage final. Cela concerne principalement la pierre de ciment sans agents complexants. Le choix des coefficients de distribution tirés de travaux originaux est expliqué,

permettant ainsi de retracer l'origine des données. Lorsque les informations souffraient de lacunes, les hypothèses introduites sont présentées de façon explicite. Pour les radionucléides significatifs du point de vue de la sûreté et pour lesquels on manque pour l'heure encore de valeurs publiées, les coefficients de distribution ont été choisis par analogie chimique avec d'autres éléments chimiques.

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1 INTRODUCTION

The aim of this work is to derive realistic sorption data sets for safety relevant radionuclides present in a cement/concrete based repository for low- and intermediate-level radioactive waste. This report is the documentation to the data sets chosen. It is important to realise that the sorption databases and the accompanying documentation always belong together, otherwise the values in the data sets are merely a series of "numbers".

The critical point about databases of any sort which are to be used in safety analyses, is that the values chosen should, wherever possible, be justified. This is almost invariably a rather difficult task since the information required to justify the choices is often incomplete.

In the vast majority of cases distribution ratios are obtained from batch type experiments on crushed material and are represented in terms of distribution ratios, R_d (see Chapter 2). These are empirical parameters measured under a specific set of conditions and mainly, only "point values" are available. In rare instances, sorption data may be available as a function of equilibrium radionuclide concentrations, usually expressed as a Freundlich isotherm. Isotherms are also comprised of empirical data. In this sense they are no better (or worse) than single R_d values, though, of course, they contain more information.

The point here is that the sorption behaviour of a radionuclide, in an often extremely complex system, is reduced to a single parameter (R_d). The only chance of being able to **justify fully** such a procedure is when the sorption mechanism(s) is (are) known and can be expressed in terms of models which have a demonstrated ability to predict sorption over the range of conditions which represent the real system (verified mechanism(s)/models). At the present time, and for the foreseeable future, this is unlikely to be the case for cementitious systems, and therefore, we cannot speak of a **fully** justified sorption data set.

Despite being unable to fulfil the "ideal" briefly described above, there is, worldwide, a large pool of data, information and experience on "sorption" which has been accumulated over the past two or three decades and upon which we can draw. It is of course true that any conclusions drawn from this data pool (ultimately this is the selection of an R_d value) are highly dependent on the quality of the data and its completeness. Judgements have to be made upon which data should be chosen from which a single distribution ratio is ultimately

selected for the database. This judgement/selection process is carried out in all cases by individuals or groups of individuals who are generally recognised "experts" and who, on the basis of their knowledge and experience, offer "expert judgement". When carried out properly, this is the best procedure available to us at the moment; there is currently no viable alternative.

However, it should not be expected that the judgement of experts is accepted blindly by third parties. In our view it is totally unacceptable that experts present only the results of their deliberations (in this case in the form of a set of distribution ratios) without describing, in as much detail as possible, the thought processes, reasoning and assumptions (implicit or explicit) which lie behind the choices made. One of the major problems with sorption databases compiled in the past is that the above has not been documented at all or, at best, insufficiently, so that third parties have not been given the opportunity to judge for themselves the validity of, or the uncertainties associated with, the values given (see for example McKINLEY & SCHOLTIS 1991). Phrases often used in the documentation to sorption databases are "it is reasonable that....." or " it is expected that.....", without further comment. If something is "reasonable" or "expected", then any third party reading the document is entitled to know why.

A further point worth mentioning is that a feature common to most reports concerning sorption databases is a section on radionuclide speciation. At best such calculations, which are relatively easy to do (whether they represent reality is another matter), enable the author to estimate in very general terms whether the radionuclide is likely to exhibit weak, moderate or strong sorption on the basis of the species present and their charge. The speciation calculations alone are not capable of yielding any justification for the magnitude of the value chosen. Indeed, the "standard speciation section" is often a "stand alone" section and is never referred to again in connection with the choice of distribution ratios. We are not saying that speciation calculations are irrelevant for understanding sorption processes, quite the contrary. However, when speciation data are given, they should not be there as a "report filler" or a "stand alone section" but rather the connection with, and relevance to, the distribution ratios chosen must be made. If there is no connection made then there is no reason to give speciation data.

One of our aims in writing this report is to describe, as fully as possible, the reasoning and reasons behind the choices made and where necessary to state clearly any associated assumptions. We already foresee that this procedure will

lead to criticism (constructive, we hope) and to further discussion. We welcome this as a positive way forward and as a means of improving future sorption databases and identifying critical areas where our current knowledge is inadequate.

2 BACKGROUND

2.1 Preamble

The pool of sorption data available comes predominantly from laboratory batch tests in which a known quantity of a radio-tracer is added to a known mass of crushed material in contact with a known volume of solution of known composition. In principle such experiments are easy to perform and distribution ratios (R_d) can be extracted from the relation:

$$R_d = \frac{\text{Quantity of radionuclide sorbed per unit mass of solid}}{\text{Equilibrium concentration of radionuclide in solution}} \qquad (1)$$

$$= \left(\frac{C_1 - C_2}{C_2}\right) \cdot \frac{V}{m}$$

where C_1 = initial aqueous concentration of radionuclide
C_2 = final ("equilibrium") aqueous concentration of radionuclide
V = volume of solution
m = mass of crushed solid phase present

In practice, batch sorption experiments are difficult to perform properly and the results obtained can be highly dependent on the experimental techniques used. Different experimental procedures can lead to vastly different distribution ratios.

Distribution ratios can also be deduced from dynamic tests e.g. column and through-diffusion type experiments. However, data from such sources are less frequently available since the experiments are far more time consuming. Also, it is important to realise that in order to extract an R_d value from an experiment in which retardation is measured, a model is required. The extracted R_d values are thus model dependent (BRADBURY et al. 1990).

It is self-evident that at any given point in time the pool of data from which selected values can be taken is fixed and that the selected sorption data is a subset of the available data. If important data are missing, or have not been measured under equivalent conditions to some stage in the evolution of the repository, then means have to be found whereby realistic values can be estimated.

Some of the major questions/considerations involved in the selection of the best available values for a sorption database for safety analysis purposes are:

(1) The quality of the experimental data
(2) Are the selected quality data relevant for our specific conditions?
(3) How can the selected relevant quality data from laboratory experiments on crushed material be applied to the repository situation?

Points (1) and (2) will be briefly discussed together since they are often considered in parallel. The discussion regarding point (3) will be treated separately.

2.2 Data Quality and Relevance

When starting to set up a sorption database the most obvious place to begin is with those which have been compiled in the past. For cementitious material a number are available e.g. ALLARD (1985), ALLARD & ANDERSSON (1987), EWART et al. (1988), EWART et al. (1989) NANCARROW et al. (1988), ALLARD et al. (1991). In addition, there are various reports which compare the database compilations, the latest of which is a review by McKINLEY & SCHOLTIS (1991). Comparing databases is a useful **first step** in obtaining a rapid overview of the considered expert opinions of others and to see whether or not there are any major discrepancies in the data sets. McKINLEY & SCHOLTIS (1991) note that there is generally good agreement between databases for cementitious material. However, this apparently good agreement is, in itself, no criterion for the acceptance of the values given as being the "best available". As mentioned before, part of the problem here is the generally poor documentation of the procedures involved in the choices made. The consistency amongst the different databases can be viewed in two ways. In a positive sense, in that the consistency is an encouraging indicator that expert deliberation world wide has led to very similar conclusions. On the negative side, the consistency may be interpreted as being a consequence of "experts" copying from each other. In any event, the values given in existing databases cannot form the basis for any independent data evaluation. At best they can act as a guide, at worst they can be misleading. Rather, the original source literature is the only basis upon which judgements can be made. Here the decisive factor is "quality". An evaluation of the quality of a piece of experimental work, and thereby the quality of the results obtained, lies in the realm of expert judgement. To a certain extent expert judgement is subjective and depends upon the experience, knowledge, interpretative abilities and biases of the individual expert. However, biases and gaps in knowledge which may influence the individuals choice and judgement can be revealed and corrected by peer review if

the expert states the reasons for his choices. Thus, peer review and feedback are an essential component and check involved in expert judgement.

"Quality" is a difficult term to define, and rather than attempting to do so we will try to describe, in the context of this work, some of the processes and considerations involved in making "quality judgements".

The quality of a piece of experimental work has its foundations in the planning of the work, in having clearly defined aims and, perhaps most important, in the experimental methodology. For example, in the case of batch type experiments (the source of most sorption data), certain critical questions spring to mind when reading a paper or report:

(a) To what extent has the *solid* phase been characterised?
(b) To what extent has the *liquid* phase been characterised?
(c) Has the water chemistry been checked at the beginning and end of the experiment?
(d) Are there good reasons for believing that the solid and liquid phases were in equilibrium, or at least in steady state, during the experiment.
(e) In sorption experiments, pH is a particularly important parameter. Was this constant?
(f) Were the experiments performed under controlled atmosphere conditions? ((f) is strongly connected with points (c), (d) and (e))
(g) Were the experiments carried out under controlled temperature conditions?
(h) How and in what form was the tracer added?
(i) Was the radionuclide concentration definitely below the solubility limit? (Precipitation and sorption are often impossible to distinguish unless an isotherm is measured)
(j) What rôle did kinetics play in the experimental measurements?
(k) What methods were used for solid/liquid phase separation? If filtration methods were employed, what was the filter pore size? Was sorption on filter substrates considered? For centrifugation, how was the particle size cut off determined?
(l) Was sorption on container walls considered/corrected for? How?
(m) Are errors considered, and, if so, how were they calculated?
(n) How relevant is the experimentally investigated system to our particular system?

For redox sensitive radionuclides the Eh is clearly an important parameter which is not listed above explicitly. In most cases the experimental conditions are described in general terms as being aerobic or anaerobic which says virtually nothing quantitatively about the redox state of the system.

Depending on the answers to a check list of the sort given above, a picture as to the quality of the measured data can be formed. Other factors such as interpretation, internal consistency of the data and comparison with other work are also taken into account.

In addition, the core of experimentalists working in radioactive waste management in a specific area is not very large, and the people are generally known to one another. Through personal contact, discussions at conferences and laboratory visits, impressions are formed with time as to the strengths and weaknesses of various institutes and the individuals working there. Judgements are formed as to the competence, thoroughness and reliability of the work carried out by various investigators and these naturally play a rôle in the overall quality assessment procedure. Though this lies on the subjective side of "expert judgement", it is nevertheless an important factor.

One final comment; a question which is often put to the compilers of databases is "Why didn't you choose the lowest value for the sorption database which has ever been measured? Isn't that the most appropriate conservative value"? The answer to this question lies in the discussion above. Experts and expert judgement is not required to find "lowest distribution ratios", a monkey or a computer would be sufficient.

2.3 Laboratory Sorption Data and their Relevance to the In-Situ Repository

A criticism often made concerning laboratory generated sorption data is that some of the conditions under which the measurements are made are so vastly different from the expected repository conditions that they are, at worst, not relevant at all, or at least, must be strongly modified in a well justified manner to make them relevant. Two of the most obvious differences between laboratory and "real" conditions are that in the former case crushed material and high liquid to solid ratios are used whereas, in the latter, monolithic blocks and liquid volumes comparable to the material porosities are involved.

We will attempt to address this question in this section with specific reference to cementitious materials. Let us be clear at the outset that the validity of the criticism stated in the opening paragraph cannot be absolutely proven or disproven. Again, like it or not, we have to rely on expert judgements made on the basis of available evidence and reasoned arguments.

In the case of cementitious materials we are in the rather fortunate position that the basic chemistry of hardened cement paste, the binding material in concretes and blends, has been the subject of investigation for many decades in the building and cement industries and is relatively well known in general if not in detail (see for example LEA 1988). Because of its extensive use in the building industry, the cement powder is produced under well defined conditions and must conform to stringent national standards. Thus, if a certain cement powder is used to make a concrete to a certain recipe, then whether that concrete is produced in land A or land B the hardened cement paste in the product will be very similar with respect to the quantity and composition of the mineral phases formed during hydration. Also, since the pore water composition in the concrete is determined almost exclusively by the mineral phases formed in the hardened cement paste, then the chemistry of the water in "equilibrium" with the cementitious product will also be very similar. **In other words, the basic liquid-solid system at "equilibrium" is well defined and will not vary appreciably from investigator to investigator.**

Given that the cement/pore water system is intrinsically well defined, let us turn first to the effect that crushing may have on sorption properties. In batch sorption tests crushed materials are most often used in order to speed up the sorption experiments. That is, crushing is intended to expose the internal surfaces of a solid which under normal circumstances could only be reached via diffusion through the pore water, usually a very slow process particularly for strongly sorbing species. The critical question with crushing is whether or not new and atypical surfaces are created (with possibly different and stronger sorption properties) and whether the surface area for sorption has been increased over and above that available in the original solid. During the hydration of cement a calcium-silicate-hydrate (CSH) gel layer builds up on the outside of the cement powder particles and forms an interconnected network on a fine scale between which lies the excess water which has not been used in the hydration process. CSH gel mainly forms the boundary between the internal fluid and the solid phases. Hardened cement pastes are fine grained microporous solids, usually with porosities in excess of 20% which implies exceedingly large internal pore

surface areas. During crushing, fracture is most likely to occur along planes of weakness i.e. along pores and at junctions where the filaments of CSH gel from adjacent particles have met. In the less likely event that transgranular fracture across partly hydrated grains takes place, then the "new surfaces" exposed will rapidly form a CSH gel layer upon contact with water. Thus the types of surface exposed as a result of crushing will not differ in any significant way from those existing internally in the cement block.

Does the area available for sorption increase as a result of crushing? ROWAN et al. (1988) investigated this question by measuring the BET surface areas of three types of hardened cement paste blends in the form of half inch diameter disc coupons weighing 3-5 g or similar discs which were broken up and sieved to create different particle sizes. The BET surface area results were similar for the three different blends considered, with values of 55 ± 5 $m^2 g^{-1}$ (coupons), 90 ± 10 $m^2 g^{-1}$ (0.5-1.0 mm particle size range), 85 ± 5 $m^2 g^{-1}$ (125-250 µm) and 75 ± 5 $m^2 g^{-1}$ (50-125 µm). Thus, the conclusion from this study was that crushing did not significantly influence the available surface area and, by inference, sorption.

In the relatively small number of cases where cement particle size effects have been systematically studied in sorption tests, few or no significant effects have been found, as would be expected from the above. (See for example the studies of ATKINSON & NICKERSON (1988) on Cs, Sr and I; BAYLISS et al. (1991) on Am; and the results reported in ATKINSON et al. (1988b) on Am and Pu. In this context the results reported in ATKINSON et al. (1988b) and by BAYLISS et al. (1991) are particularly interesting. Discs, into which Am and Pu had diffused, were sectioned by grinding and R_d values calculated for the penetration depth only. The R_d values determined in this manner were very similar to those obtained in crushed cement batch tests.

With respect to the effect of liquid to solid ratio, it is somewhat less easy to give a clear cut answer since all possible influences have been reported at one time or another in the literature; no effect, increases and decreases in sorption. At the present time, we know of no reliable systematic investigations which have yielded a plausible general explanation. Indeed, there is probably no single explanation. Under these circumstances we are forced to rely on our current understanding of sorption processes and to deduce whether or not the high liquid to solid ratios used in the laboratory experiments are most likely to lead to con-

servative or non-conservative distribution ratios with respect to the repository situation where the pore water to solid ratio is low.

Generally speaking, if the composition of the liquid phase does not represent that which is in equilibrium with the solid phase, then when the two are brought together a solid/liquid interaction will occur and the system will adjust in the direction of a new equilibrium state involving not only macro and micro changes in liquid phase composition but also changes to the solid phase (the former can be detected, the latter is very much more difficult, if not impossible, to estimate or quantify). Depending on the nature and magnitude of the initial imbalance, the liquid phase or the solid phase or both can drive the changes. The sort of macro effects which may occur are dissolution/precipitation reactions. A minor phase may change from being saturated to undersaturated if the volume of liquid is sufficiently great to dissolve it completely. Sorption/desorption of ions may occur on and from the solid phase. If these ions are competitive with the generally low levels of radionuclide added, then this will influence the subsequent sorption measurements. If the solid phase contains soluble organic matter, then its concentration in solution will depend on the liquid to solid ratio and therefore influence speciation and thereby sorption. The above is by no means an exhaustive list, but nevertheless serves to illustrate that differences in liquid to solid ratios may in fact lead to sorption studies on effectively different systems. The effects may be even more complicated if the systems are evolving in time during the actual sorption measurements.

In our view the above is one of the two major causes of liquid to solid ratio effects in experimental studies. However, for cement systems, it is not likely to be **the major effect** since the solid acts as an extremely powerful buffer and effectively determines the liquid composition.

Virtually all of the studies in which a sorption dependency on liquid to solid ratio has been found, have relied on isolated single measurements i.e. in experiments where the initial concentration of radionuclide has been fixed and the liquid to solid ratio varied. Under these circumstances changes in distribution ratio with liquid to solid ratio **would be expected** where the radionuclide is sorbing non-linearly since the equilibrium concentrations at the different liquid to solid ratios are different. In general, increased sorption would be anticipated with decreasing liquid to solid ratio. Cause and effect have been confused. The effect is an apparently inexplicable dependency of sorption on liquid to solid ratio, whereas the cause is the non-linearity of the sorption process itself, a well

known and well documented phenomenon. The confusion has arisen because of either poor experimental technique (the liquid and solid phases are not in equilibrium) or because single measurements at different liquid to solid ratios have been compared. In the latter comparisons, like has not been compared with like since the equilibrium concentrations are different.

Our conclusion is that the "liquid to solid ratio effect" often reported is an apparent effect and is not due to the liquid to solid ratio per se, but has other causes, predominantly those listed above. (See also BRADBURY & BAEYENS 1992). In the relatively few cases where the non-linearity of sorption has been taken into account and results at different liquid to solid ratios plotted as part of a sorption isotherm (AKSOYOGLU et al. 1990) or where attempts have been made to keep the equilibrium radionuclide concentration constant at different liquid to solid ratios (for example ATKINSON et al. 1988b) no significant effects have been found. The only circumstances under which the liquid to solid ratio may have a real effect on measured distribution ratios is when the conditions of the experiment are such that sorption site saturation occurs. If this is the case, then the measured R_d should decrease in direct proportion to the inverse of the concentration measured in the solution at the end of the experiment. Where isotherms are measured, this effect would be evident. Unfortunately the determination of sorption isotherms is the exception rather than the rule.

2.4 General Conclusions

On the basis of the discussions given in section 2.3, we have drawn three general conclusions for cementitious systems:

(i) The crushing of cement, at least for particle sizes > 50 μm (ROWAN et al. 1988), does not in any significant way influence sorption. Crushing makes available surfaces for sorption which already exist within the bulk material and which normally could only be reached by diffusion. Distribution ratios obtained from properly performed laboratory batch tests on crushed cement (see sections 2.2 and 2.3) are valid for the in situ bulk cement.

(ii) The liquid to solid ratio has no effect per se on sorption. If the non-linearity of sorption is taken into account, and like is compared with like at different liquid to solid ratios, then the R_d values measured are the same.

(iii) **The corollary to point (ii) is that it is incorrect to scale up distribution ratios from laboratory experiments to the in-situ conditions on the basis of the liquid to solid ratios in the two systems.**

3 DO DIFFERENT CEMENTS AND CEMENT MIXES HAVE A SIGNIFICANT INFLUENCE ON SORPTION?

The different cements and cement mixes which may eventually be present in a Swiss low- and intermediate-level waste repository are summarised in Table 1 (NEALL 1994).

The majority of the sorption data presented later in this report were not obtained on these particular cement/concrete types. Most of the data were taken from Swedish and British investigations. In the former case the sorption of actinides, I and Cs was measured on seven mixes: Ordinary portland cement, ordinary portland (French mixture), sulphate-resisting cement, blast furnace slag cement, high alumina cement, fly ash cement and silica cement (see ALLARD et al. 1984 for details of the mixes).

The general conclusion from this work was that, "The differences in sorption between the various types of concrete used in the present study were usually minor with a few exceptions" (ALLARD et al. 1984, p. 22). The "exceptions" discussed by Allard do not materially affect the conclusion.

AEA at Harwell has carried out similar studies on cement blends such as ordinary portland cement + blast furnace slag, ordinary portland cement + pulverised fly ash (both at various ratios) as well as on ordinary portland cement and sulphate resisting cement. In a position paper (ATKINSON et al. 1988b) they write, "It may be concluded that the sorption coefficients of these two nuclides (Am and Pu)..... are almost independent.....of the cement formulations studied". The evidence from the studies of Allard and Atkinson on a wide range of concrete mixtures indicates strongly that the cement composition at pH > ~12.5 has only a second order effect on actinide sorption i.e. the dominant sorbing substrate is the cement itself. For mono- and bivalent fission and activation products the above statement is also generally valid but each radio-element needs to be looked at individually.

In this report we have tried, wherever possible, to favour the data obtained on "pure" hardened cement pastes i.e. ordinary portland cement (OPC) or sulphate-resisting portland cement (SRPC).

Table 1: Summary of cement types and concrete blends foreseen to be present in a Swiss low- and intermediate-level radioactive waste repository (NEALL 1994).

		Waste	Backfill	Container Walls	Cavern Lining
HTS[1]	[kg/m³]	550			
OPC[2]	[kg/m³]				350
Sulfacem[3]	[kg/m³]		285	350	
Trass[4]	[kg/m³]	150			
Water	[kg/m³]	300	113	150	150
Ballast material	[kg/m³]	1000	1520	1950	1950
Total	[kg/m³]	2000	1918	2450	2450
W/C[5]		0.43	0.40	0.43	0.43

1 French sulphate resistant cement: Ciment Portland Artificiel, CPA 55, Haute Teneur en Silice, Ciments Lafarge, France

2 Ordinary Portland cement

3 Swiss sulfate resistant portland cement (Sulfacem, Olten, Switzerland)

4 Rhenish volcanic tuffs

5 Water to cement ratio

4 CHEMICAL ANALOGUES AND REPOSITORY CONDITIONS

4.1 Chemical Analogues and Sorption Mechanism

In attempting to compile a sorption database for safety assessment studies, it quickly became apparent that sorption data for all safety relevant radionuclides under the different conditions which occur during the lifetime of the repository do not exist. Nevertheless these data are required for safety analysis calculations. It is important that the reasoning and assumptions behind the procedures for assigning values to "gaps" in the sorption data are clearly stated.

We begin with a list of safety relevant radionuclides for a Swiss low- and intermediate-level waste repository derived from KEMAKTA (1989) according to their foreseen importance.

Table 2: Radionuclides listed according to their foreseen importance for safety assessment.

High Priority:	H, CO_3^{2-}, Cl, Ni, Se, Sr, Zr, Tc, Sn, I, Cs, Ra, Th, U, Np, Pu, Am
Medium Priority:	Mn, Nb, Mo, Pd, Ag, Pb, Pa, Cm
Low Priority:	Be, C_{org}, Na, K, Ca, Fe, Co, Sm, Eu, Ho, Po, Ac (sorption for these elements is briefly discussed in Appendix D)

We have taken the above radionuclides (high and medium priority) and regrouped them according to their position in the periodic table of elements and according to their major chemical characteristics (SMITH & MARTELL 1976), Table 3. The bracketed elements are ones which have no primary relevance to waste disposal but whose chemical behaviour is expected to be similar to those which do. The major chemical characteristics considered are redox sensitivity, hydrolysis and ion pair formation.

Table 3: Radionuclides grouped according to their major chemical characteristics.

Groups	Elements	Major characteristics
Alkali metals	Cs	• not redox sensitive • no tendency to hydrolysis • low tendency to form ion pairs
Alkali-earth metals	(Mg),(Ca),Sr,(Ba),Ra	
Lanthanides + Am,Ac Cm	(La),(Ce),(Nd),(Sm),(Eu),Am,(Ac) Cm	• not redox sensitive • tendency to hydrolysis • tendency to form ion pairs
Group IVA elements	Zr,Th	
Transition elements	*Ni Pd,Ag *Nb,*Mo Mn,Tc	• redox sensitive • tendency to hydrolysis • tendency to form ion pairs
Group IVB elements	Sn,(Pb)	
Actinides	Pa,U,Np,Pu	
Halides	Cl,(Br),I	• redox sensitive
"Anion species"	C,Se	• redox sensitive

* Stable oxidation states for expected Eh/pH ranges

Table 3 gives a first broad overview of groups of elements having chemically similar properties and which would therefore also be expected to exhibit similar sorption properties. The table is intended as a guide, only. Americium, curium and thorium could equally well be grouped together with the actinides for example, but, because of their insensitivity to redox conditions, they have been included with the Lanthanides and group IVA elements, respectively.

Are there other "indicators" or means of classifying groups of elements which should exhibit similar sorption properties and which could help in assigning

realistic distribution ratios and/or ensuring consistency in the sorption database?

In non-cementitious systems there are strong indications in the open literature that sorption, particularly at pH values above 8, is correlated positively with the tendency of radionuclides to hydrolyse. ALLARD (1982), in an extensive study of the sorption of Am, Np and Pu on 40 different minerals as a function of pH, concluded that, "for all systems the sorption is drastically increased when hydrolysis starts. Sorption maxima are generally obtained in the pH range where neutral hydroxy complexes would dominate in solution".

In the metal (hydrous) oxide literature, where sorption data have been interpreted in terms of surface complexation models for the past 20 years or so, a linear correlation between cation surface complexation constants and the first hydrolysis constant has been found (see for example SCHINDLER 1984, BUFFLE 1988, DZOMBAK & MOREL 1990).

Though the examples given above are not directly relevant to cement systems, and there are no investigations of which we know where attempts have been made to investigate sorption mechanisms on cement, we believe that surface complexation is most probably a major sorption mechanism in cementitious systems. Many of the predominantly amorphous phases formed during cement hydration, and included under the general heading of calcium-silicate-hydrate gel, have large surface areas rich in surface "SOH" type groups, where "S" represents for example Si, Ca, Al (see LEA 1988). The high pH, favouring hydrolysis in the liquid phase, and the above characteristics of the gel, constitute favourable conditions for surface complexation. On the basis of this assumption, it would then follow that the readiness with which a radionuclide forms surface complexes may be related to the first hydrolysis constant.

There is an interesting plot (reproduced in Figure 1) given in BAES & MESMER (1986), where the first hydrolysis constant (K_{11}) is plotted against the ratio of charge to bond length (z/d) for a wide range of metal hydroxy species. The z/d value can be taken as a "bond strength" indicator i.e. large z/d ratios represent "strong" bonding and vice versa. The reason that this plot is interesting is that for those radionuclides where sorption has been measured (see Chapter 5), the magnitude of the sorption qualitatively correlates with the position occupied by the radionuclide in Figure 1. That is, a strong tendency to hydrolyse (high K_{11} value) coupled with a high value for z/d is associated with high distribution ra-

tios measured on cement. Low K_{11} and z/d values correlate with low sorption and intermediate values with intermediate sorption.

Though this is all rather empirical, it does make sense in terms of a surface complexation sorption mechanism for cement. Table 3 and Figure 1 will be used later in this report in the sections describing the selection procedures for radionuclide distribution ratios.

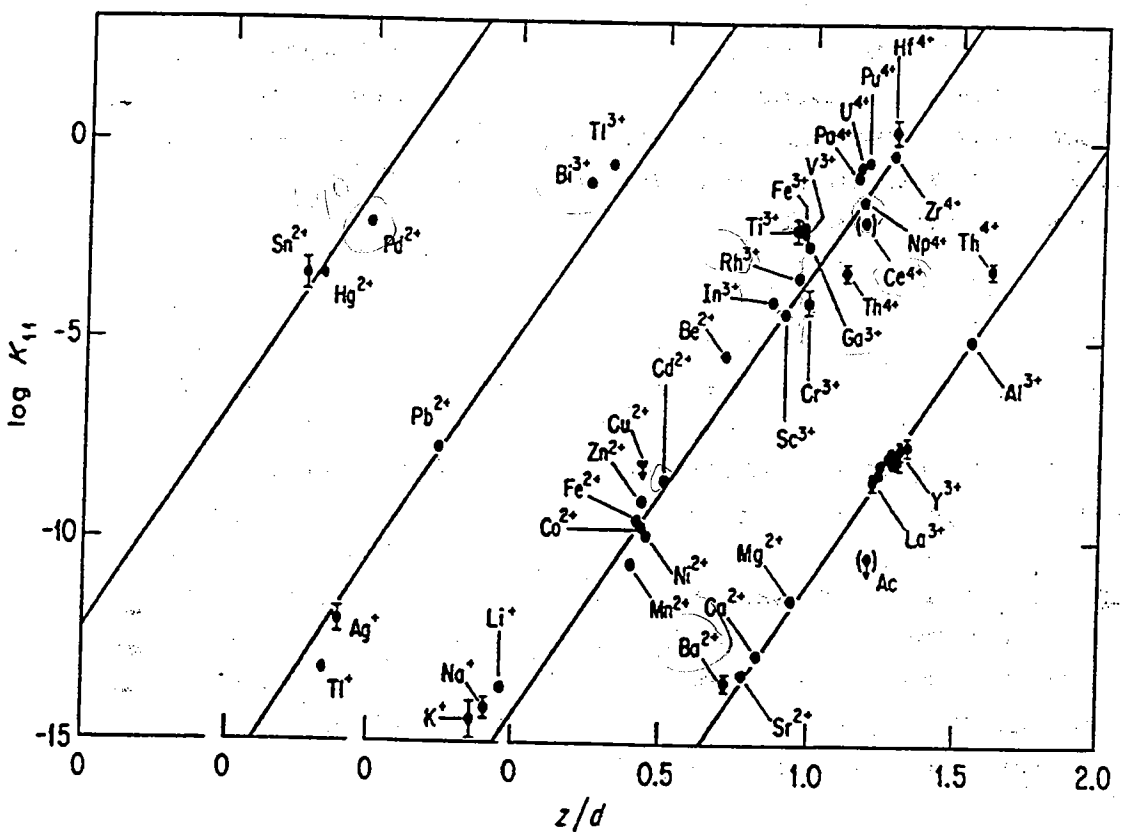

Fig. 1: The linear dependence of log K_{11} on the ratio of the charge to the M-O distance for four groups of cations (From BAES & MESMER 1986, Figure 18.4, page 408).

4.2 Redox

For many radionuclides, in particular the actinides, the redox state of the system can have a significant effect on speciation and solubility limits and thereby on the sorption properties.

We believe that it is fair to say that there are no reliable sorption data existing in the open literature where measurements have been made under well defined and constant redox conditions for cement systems. Almost all measurements have been made under oxidising (aerobic) conditions. Sometimes the conditions are reported as anaerobic (which often means "in a glove box") or reducing; both of which have little quantitative meaning. Here is neither the time nor the place to discuss how and why this situation has arisen when strongly reducing conditions (Eh ~ -300 to -500 mV) are expected to develop relatively rapidly after repository closure nor is a discussion on the difficulties of establishing well defined redox conditions in the laboratory appropriate. The fact of the matter is that effectively no sorption measurements have been made under the appropriate redox conditions.

In order to estimate what the sorption of redox sensitive radionuclides is likely to be when they are in a reduced state, we have to rely on measured sorption data available from oxidising conditions and chemical analogy. For example, under oxidising conditions the valence states of the actinides are:

Element	Expected valence state under oxidising conditions
Pu	5+
U	6+
Am	3+
Th	4+
Np	5+
Pa	5+

Their valencies in the reduced state together with their respective analogues are taken to be:

Element	Expected valence in the reduced state	Analogue element
Pu	4+	Th (4+)
U	4+	Th (4+)
Am	3+	Lanthanides
Th	4+	-
Np	4+	Th (4+)
Pa	4+	Th (4+)

4.3 Evolution of the Cement Pore Water Composition: Degradation of Cement

Over long periods of time in contact with ground water, cementitious materials are unstable. In broad general terms the evolution of the pore water composition during leaching can be characterised in terms of the pH into three regions illustrated in Figure 2.

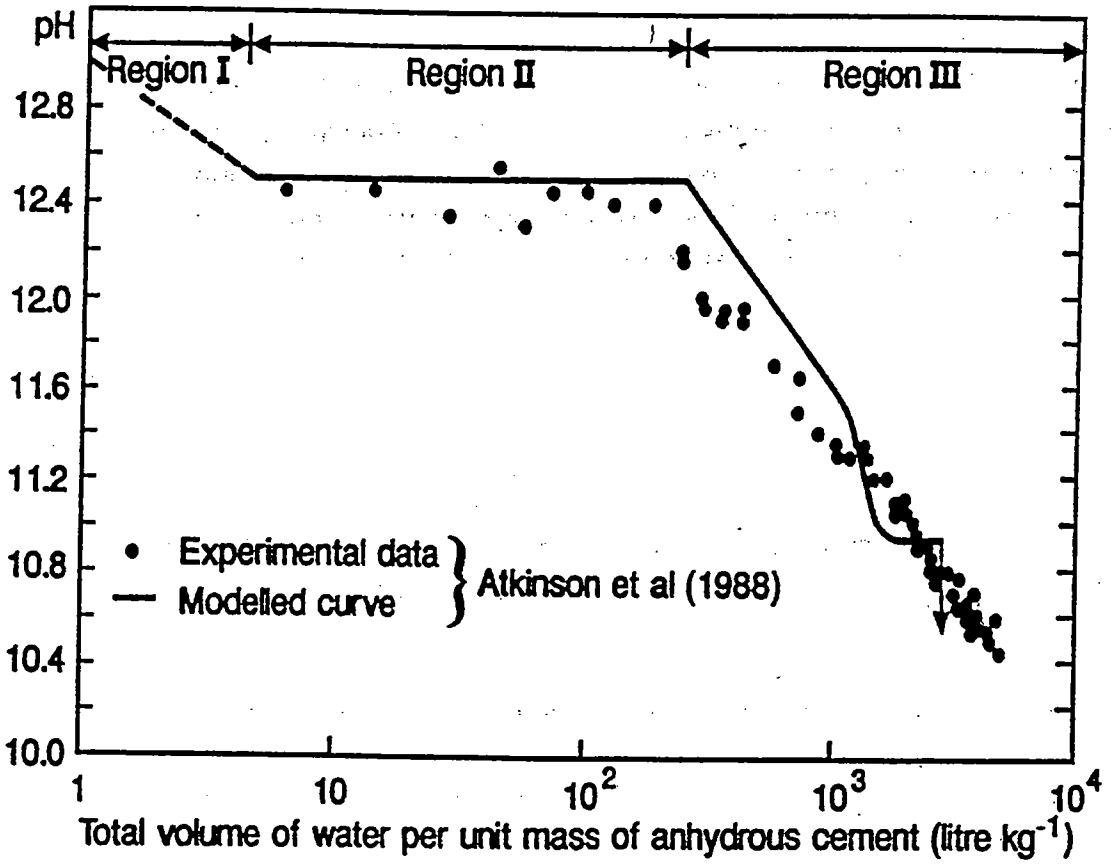

Fig. 2: The pH of the aqueous phase in contact with SRPC paste during leaching with water; after ATKINSON et al. (1988a). (See also BERNER 1990)

Region I

The pH lies between ~13.3 and 12.5. The pore water composition is dominated by (K, Na) OH. The solution is saturated with respect to portlandite ("$Ca(OH)_2$" ~$2 \cdot 10^{-3}$ M). The major solid phases present in cement have already formed, though hydration may be continuing.

Region II

Contact with "flowing" groundwater has removed virtually all of the highly soluble (K, Na) OH. The pore water composition is now dominated by portlandite ("$Ca(OH)_2$" ~$20 \cdot 10^{-3}$ M) which fixes the pH at ~12.5. The portlandite is also being slowly removed by groundwater flow but the quantities contained in the cement are so large that this phase buffers the system over very long periods of time. There are no significant changes in the major solid phases present in region I and II.

Region III

The removal of "$Ca(OH)_2$" has become significant and the pH falls continuously. The CSH gel is no longer stable and begins to dissolve incongruently. The Ca^{2+} concentration decreases continuously to ~1 to $5 \cdot 10^{-3}$ M at pH ~11.

The overall picture given above is supported by some experimental (see Figure 2) work by ATKINSON et al. (1988a) and references therein. BERNER (1990) and NEALL (1994) have carried out an extensive modelling study on different cement types and groundwater chemistries directly relevant to Swiss disposal concepts. These reports are recommended for more detailed descriptions of the processes occurring during cement degradation by groundwater.

4.4 Material Inventory of a Low- and Intermediate-Level Waste Repository and Perturbation of the Near-Field Influencing Sorption

A L/ILW waste repository is not a "clean" system made up only of cementitious materials and radionuclides. Rather, as indicated in Table A-1 (Appendix A), taken from ALDER & McGINNES (1994), it is a complex system comprising many and varied components arising from the different waste sources and reprocessing waste streams.

We have chosen an approach whereby we first consider the sorption properties of the "unperturbed" system i.e. cementitious material in equilibrium with its own pore water in contact with radionuclides. The majority of the measured data available are for this "unperturbed" case. Using the procedures outlined in Chapters 2 to 4.3 we have produced a sorption data base for the radionuclides listed in Table 2 taking into account the degradation of cement and redox conditions, Table 4. The distribution ratios given in Table 4 will be influenced to a greater or lesser extent, depending on the radionuclide, by certain perturbation effects present in the near-field repository environment. The source of these perturbation effects can be found in the waste inventory (see Table A-1) e.g. complexation of radionuclides with the degradation products from cellulose, or in the cement/concrete mix formulations e.g. organic cement additives (plasticisers/retarders) complexing with radionuclides, or in the temporal evolution of the repository e.g. possible re-crystallisation of the CSH gel leading to a reduction of available sorption sites. The influence of these and other processes identified as major perturbation effects are evaluated in Chapters 6 to 12 with respect to their potential influence on sorption.

5 SORPTION DATABASE ("unperturbed" cementitious material)

5.1 Introduction

In this section we will give what we consider to be the best available realistic distribution ratios on the basis of the existing data for an "unperturbed" near-field. In making these selections we will rely heavily on the discussions given in the previous four sections and it should be "taken as read" that the factors listed there have been taken into consideration.

The term "realistic" is somewhat undefined. From the discussions given in section 2.3 with reference to section 2.2, we are of the opinion that laboratory sorption measurements on crushed cement/concrete are directly relevant to monolithic cement/concrete existing in a repository. In this sense, the laboratory data represent "realistic" distribution ratios for the repository. The term "best available" is a matter for "expert judgement" and this has been discussed in section 2.3. In many instances, particularly for the actinides, where a range of very high distribution ratios have been reported, we have tended to make selections in the lower half of the range i.e. to select conservative values even though the larger values may be valid. Where radionuclides sorb very strongly the exact magnitude of the sorption parameter is exceedingly dependent on the phase separation method. Where precipitation effects can be ruled out, the better the phase separation technique, the higher the sorption (generally).

In section 2.3 where the liquid to solid ratio was discussed, we argued that it was an effect rather than a cause. No "effect" would be expected for linearly sorbing radionuclides whereas an "effect" would be expected for non-linearly sorbing tracers. In the latter case, if the equilibrium concentrations measured in the laboratory are very much less than those which may actually be present in the repository then it could be argued that laboratory sorption data are too high. However, the maximum possible aqueous concentration which can be present in any waste container may be strongly dependent on the particular inventory. Some recent calculations, which took into account the waste specific inventories of radionuclides and their sorption on cement, indicated that the aqueous concentrations expected are very low (in general much lower than the solubility limits) and of the same order as the equilibrium concentrations in laboratory experiments (see Table C-1, Appendix C). Also, if it is accepted that the most likely sorption mechanism is surface complexation (section 4.1) and that hardened cement paste has a high surface density of sorption sites per unit mass

(BET surface areas > 50 $m^2 g^{-1}$, section 2.3) then the above conditions i.e. limited inventory of radionuclides, large masses of cement with high surface density of sorption sites, are those which lead to linear (Langmuir type) sorption (see for example BRADBURY & BAEYENS 1992). Under these circumstances the selection of a single R_d to represent sorption at low concentrations may not be a bad approximation of reality.

For those radionuclides which are redox sensitive (see Table 3), distribution ratios for the reduced state of the nuclide are derived according to the chemical analogy as outlined in section 4.2. The calculations of SHARLAND et al. (1987), based on the anaerobic corrosion of steel, indicate that reducing conditions in the cement pore water in the repository will exist after relatively short times following closure (of the orders of 100 years). The evolution of the cement pore water chemistry with time was briefly discussed in terms of three regions in section 4.3. The solid phases present in regions I and II are not significantly different and here an influence of degradation on sorption is only expected for those radionuclides where pH variations in the range 13.3 to 12.5 have large effects on speciation and/or where the cations Na^+, K^+ and Ca^{2+} are anticipated to have strong competitive effects on the sorption of the radionuclide in question. In terms of time scales, the repository will be in region II for very much longer than region I, (NEALL 1994), and from this point of view region II sorption behaviour is far more important.

In region III the CSH gel begins to dissolve incongruently and additional mineral phases begin to form and become significant depending on the composition of the groundwater (see BERNER 1992 and NEALL 1994). No sorption measurements are available in this region, therefore estimates must be made.

We have made one of two assumptions depending on the data available:

(i) When the major part of the CSH gel has been removed, the ballast remains. We assume the ballast to be approximated by a quartz sand and the distribution ratio taken is that on pure quartz at pH~10.

(ii) Where no data for the sorption on quartz at pH~10 are available we have assumed a linear decrease in sorption with decreasing CSH gel content. An average value for region III is given based on the removal of 90% of the CSH gel, i.e. the average sorption in region III is taken as being a factor of 10 less than that in region II. The exception to this is the alkali and alkali-earth metals where the major sorbing substrate is likely to be

the ballast and not the cement. The removal of the CSH gel and decreasing levels of competing ions in solution are likely to increase, rather than decrease, sorption in region III. The latter is somewhat academic since, on the timescales involved in reaching region III, such radionuclides will have either decayed or disappeared from the repository due to their low sorption in region I and II.

As is evident from the above, we are not taking into account, at this stage, any "disturbance effects" such as the influence of organic compounds or the degradation products from organic materials. These will be discussed in subsequent chapters.

5.2 Selected Sorption Data

5.2.1 Actinides

5.2.1.1 Pu, Np, Am, Th, U

The main sources of sorption data for actinides were the reports of ALLARD et al. (1984), ALLARD & ANDERSSON (1987), EWART & TASKER (1987), EWART et al. (1988), ATKINSON et al. (1988b), BAYLISS et al. (1991), ALLARD et al. (1991), EWART et al. (1991) and references contained therein.

All authors report high distribution ratios for actinides. For example EWART et al. (1988) state that: "Pu(4), Am(3)... consistently showed sorption ratios between 10 and 60 $m^3 kg^{-1}$". The Pu and Am concentrations in the above determinations were "set to be approximately five to ten times lower than the solubility limits...." (ATKINSON et al. 1988b). The equilibrium concentrations were ~$1\text{-}2 \cdot 10^{-11}$ and ~$3\text{-}6 \cdot 10^{-11}$ M for Am and Pu respectively. BAYLISS et al. (1991) report an R_d(Am) ~12 $m^3 kg^{-1}$ obtained from diffusion experiments on discs of cement which were subsequently sectioned. The reservoir concentration in these diffusion experiments on intact cement samples was held constant at ~$2 \cdot 10^{-11}$ M.

Distribution coefficients for Th, U, Np, Pu and Am measured by ALLARD et al. (1984) after long contact times (> 100 days) on a variety of different cement mixtures under "oxidising" conditions were all generally > 1 $m^3 kg^{-1}$. Approximate equilibrium concentrations in these experiments were:

Np(V)	$4 \cdot 10^{-9}$	M
Pu(V)	$1 \cdot 10^{-11}$	M
Am(III)	$1 \cdot 10^{-11}$	M
U(VI)	$4 \cdot 10^{-9}$	M
Th(IV)	$3 \cdot 10^{-12}$	M

The pH range covered in these experiments was ~13.4 to ~12.7. Some tests were made with $Ca(OH)_2$ saturated solutions (pH~12.5). If anything, the sorption measured at pH~12.5 was larger than at the higher pH values.

There is no doubt that the actinides Pu, Np and Am (particularly Am) sorb extremely strongly on cementitious material. The sorption data for Th is somewhat less extensive, but nevertheless clearly show a very similar magnitude to

that for Pu and Np. The (limited) results available for U indicate high sorption but slightly weaker than for the other actinides (see Table 7 in ALLARD et al. 1984). There does not appear to be any major influence of pH for values > 12.5 and at the low levels of actinides expected in the repository (see section 5.1) concentration variations will have only a second order effect.

On the basis of the above we see no compelling reason to change the distribution ratios given in ALLARD (1985) for Am, Pu, Th and Np in the pH range > 12.5 i.e. 5 $m^3 kg^{-1}$. Indeed, the bulk of experimental evidence indicates that this is a rather conservative value. It should be remembered that for such high R_d values, where precipitation can be excluded, phase separation plays a critical rôle. Less complete separation will lead to lower (conservative) R_d values.

As stated previously, U appears to sorb less strongly than the other actinides and we therefore feel that it is justified to downgrade the value given in NTB 85-21 to 2 $m^3 kg^{-1}$.

From the arguments given in section 4.3 the values given above are taken as being appropriate for regions I and II (Figure 2) under oxidising conditions. Values for reducing conditions are derived according to the method given in section 4.2 (see the summary table, Table 4).

The situation with respect to region III is more complex and less clear. Though the pH has fallen, it is still generally high (> 10) for most of this region. The calcium-silicate-hydrate compounds (CSH gel) have been depleted and products such as brucite and calcite formed (see BERNER 1990) through reactions with the groundwater. The ballast (e.g. quartz sand) in the concrete will remain. Because of the high pH, low levels of carbonates in solution and the presence of the ballast, the degraded concrete may still have a significant sorption capacity. Also, for most of region III some CSH gel will still be present.

We take a conservative view of sorption in this region and assume that the uptake of radionuclides by the solid phases is only occurring on the ballast (assumed to be sand). The data given by ALLARD (1982) for the sorption of Am, Pu and Np on quartz in a groundwater containing relatively high carbonate concentrations are used. The distribution ratios measured at the highest pH values in this work are taken.

Am	(pH~9.5)	R_d (Quartz) ~1	$m^3 kg^{-1}$
Pu	(pH~9)	R_d (Quartz) ~1	$m^3 kg^{-1}$

Np (pH~7.5) R_d (Quartz) ~0.1 $m^3 kg^{-1}$

(The trend in the data for Np indicates increasing sorption with pH)

Hence, in region III for oxidising conditions, a (conservative) distribution ratio of 1 $m^3 kg^{-1}$ is selected for Am, Pu and Th (Th is taken to be similar to Pu) and a value of 0.1 $m^3 kg^{-1}$ for Np and U.

The redox is treated as described in section 4.2 (see Table 4).

5.2.1.2 Protactinium

Only one study of Pa sorption on cement is known to the authors (BERRY et al. 1988). The solubility and sorption experiments reported in this work were beset with wall sorption, filtration and possibly precipitation effects. Sorption appeared to increase with increasing initial Pa concentration and decreasing filter size. The filtration effect was explained in terms of the continual formation and disaggregation of "large size species" with little or no discussion of potential sorption on CSH gel colloids suspensions in solution. Also no satisfactory explanation was given for the rather unusual observation that sorption increased with increasing concentration (precipitation?). Distribution ratios between 0.1 and > 30 $m^3 kg^{-1}$ are reported depending on the experimental method and conditions used in the tests. The main impression generated from this work is that the Pa / cement pore water / cement system is experimentally extremely difficult to work with and the "effects" observed are poorly understood.

Given the uncertainties in the one sorption study on Pa and an otherwise total lack of data, we choose to select a distribution ratio based on chemical analogy and particularly the diagram from BAES & MESMER (1986) given in Figure 1, section 4.1.

From Figure 1 Pa^{4+} has a high first hydrolysis constant and a high z/d ratio. Following the discussion in section 4.1 it would therefore be expected to exhibit significant sorption at high pH. In addition Pa is closely grouped together with U^{4+}, Pu^{4+} and Np^{4+}. Pa may exist in the 5+ and 4+ state under oxidising and reducing conditions respectively and in this respect is similar to Np. The analogy with Np is therefore taken to give "best estimate" distribution ratios of 5 $m^3 kg^{-1}$ for this element in Table 4.

5.2.1.3 Curium

No data are available for trivalent Cm. The analogy with Am^{3+} is taken to estimate the distribution ratios for Cm.

5.2.2 Zirconium

No sorption data for Zr could be found. The Zr^{4+} ion exhibits a high first hydrolysis constant, a high z/d ratio and is closely grouped together with Th^{4+}, U^{4+}, Pu^{4+} and Np^{4+} in Figure 1. For these reasons, and since Zr is redox condition insensitive, we assign it the same distribution ratios as Th^{4+} in Table 4.

5.2.3 Nickel and Manganese

Very little reliable and appropriate sorption data for Ni on cement is currently available. The sorption data for Ni given in Table 4 has been taken from a well documented study of Ni sorption on cement/concrete by PILKINGTON & STONE (1990). Again there appear to have been problems with Ni sorption onto container walls, filtration effects and liquid to solid ratio effects. In most cases filtration was performed with an 0.45 µm membrane. (Such a large pore size is likely to produce relatively conservative R_d values because of colloidal material in the solutions in cement batch sorption tests). Distribution ratios in the range 0.5 to 1 $m^3\,kg^{-1}$ were measured. (The method used for wall sorption corrections to yield the most pessimistic distribution ratios given is considered to be far too conservative.). PILKINGTON & STONE (1990) give a best estimate value of 0.1 $m^3\,kg^{-1}$. We accept this value as being a realistic best estimate from their results and also because of the inbuilt conservative factor introduced by the filtration procedure chosen. The composition of the different concrete mixtures used had little or no effect on the distribution ratios measured. From this it would appear that the main sorbing phase is the hardened cement paste.

In a Finnish report (HIETANEN et al. 1984) Ni distribution ratios measured on crushed concrete (< 4 mm particle size) were in the range 0.5-3 $m^3\,kg^{-1}$. They conclude, on the basis of radiographs, that the Ni is equally distributed between cement phases and sand ballast. (This is in contrast to the deduction made above. The type of ballast material may have been important in these experiments).

For region III, section 4.3, we have assumed, somewhat pessimistically, that Ni sorption decreases in proportion to the quantity of CSH gel present. We give an average value of 0.01 $m^3 kg^{-1}$ for this region corresponding to a 90% removal of CSH gel.

No sorption data for Mn on cementitious materials have been found. In order to estimate a distribution ratio for Mn we again rely on Figure 1 where it can be seen that Mn lies grouped with Ni^{2+}, Co^{2+}, Fe^{2+}, Zn^{2+} and Cu^{2+}. The sorption of Mn is taken to be the same as for Ni^{2+} and therefore we assign a value of 0.1 $m^3 kg^{-1}$ (region I and II) and 0.01 $m^3 kg^{-1}$ (region III). It is also apparent from Figure 1 that the above group of elements lies below and to the left of the actinides. The selected value for Ni^{2+} and Mn^{2+} is 0.1 $m^3 kg^{-1}$ and those for the actinides lie in the range 1-5 $m^3 kg^{-1}$. This is qualitatively consistent with what would be expected from Figure 1.

5.2.4 Caesium

Caesium is the major radioactive alkali metal of importance in Nagra safety assessment studies and is probably the most studied of all radionuclides. There is no doubt that the sorption of Cs on hardened cement pastes at pH > 12.5 is weak. Cs diffusion measurements on hardened HTS (see Table 1) cement paste discs by SAROTT et al. (1992) yielded distribution ratios of ~$3 \cdot 10^{-3}$ $m^3 kg^{-1}$ at pH~13.3 in the equilibrium concentration range 10^{-10} to 10^{-8} M. ATKINSON et al. (1984) give a similar value for hardened sulphate-resisting cement paste. In the concentration range > 10^{-5} M, EWART et al. (1985) give a value of ~$2 \cdot 10^{-4}$ $m^3 kg^{-1}$. In region I, provided Cs concentrations do not exceed ~10^{-5} M, a distribution ratio of $2 \cdot 10^{-3}$ $m^3 kg^{-1}$ is selected. At higher concentrations, a reduction in R_d by a factor of ~10 would seem appropriate i.e. practically no sorption.

In region II, the concentrations of (Na, K) OH have decreased by orders of magnitude and their competitive effect on Cs sorption has been correspondingly diminished. Many authors have reported increased sorption at pH~12.5 and noted that the ballast, and not the cement paste, is the factor which determines the magnitude of the sorption (e.g. ANDERSSON et al. 1983; HIETANEN et al. 1984; EWART et al. 1985). Various values from ~0.01 to ~0.2 $m^3 kg^{-1}$ have been reported but it should be stressed that the type of ballast will be the deciding factor here and also the concentration of K (and Na). The sorption of caesium appears to be non linear and EWART et al. (1985) suggest the follo-

wing FREUNDLICH equation for the equilibrium concentration range ~$5 \cdot 10^{-6}$ to $5 \cdot 10^{-2}$ M:

$$X = 1.6\ [mg^{0.2}\ ml^{0.8}\ g^{-1}]\ C^{0.8}$$

where: X = amount of solute sorbed per unit mass of solid [mg/g]
C = equilibrium concentration in solution [mg/ml]

In view of this evidence, we consider that an increase in the distribution ratio for Cs for region II and III compared with region I, by one order of magnitude is justified.

5.2.5 Strontium and Radium

EWART et al. (1985) report Sr distribution ratios for hardened cement paste and concrete between 1 and $4 \cdot 10^{-3}$ $m^3\ kg^{-1}$ with very little dependency on concentration. ATKINSON & NICKERSON (1988) summarised the results from different types of tests (batch, "through" diffusion, in/out diffusion) and give a best estimate range for Sr of 3 to $6 \cdot 10^{-3}$ $m^3\ kg^{-1}$.

A value of 10^{-3} $m^3\ kg^{-1}$ is chosen to apply to both hardened cement paste and concretes. Most of the above results were obtained at pH~12.5 where Ca^{2+} concentrations (and hence the competitive effect on Sr sorption) is greatest. The value is therefore considered to be conservative and to apply to all three regions. As with Cs, the type of ballast chosen for conerete can potentially influence the sorption of Sr in a positive way. (The most likely sorption mechanism for Sr is ion exchange, hence the potential dependence on the ballast material).

BAYLISS et al. (1989) have measured distribution ratios for Ra on hardened sulphate-resisting cement paste at low concentrations. (The equilibrium concentrations were certainly $<< 10^{-6}$ M but could not be calculated from their data since the liquid to solid ratio was not given.) The sorption is significant, R_d ranging in value from $5 \cdot 10^{-2}$ to $5 \cdot 10^{-1}$ $m^3\ kg^{-1}$. There appears to be a slight, but by no means conclusive, concentration dependency. These results, when compared with those for Sr, seem at first sight to be rather surprising since from a chemical point of view Ra and Sr are expected to behave very similarly and to sorb by the same (cation exchange) mechanism. We can offer no definitive explanation for this difference in behaviour except to note that the equilibrium

concentrations in the two cases are very different. In EWART et al. (1985), the lowest equilibrium Sr concentration measured was $2 \cdot 10^{-6}$ M compared with the highest concentration for Ra of $< 10^{-8}$ M. Low initial concentrations for Ra were used in the sorption experiments because of its limited solubility in cement pore water: ~10^{-7} M. (Precipitation effects can be ruled out in these tests.) It may well be that in cement, as in many natural minerals, there are a range of sorption sites with different capacities and affinities. At very low concentrations, as in the case for Ra, sorption may be occurring on the more active sites (which may be "impurities" in the cement) leading to high R_d values whereas at higher concentrations these sites become saturated and sorption is occurring predominantly on the low affinity sites leading to lower R_d values (the case for Sr).

In addition to, or instead of, the above hypothesis, the hydrolysis behaviour of Ra may be playing a rôle. Alkali-earth metals show less tendency to hydrolyse in the order Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Ra^{2+}. If indeed the main sorption mechanism is cation exchange, then the formation of hydroxy species would tend to decrease sorption, and since Ra hydrolyses less than Sr this could explain the higher sorption of Ra.

Although we can only speculate as to why Ra and Sr appear to exhibit markedly different sorption behaviour, we consider that the experimental data presented by BAYLISS et al. (1989) are genuine results, and not due to artefacts or poor technique. We err on the conservative side and choose an R_d value for Ra across the three regions of $5 \cdot 10^{-2}$ m^3 kg^{-1}.

5.2.6 Iodide and Chloride

Iodine is assumed to be present as I^- under oxidising (Eh < 400 mV) and reducing conditions. Many studies on the sorption of I^- on cement paste at high pH indicate that its sorption is low but finite (see for example ANDERSSON et al. 1983; ALLARD et al. 1984; HIETANEN & ALALUUSUA 1984, ATKINSON & NICKERSON 1988; the review of LIU & von GUNTEN 1988; ATKINS & GLASSER 1990).

In most of the above, comparable experiments with I^- and Cs were carried out and almost invariably a higher sorption for I^- was measured. Also the results of ALLARD et al. (1984) indicate that I^- sorbs predominantly on the hardened cement paste phases. In view of the experimental evidence we consider it to be unreasonable to assign zero sorption to I^-. We assign a (conservative) value of

$2 \cdot 10^{-3}$ m^3 kg^{-1} in region I and II. In region III we assign a value of zero since I^- sorption appears to take place mainly on the cement phases which are disappearing.

In some recent Cl^- diffusion experiments on hardened HTS cement discs (SAROTT et al. 1992), the diffusion curves were analysed to yield distribution ratios for Cl^- of ~$2.5 \cdot 10^{-2}$ m^3 kg^{-1} within the concentration range $3 \cdot 10^{-5}$ to $3 \cdot 10^{-7}$ M existing across the thickness of the disc samples. It is not yet clear from these tests whether Cl^- is sorbing or being bound in phases such as aluminate monochloride. However, in these long term experiments a steady state diffusion condition was reached. This implies that the sorption or phase formation within the available pore space within the sample must also have reached a steady state. Under these conditions the retention of Cl^- in the cement matrix can be treated as sorption. Provided the inventory of Cl^- in the waste packages does not lead to pore water concentrations greater than ~10^{-5} M, the above data can be applied directly. (For Swiss waste types Cl^- concentrations of less than 10^{-5} M are anticipated).

Since the HTS cement type used by SAROTT et al. (1992) is directly relevant to the Swiss case we have selected $2 \cdot 10^{-2}$ m^3 kg^{-1} for the sorption of Cl^- in region I and II, and an order of magnitude less in region III (see section 5.1).

5.2.7 Carbon

The main sources of C-14 in a low- and intermediate level repository arise from activation products in the steels (from "reactor internals" waste and decommissioning waste), from $^{14}CO_3^{2-}$ on ion exchange resins and from organic waste streams (see, for example, JEFFERIES 1990).

C-14 in steel will be present predominantly as elemental carbon or as refractory metal carbides. Both of these forms of C-14 are extremely stable under the foreseen repository conditions (see for example SAMSONOV 1974) and are not expected to undergo any chemical reactions which would release C-14 into the aqueous phase. This source of C-14 will therefore not be considered further.

C-14 in organic waste streams will be incorporated in organic compounds which can potentially dissolve into the cement pore fluid of the near-field, directly or after degradation. A plurality of such organic compounds is expected.

At present, no statement on their sorption is possible, although there are indications that at least some of these organic compounds can sorb onto cement (see section 6.2.2).

The $^{14}CO_3^{2-}$ on the anion exchange resins can of course be released to the aqueous phase and it is this inventory of C-14 which is discussed in the following.

A number of studies e.g. ALLARD et al. (1981), BAYLISS et al. (1988), have investigated the "sorption" of C-14 as $^{14}CO_3^{2-}$ in cement/concrete systems. Generally, very high "sorption" values (~10 $m^3 kg^{-1}$) have been reported. A characteristic of such experiments is the long times required to reach a steady state "sorption" value. For instance, BAYLISS et al. (1988) carried out tests for times in excess of 200 days and even after this time $^{14}CO_3^{2-}$ was still being removed from solution. McKINLEY & SCHOLTIS (1991) make the comment that precipitation rather than sorption is probably being measured. BAYLISS et al. (1988) suggest isotope exchange with inactive CO_3^{2-} in $CaCO_3$ whereas ALLARD et al. (1981) consider a mixture of precipitation effects and isotope exchange.

It is our view that sorption, within the usual meaning of the term, is not being measured in these experiments and that the extent of removal of $^{14}CO_3^{2-}$ is very dependent on the particular cement/concrete system in question. Once the mechanism behind the removal of $^{14}CO_3^{2-}$ has been understood, then it is, in principle, possible to calculate an "effective sorption parameter" for $^{14}CO_3^{2-}$ for each particular system.

Most cementitious systems contain some $CaCO_3$ (HTS cement, for example contains ~0.6 wt-%, BERNER 1990). Because of the finely ground nature of cement powder, the $CaCO_3$ is also present in a finely divided form, more or less homogeneously distributed. The pore water in a hardened cement paste or concrete will be saturated with respect to $CaCO_3$ (albeit at low levels). The concentration of CO_3^{2-} ions will be pH dependent and influenced, via the solubility product, by the Ca^{2+} concentration arising from other saturated phases predominantly "$Ca(OH)_2$". This is the situation which $^{14}CO_3^{2-}$ from the anion exchange resins will "see".

In the long term, the dominant removal mechanism of $^{14}CO_3^{2-}$ from solution is isotope exchange with the finely divided solid $CaCO_3$ phase. We propose that an effective sorption parameter for $^{14}CO_3^{2-}$ can be calculated in the following manner.

Consider a cementitious mix containing Q kg of cement which in turn contains Z mol/kg of inactive carbonate, present, as mentioned earlier, in a homogeneously distributed finely divided form.

Let the inventory of C-14 from the anion exchange resins be ^{14}X mol of $^{14}CO_3^{2-}$ and the inactive CO_3^{2-} component, Y mol.

Let the concentration of CO_3^{2-} in the pore water be S mol l^{-1} (determined by the solubility limit of $CaCO_3$).

In such a system the total quantity of CO_3^{2-} present is therefore:

$$ZQ + {}^{14}X + Y \quad \text{moles} \tag{2}$$

of which SV mol are in solution, where V is the pore volume in litres.

Assume that the system is closed and, in time, becomes well mixed.

Given sufficient time the $^{14}CO_3^{2-}$ will distribute itself between solid phases containing CO_3^{2-} and the liquid phase by isotope exchange such that the ratio of $^{14}CO_3^{2-}$ to CO_3^{2-} in both phases is the same.

In equation (2), ZQ will normally be much greater than $^{14}X+Y$. The total carbonate inventory can then be approximated by ZQ and thus the ratio of active carbon to inactive carbon in the system is:

$$\frac{{}^{14}CO_3^{2-}}{CO_3^{2-}} = \frac{{}^{14}X}{ZQ} \tag{3}$$

At equilibrium, the same ratio will exist in the liquid phase and the concentration of $^{14}CO_3^{2-}$ in solution is therefore

$$S \cdot \frac{{}^{14}X}{ZQ} \quad \text{moles } l^{-1} \qquad \text{(liquid phase)} \tag{4}$$

In almost all conceivable cases the quantity of ^{14}C in the solid phase is much greater than the quantity in solution i.e.

$${}^{14}X \gg \frac{S \cdot {}^{14}X \cdot V}{ZQ} \tag{5}$$

Therefore, to a good approximation the quantity of $^{14}CO_3^{2-}$ in the solid phase is ^{14}X mol. Thus, the quantity of $^{14}CO_3^{2-}$ per kg of cement is simply:

$$\frac{^{14}X}{Q} \text{ moles kg}^{-1} \qquad \text{(solid phase)} \qquad (6)$$

Hence, using equations (4) and (6) an effective sorption coefficient for ^{14}C as $^{14}CO_3^{2-}$ can be calculated i.e.

$$\text{Effective } R_d(^{14}CO_3^{2-}) = \frac{\frac{^{14}X}{Q}}{\frac{S \cdot ^{14}X}{ZQ}} = \frac{Z}{S} \text{ l kg}^{-1} \qquad (7)$$

Given the assumptions stated, the conclusion is that the effective sorption parameter for C-14 as $^{14}CO_3^{2-}$ in any system after long times is simply the ratio of the quantity of CO_3^{2-} contained in the cement (Z mol kg^{-1}) to the solubility limit of $CaCO_3$ in the pore water solution. The effective sorption parameter for C-14 (as $^{14}CO_3^{2-}$) is fixed by the system itself and is independent of the $^{14}CO_3^{2-}$ inventory.

Just as a minor illustration of the above, BAYLISS et al. (1988) present the following data:

The solubility limit for $CaCO_3$ (S) in their pore water at pH 12.2 to 12.6 was $8.5\ 10^{-5}$ mol l^{-1} and the stable carbon content (assumed to be present as carbonate) in the samples was given as 7.4 wt-% which yields a CO_3^{2-} content of ~37 wt-%. i.e. Z ~6 mol CO_3^{2-} kg^{-1}. (Note that the large quantities of CO_3^{2-} arise from the limestone aggregate).

Hence, by applying equation (7), the effective $R_d(^{14}CO_3^{2-})$ is predicted to be $7 \cdot 10^4$ l kg^{-1} (70 m^3 kg^{-1}).

After ~100 days BAYLISS et al. (1988) measured an R_d of ~10^4 l kg^{-1} (10 m^3 kg^{-1}) and the R_d vs time plot showed no indications of levelling off.

Equation (7) assumes that the whole of the solid CO_3^{2-} is available for exchange with $^{14}CO_3^{2-}$ which, when the carbonate is present in a very finely divided form and sufficient time is available for equilibration, may be a realistic assumption. However, for effective sorption parameter calculations for $^{14}CO_3^{2-}$ for safety analyses we suggest that the result from equation (7) should be re-

duced by a factor of ~10. (The suggested reduction implies that about ten percent of the mass of solid CO_3^{2-} is available for isotope exchange).

No distribution ratios for C-14 have been given in Table 4 since they will be system dependent and can be calculated by the method shown for each individual case. In Appendix F distribution ratios of CO_3^{2-} as a function of pH are calculated for the degradation of HTS cement in both $NaHCO_3$ and NaCl type groundwaters.

With respect to the degradation of cement by a marl pore-water it should be noted that BERNER (1990) has predicted an increasing $CaCO_3$ solid phase content in the cement throughout its lifetime. This will influence the sorption of C-14 in a positive direction.

5.2.8 Niobium

Only one study on the sorption of Nb on cementitious material was found (PILKINGTON & STONE 1990). The range measured for R_d(Nb) was 0.5 to 80 $m^3\ kg^{-1}$ with a best estimate value of 1 $m^3\ kg^{-1}$. Because of the experimental difficulties reported to be associated with these measurements, and the rather erratic sorption results as a function of liquid to solid ratio, we select the minimum measured distribution ratio for Nb of 0.5 $m^3\ kg^{-1}$ as a conservative value. The solubility of Nb_2O_5 may be quite high (see PILKINGTON & STONE 1990) and R_d measurements were made at "trace" concentration levels. The above conservative value was chosen to allow for possibly lower sorption at higher concentrations. Nb exists primarily as $Nb(OH)_6^-$ across the whole pH/Eh range of interest (see BAES & MESMER 1986). Following the discussion in section 5.1 we assume that sorption is occurring predominantly on the CSH phases and a distribution ratio of $5 \cdot 10^{-2}$ $m^3\ kg^{-1}$ is estimated for region III.

5.2.9 Tin

As with Nb, only one set of sorption data for Sn was found (BAYLISS et al. 1989). The distribution ratios measured depended very strongly on, amongst other factors, phase separation. (Unfiltered, R_d(Sn) ~0.5 $m^3\ kg^{-1}$; 0.45 μm filter, ~36-44 $m^3\ kg^{-1}$; 30,000 MWCO filter, 50-62 $m^3\ kg^{-1}$). In the same paper, solubility data are reported for SnO, SnO_2 and Sn metal as solid phases. The solubilities were high, ~10^{-4} M and similar for all of these solid phases, which suggests

that the same solid phase in each case was ultimately determining the solubility limit. Sn solubilities were not affected by the range of redox conditions examined. Solubility results presented in a later paper (BAYLISS et al. 1991) suggest that cassiterite (SnO_2) may be the solubility limiting phase with a solubility limit in the range 10^{-9} to 10^{-6} M, i.e. a different, and lower solubility limit than in their earlier paper.

It appears from this work that tetravalent Sn is stable under repository conditions. By analogy with the tetravalent actinides and Zr, plus the tendency of Sn^{4+} to form very strong hydroxy complexes, significant sorption for Sn on cementitious materials is to be expected. On this basis and the measurements of BAYLISS et al. (1989), we have selected a conservative R_d(Sn) of 1 $m^3\ kg^{-1}$ for regions I and II falling to 10^{-1} $m^3\ kg^{-1}$ in region III (see section 5.1) with no redox dependency.

5.2.10 Technetium

Sorption data for Tc on cementitious materials are sparse. Under oxidising conditions, distribution ratios of TcO_4^- in the range 10^{-3} to 10^{-2} $m^3\ kg^{-1}$ have been reported (see for example ALLARD et al. 1985). We have selected a value of 10^{-3} $m^3\ kg^{-1}$ for regions I and II and zero for region III.

Under "reducing" conditions technetium is present as hydrolysed Tc (IV) species and the solubility limit over technetium dioxide has been measured to be ~10^{-7} M (PILKINGTON 1990). In some recent work, using Tc (IV) at trace levels (< 10^{-11} M) and sodium dithionite as reducing agent, distribution ratios of ~5 $m^3\ kg^{-1}$ have been reported (BAYLISS et al. 1991). For similar reasons as those given for Sn, Tc might be expected to sorb strongly under reducing conditions at high pH. As a conservative value we select a distribution ratio under reducing conditions of 1 $m^3\ kg^{-1}$ for region I and II, falling to 10^{-1} $m^3\ kg^{-1}$ in region III (see section 5.1).

5.2.11 Selenium, Palladium and Molybdenum

No sorption data at all could be found for Se, Pd and Mo in cement systems.

Under the redox and pH range appropriate to the repository Se and Mo are likely to exist predominantly as anionic species (SeO_4^{2-}/SeO_3^{2-}/HSe^- and

MoO_4^{2-}). Because no sorption data were found, a nominal value of 10^{-4} m^3 kg^{-1} was assigned to both across the whole range of conditions for region I and II, and zero for region III.

The currently available thermodynamic data (see for example BAEYENS & McKINLEY 1989) would predict relatively low Pd solubilities at high pH for PdO. The major aqueous species is likely to be $Pd(OH)_2^0$. For the sorption of Pd we take its behaviour to be analogous to that of Ni^{2+} and assign the same values.

5.2.12 Silver

No sorption data are available for Ag. We assume that Ag is present predominantly as Ag^+. In region I the competitive effect of Na and K will be extremely strong and therefore weak sorption would be expected. In region II and III such a competitive effect will diminish and sorption is more likely to be determined by the ballast material rather than the cement paste itself (c.f. caesium). Because of the lack of data, we assign a nominal value of 10^{-3} m^3 kg^{-1} across the whole range.

5.2.13 Lead

BAYLISS et al. (1988) have measured the sorption of Pb on crushed sulphate-resisting portland cement (SRPC) and ordinary portland cement/blast furnace slag (OPC/BFS) pastes in the concentration range from 10^{-9} M to ~10^{-3} M and within a (reported) Eh range of +50 to -500 mV. The main findings of this work were that the sorption is concentration and cement composition dependent. Phase separation had a strong influence on sorption (Pb colloids suggested) but no Eh dependency was reported. From the data presented in this paper we have chosen a conservative R_d value of 0.5 $m^3 kg^{-1}$ measured at Pb concentrations near the solubility limit on SRPC based cement blend using a 0.45 µm filter for phase separation. Higher values would be expected at lower Pb concentrations and any filtration action by bulk cement would also increase the retention of Pb. The sorption in regions I and II is considered to be the same whereas a factor of 10 reduction is proposed for region III.

5.2.14 Tritium

Tritium will predominantly be present in the aqueous phase as a dissolved gas or as tritiated water. Tritium, in the dissolved gaseous form, will not sorb at all, whereas tritium as tritiated water can undergo isotope exchange reactions with bound protons, OH^- ions and water. The "sorption" resulting from isotope exchange will, to a first approximation, be dependent upon the ratio of "bound accessible" water to free water (c.f. $^{14}CO_3^{2-}$ behaviour in section 5.2.7). Although a considerable quantity of water is "bound" during the hydration of cement, it is an open question as to what proportion of this water is accessible. Although some (low) sorption of tritium is likely, we set the distribution ratio to zero over the three regions.

5.2.15 Summary of Sorption Data

Based on the information and discussions given in sections 5.2.1 to 5.2.14 we present in Table 4 a summary of distribution ratios for the radionuclides listed in Table 2 as a function of cement degradation (sections 4.3 and 5.1) and redox (section 4.2) for an **"unperturbed"** repository (see Chapters 6 to 12 for estimates of the influence on sorption of various "perturbance" factors).

Table 4: Sorption Database.

Element	State of Cement Degradation (see Fig. 2)					
	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					
Cl	$2 \cdot 10^{-2}$	$2 \cdot 10^{-2}$	$2 \cdot 10^{-2}$	$2 \cdot 10^{-2}$	$2 \cdot 10^{-3}$	$2 \cdot 10^{-3}$
Mn	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	10^{-4}	10^{-4}	10^{-4}	10^{-4}	0	0
Sr	10^{-3}	10^{-3}	10^{-3}	10^{-3}	10^{-3}	10^{-3}
Zr	5	5	5	5	1	1
Nb	$5 \cdot 10^{-1}$	$5 \cdot 10^{-1}$	$5 \cdot 10^{-1}$	$5 \cdot 10^{-1}$	$5 \cdot 10^{-2}$	$5 \cdot 10^{-2}$
Mo	10^{-4}	10^{-4}	10^{-4}	10^{-4}	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	10^{-3}	10^{-3}	10^{-3}	10^{-3}	10^{-3}	10^{-3}
Sn	1	1	1	1	10^{-1}	10^{-1}
I	$2 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	0	0
Cs	$2 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	$2 \cdot 10^{-2}$	$2 \cdot 10^{-2}$	$2 \cdot 10^{-2}$	$2 \cdot 10^{-2}$
Pb	$5 \cdot 10^{-1}$	$5 \cdot 10^{-1}$	$5 \cdot 10^{-1}$	$5 \cdot 10^{-1}$	$5 \cdot 10^{-2}$	$5 \cdot 10^{-2}$
Ra	$5 \cdot 10^{-2}$	$5 \cdot 10^{-2}$	$5 \cdot 10^{-2}$	$5 \cdot 10^{-2}$	$5 \cdot 10^{-2}$	$5 \cdot 10^{-2}$
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	5	5	5	5	1	1
Cm	5	5	5	5	1	1

The elements are listed according to increasing atomic number. All distribution ratios are in units of $m^3\ kg^{-1}$. Data selection procedures are described in the text.

6 INFLUENCE OF CELLULOSE ON SORPTION IN CEMENT

6.1 Introduction

A low- and intermediate-level radioactive waste repository (L/ILW repository) may contain a large proportion of solid organic matter of various types (ALDER & McGINNES 1994) (see also Table A-1, Appendix A). Under the high pH conditions existing in the repository, this organic matter will undergo degradation thereby releasing organic molecules into the aqueous phase. Such soluble organic degradation products have the potential to complex with radionuclides and hence to influence radionuclide speciation, solubility limits and sorption processes. The central problem with which we are concerned here is the latter, and how this may be estimated/quantified.

The only relevant source of experimental data on this topic is the ongoing work of AEA at Harwell which was started in the mid eighties. Having to rely on the data produced from one source is intrinsically undesirable but in this case there is no choice.

Broadly speaking, the research of AEA at Harwell has shown that the degradation products from cellulose containing materials (e.g. wood, paper) have a far greater influence on radionuclide chemistry/sorption than those from other organic materials such as plastics, which are also present. Consequently we will discuss the potential influence of cellulose degradation products on sorption first and the effect of "plastics" and other organic complexants in the following chapter.

6.2 The Influence of the Degradation Products from Cellulose on Radionuclide Sorption in Cement

6.2.1 Background

It is not the intention in this chapter to review the many tens, if not hundreds, of experiments which have been carried out by AEA at Harwell. However, a very brief description of the general types of tests which have been carried out may be useful.

Basically, they have performed accelerated chemical degradation tests, at 50 to 80°C, of cellulose materials incorporated in various cement mixtures for times

as long as ~500 days. Cellulose loadings in the range 0.1 to 10 wt-% have been used and the influence of γ and α radiation on the degradation process has been investigated at dose rates far higher than expected in the real L/ILW repository situation. (An important general conclusion from these investigations was, that chemical degradation was by far the most important process under repository conditions.) The leachates from such experiments were used in further tests in which radionuclide solubility limits and sorption were measured. The bulk of the work was performed with Pu though there are data available for Am, Th, U, Np, Tc and Ni.

Increases in solubility limits by several orders of magnitude have been reported in these leachates (for Pu in particular). Relatively fewer data are available for the effect on sorption, where decreases of two to three orders of magnitude (for Pu) have been reported i.e. the influence of cellulose degradation products on solubility limits appears to be far greater than on sorption, EWART et al. (1991). These results have been **interpreted by AEA** at Harwell in terms of a powerful complexation reaction between the radionuclide and an organic degradation product from cellulose. It is important to realise that this organic molecule has not, as yet, been identified. In simulation tests it has been shown that iso-saccharinic acid, for example, has an apparently similar influence on Pu solubilities to "ingredient X" in the cellulose leachates. The degradation mechanism of cellulose under alkaline conditions and the possible end products are known in general but not in detail (see GREENFIELD et al. 1990; ALLARD & BORÉN 1991).

Though the above work has indicated that there is a "strong effect" on solubility and sorption of cellulose degradation products, there are still many open questions. To our knowledge no general principles from the "measured effects" have been distilled out of these investigations. Though the experiments themselves are relatively simple, they are virtually impossible to interpret because many (unquantified) factors are influencing the end result e.g. kinetics (short experimental time scales in sorption, precipitation/dissolution tests), dilution effects, sorption capacities of the cement for organics and radionuclides, saturation effects, identity and concentration of the complexing organic molecule, whether this organic molecule is the end member of the degradation chain or whether degradation continues further, lack of thermodynamic complexation constant measurements/data.

The message which we wish to convey is that though AEA at Harwell has reported a strong effect of cellulose degradation products on radionuclide solubility limits and sorption behaviour in their tests, **for the experimental procedures used,** the origin of these increases (decreases respectively) has, in our view, not been unambiguously identified and there is no convincing model, with the associated thermodynamic data, which is capable of describing the data.

As stated previously, the results of AEA at Harwell are the only data available on this topic. In order to develop a procedure for estimating the influence of cellulose degradation products on the sorption of radionuclides on the basis of the limited data available, we are forced to make certain assumptions.

Assumption 1

We assume that the data from AEA at Harwell are valid and that the effects measured are primarily due to an extremely strong complexation reaction between radionuclides and an "organic molecule X" which results from the degradation of cellulose. (There could however be more than one strongly complexing organic molecule.)

Assumption 2

We take iso-saccharinic acid to be the model end member of cellulose degradation i.e. we assume that the complexation characteristics of the "organic molecule X" are very similar to that of iso-saccharinic acid (see GREENFIELD et al. 1992).

Assumption 3

We assume that the data given by GREENFIELD et al. (1992) in Figure 5 of their report, and partly reproduced in Figure 3 here, represent the increase in Pu solubility through complexation by iso-saccharinic acid ("organic molecule X").

Assumption 4

It is known from literature that, in general, the alkaline degradation of cellulose can cease due to a competing reaction called a "stopping reaction" (see VAN LOON 1993 and references therein) leading to a product which is stable under alkaline conditions. However, the degradation of cellulose under the conditions in a cementitious repository near-field is not yet completely understood. For this reason, and because we have not seen any reports which indicate that cellulose degradation product concentrations may be solubility limited in the repository environment, we assume, as a starting condition for the calculations given later, that all the available cellulose in each sub-system will ultimately degrade completely. Following assumption 2, we further assume that cellulose degrades to the equivalent quantity of iso-saccharinic acid and that no further degradation occurs.

It should be recognised that many of these assumptions are particularly stringent, and in all probability represent an extreme worst case situation.

In the following we first consider the sorption of iso-saccharinic acid ("organic molecule X") on cement. This will influence the free concentration of organic complexant available for complexation with radionuclides as a function of the cellulose loading in each waste canister. The effect of cellulose degradation products (iso-saccharinic acid) on sorption is then discussed for the general case.

6.2.2 Sorption of Iso-Saccharinic Acid on Cement

In GREENFIELD et al. (1992) an experiment is described in which a 10^{-2} M solution of iso-saccharinic acid is contacted with a cement mixture at a very low liquid to solid ratio of 3:2. Aliquots of the solution were taken from this experiment as a function of time and the Pu solubility in each aliquot was measured as an indicator of the complexation capacity (concentration) of iso-saccharinic acid (the actual concentration of iso-saccharinic acid was not measured). The form of the curve, reproduced in Figure 4, suggests that iso-saccharinic acid is either degrading to a less powerful complexant or a precipitation process is occurring or it is sorbing on the cement. The former two possibilities are considered to be unlikely since previous experiments (also described in GREENFIELD et al. 1992) showed iso-saccharinic acid to be stable in similar solutions.

However, they cannot be ruled out. With the aid of Figure 3, Pu solubility limits in Figure 4 can be converted to equivalent iso-saccharinic acid concentrations. From such a cross plot, and under the assumption that the decrease in iso-saccharinic acid is indeed due to sorption, an R_d(iso-saccharinic acid) of ~1 $m^3 kg^{-1}$ can be estimated at a iso-saccharinic acid concentration of ~10^{-5} M. The curve in Figure 4 has not yet reached steady state, so the value of ~1 $m^3 kg^{-1}$ is probably an underestimate of the sorption.

Assumption 5

These experiments were carried out on an OPC/BFS blend cement and we assume that the distribution ratio given above can also be applied to Swiss cement blends (see also section 3).

From the data available it is not possible to deduce how the sorption of iso-saccharinic acid varies with concentration. One approach would be to make very conservative assumptions i.e. to assume that the sorption of iso-saccharinic acid is constant up to concentrations of the order 10^{-5} M with a value of ~1 $m^3 kg^{-1}$ (see above) and thereafter that the sorption capacity of the cement remains constant at ~$1 \cdot 10^{-2}$ mol kg^{-1}. The sorption capacity is obtained from the product: distribution ratio × equilibrium iso-saccharinic acid concentration, and represents the maximum amount of iso-saccharinic acid which can be sorbed by the cement (sorption capacity = $R_d \cdot C = 1 \cdot 10^3$ (l kg^{-1}) · $10^{-5} = 1 \cdot 10^{-2}$ mol kg^{-1}).

The question of sorption capacity can be approached from another point of view. If a cement surface area of ~80 $m^2 g^{-1}$ is taken (ROWAN et al, 1988) together with a conservative estimate for the site density of ~$4 \cdot 10^{-6}$ mol of sites m^{-2} (DAVIES & KENT, 1990), this would give a site capacity for cement of ~$3.2 \cdot 10^{-1}$ mol of sites kg^{-1}. (The site density could easily be a factor of two lower and two to three times higher (GRAUER 1990)).

The initial very conservative estimate of the "iso-saccharinic acid site capacity" of ~$1 \cdot 10^{-2}$ mol kg^{-1} is only ~3% of a conservative estimate of the total site capacity. Although we have no direct supporting evidence, we would propose that a more realistic estimate of the site capacity of cement for iso-saccharinic acid might be of the order of 10^{-1} mol kg^{-1}.

Assumption 6

The above implies that, for calculation purposes, a constant R_d of 1 $m^3\,kg^{-1}$ is assumed up to an iso-saccharinic acid concentration of $1 \cdot 10^{-4}$ M. At equilibrium iso-saccharinic acid concentrations above this level, a constant site capacity of 10^{-1} mol kg^{-1} is assumed.

The relevance of the above is that each waste canister, containing different cellulose loadings, can be treated separately, and under assumptions 1-6, the maximum concentrations of iso-saccharinic acid in the pore solution can be estimated. (As will be shown later, the concentration of iso-saccharinic acid will effectively determine the magnitude of sorption for many radionuclides).

As an example of how this functions, consider a waste canister with total porosity ε which contains X kg cement, Y kg cellulose and has a volume V litres. (Note, in the cases where trass (Rhenish volcanic tuffs) is present, this mass can be included with the quantity of cement to yield an average composition for the cement + trass mixture, which is not far from that of the cement alone; BERNER 1990).

If all the cellulose present degrades to iso-saccharinic acid (assumptions 2 and 4), the number of mol of iso-saccharinic acid present in the system is:

$$\frac{Y \cdot 10^3}{165} \qquad (8)$$

(165 is the approximate molecular weight of iso-saccharinic acid). If we represent the equilibrium concentration of iso-saccharinic acid in the pore water after sorption by C_{org}, two mass balance equations can be written from which C_{org} can be calculated.

Under the condition that $C_{org} < 1 \cdot 10^{-4}$ M then

$$V \cdot \varepsilon \cdot C_{org} + R_d \cdot X \cdot 10^3 \cdot C_{org} = \frac{Y \cdot 10^3}{165} \qquad (9)$$

where $R_d = 1\ m^3 kg^{-1}$

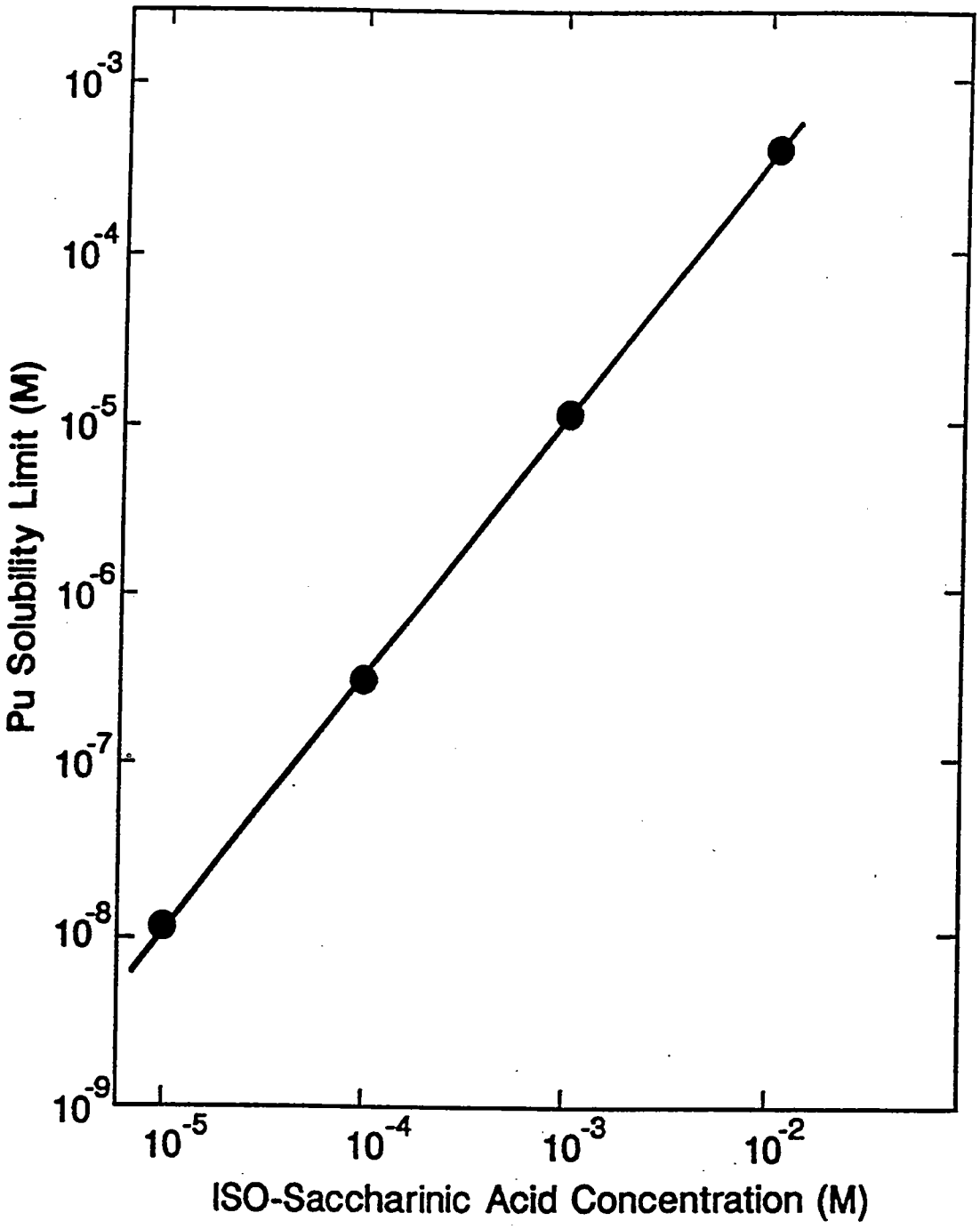

Fig. 3: Plutonium solubilities in solutions of iso-saccharinic acid at pH 12. (From GREENFIELD et al. 1992)

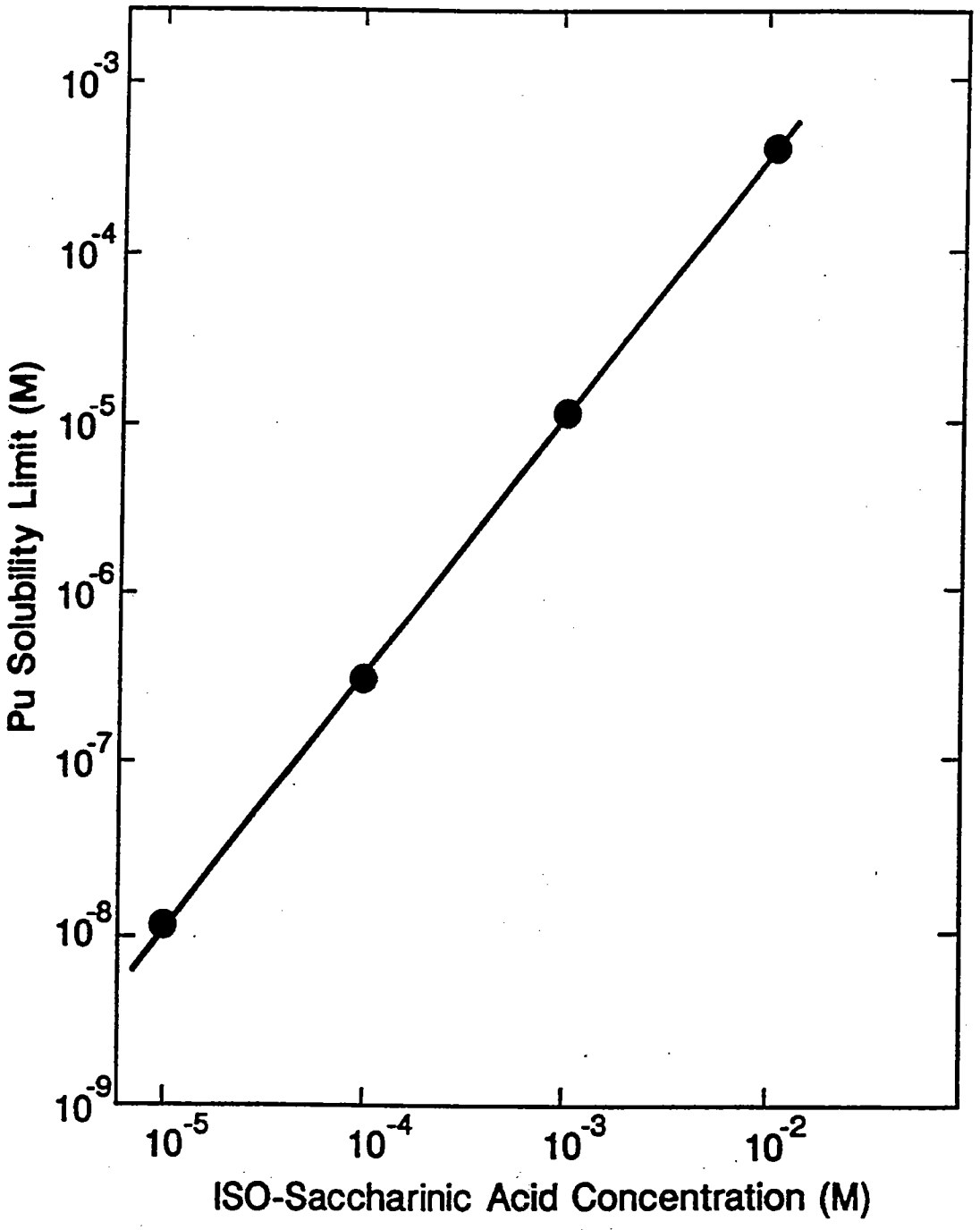

Fig. 3: Plutonium solubilities in solutions of iso-saccharinic acid at pH 12. (From GREENFIELD et al. 1992)

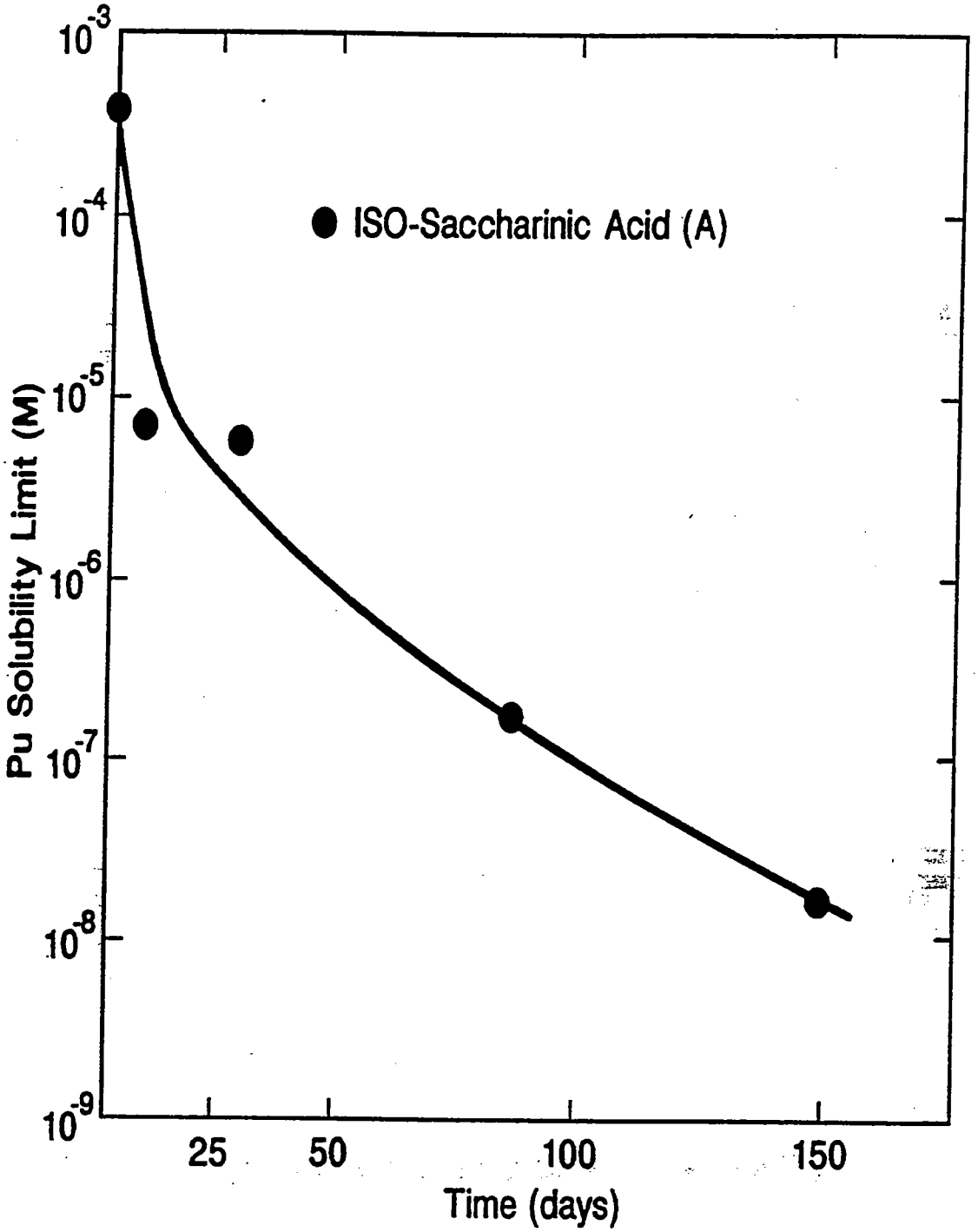

Fig. 4: Plutonium solubilities measured as a function of time in aliquots taken from a 10^{-2} M iso-saccharinic acid solution in contact with cement. (From GREENFIELD et al. 1992)

If $C_{org} > 1 \cdot 10^{-4}$ M then the capacity of the cement (10^{-1} mol kg^{-1}) has to be used instead of R_d and the equation becomes:

$$V \cdot \varepsilon \cdot C_{org} + 10^{-1} \cdot X = \frac{Y \cdot 10^3}{165} \qquad (10)$$

Which of the two mass balance equations is the appropriate one for calculating C_{org} for a specific system can only be seen by carrying out the calculations.

In general, but depending on the particular conditions, it will be seen that for cellulose loadings in the region of 1.0 wt-% or more, the **calculated** iso-saccharinic acid concentration will rise very rapidly to large values. Whether these large concentrations have any meaning in reality is open to question, but in practice calculated values > 10^{-3}-10^{-2} M effectively mean that for many radionuclides the sorption is zero (see next section).

6.2.3 Effect of Cellulose Degradation Products on Radionuclide Sorption

In the previous section we have outlined a means of estimating the concentration of iso-saccharinic acid corresponding to complete degradation of all the available cellulose in a specific waste canister. Figure 3 (taken from GREENFIELD et al. 1992), relates the increase in Pu concentration to the (effectively free) concentration of iso-saccharinic acid in solution. The slope of this plot is ~1.5 and cannot be interpreted in terms of a single Pu-organic complex of the general form Pu_nL_m. The results, as presented in Figure 3, do not alone allow any predictions to be made regarding Pu sorption. They can however be used to make such predictions, based on the following procedure.

Assumption 7

We assume here, and in what follows, that (in general) the very low concentrations of radionuclides expected in the individual canisters in a radioactive waste repository (often inventory limited) fall within a concentration range for which their sorption is linear i.e. independent of concentration.

Consider an experiment in which the sorption of a radionuclide, B, is measured in a system where organic ligands are absent. The distribution ratio, $R_d(B)$, is then given by:

$$R_d(B) = \frac{\text{Quantity of B sorbed per unit mass of solid}}{\text{Equilibrium concentration of B in solution}} \tag{11}$$

$$= \frac{B_{sorb.}}{[B]_{sol.}} \tag{12}$$

The term $[B]_{sol.}$ is the sum of all inorganic B species existing in solution.

Consider exactly the same experiment as above except that the sorption of B is measured in the presence of an organic ligand, L, which forms complexes of the form B_nL_m with radionuclide B. The concentration of such complexes in solution at equilibrium after sorption is simply:

$$\sum_{n=1}^{N}\sum_{m=1}^{M}[B_nL_m] \tag{13}$$

If the B_nL_m complexes do not sorb, it is easy to show that (Appendix B, equation (9-B)):

$$R'_d(B) = \frac{R_d(B)}{\dfrac{[B]'_{sol.} + \sum_{n=1}^{N}\sum_{m=1}^{M} n \cdot [B_nL_m]}{[B]'_{sol.}}} \tag{14}$$

where $R'_d(B)$ and $[B]'_{sol.}$ are, respectively the sorption of B and the sum of all inorganic B species in solution in the presence of a complexing organic ligand at equilibrium.

The term

$$\frac{[B]'_{sol.} + \sum_{n=1}^{N}\sum_{m=1}^{M} n \cdot [B_nL_m]}{[B]'_{sol.}} = \frac{[B]_{Tot.Aqu.}}{[B]'_{sol.}} \tag{15}$$

is the factor by which sorption is reduced in the presence of a complexing ligand concentration [L] i.e. the sorption reduction factor ($[B]_{Tot.Aqu.}$ is the total

concentration of B in solution). The aim here is to deduce such sorption reduction factors for the safety relevant radionuclides given in Table 2 in the presence of different concentrations of cellulose degradation products.

These data do not exist. The only information available are plutonium solubility limits (S.L.) as a function of iso-saccharinic acid concentration, Figure 3, i.e. $[Pu(org)]_{S.L.} = [Pu]_{S.L.} + \Sigma$ [Pu organic complexes] in the presence of a plutonium solid phase.

In Appendix B, equation (22-B), we show that, in general, the value of the ratio $[B]_{Tot.Aqu.}/[B]'_{sol.}$ (equation (15)) for 1:m complexes, at a given water chemistry and ligand concentration, is not dependent on the absolute value of $[B]'_{sol.}$. This means that we can calculate the ratio $[Pu(org)]_{S.L.}/[Pu]_{S.L.}$ ($[Pu]_{S.L.} \sim 5 \cdot 10^{-10}$ M, Table 6) using the data from Figure 3, and the value of this ratio is the same, at the same free ligand concentration [L], for other $[Pu]'_{sol.}$ concentrations i.e. for situations where no Pu solid phase is present. This can be summarised by writing:

$$[Pu]'_{sol.} + \sum_{m=1}^{M} [Pu_1 L_m] = \frac{[Pu]_{Tot.Aqu.}}{[Pu]'_{sol.}} = \frac{[Pu(org)]_{S.L.}}{[Pu]_{S.L.}} \qquad (16)$$

$[Pu(org)]_{S.L.}/[Pu]_{S.L.}$ is defined as the solubility enhancement factor for Pu at a given free organic ligand concentration, [L]. From the above, this is also equal to the sorption reduction factor, equations (14) and (15). Equation (14) can therefore be rewritten as:

$$R'_d(\text{Pu, organics}) = \frac{R_d(Pu)}{\dfrac{[Pu(org)]_{S.L.}}{[Pu]_{S.L.}}} \qquad (17)$$

$[Pu(org)]_{S.L.}/[Pu]_{S.L.}$ can be calculated at different iso-saccharinic acid concentrations using the data in Figure 3.

In order to illustrate how the above works in practice, we have used the data in Figure 3 in conjunction with equation (17) to construct Table 5.

Table 5: Calculated solubility enhancement factors[1)] and distribution ratios for Pu as a function of iso-saccharinic acid concentration.

Free iso-saccharinic acid concentration [L] (M)	Measured Pu solubility limit in presence of organics $[Pu(org)]_{S.L.}$ (M)	Ratio $[Pu(org)_{S.L.}/[Pu]_{S.L.}$ (solubility enhancement factor)*	R'_d(Pu, organics) in presence of organics at concentration [L] see equation (17) ($m^3\ kg^{-1}$)
10^{-6}	(linearly extrapolated value) $\sim 5 \cdot 10^{-10}$	~1	**5
10^{-5}	$\sim 10^{-8}$	~20	$\sim 2.5 \cdot 10^{-1}$
10^{-4}	$\sim 2.5 \cdot 10^{-7}$	~500	$\sim 10^{-2}$
10^{-3}	$\sim 10^{-5}$	~20'000	$\sim 5 \cdot 10^{-4}$
10^{-2}	$\sim 5 \cdot 10^{-4}$	$\sim 10^{6}$	~0

* $[Pu]_{S.L.}$ = Pu solubility limit in an artificial cement pore water at pH~12.5 = $5 \cdot 10^{-10}$ M (see Table 6)

** Unperturbed distribution ratio for Pu (Table 4, region II, reducing conditions)

Results for iso-saccharinic acid, of the sort presented in Figure 3, have only been reported for Pu. Consequently, it is not possible to deduce equivalent data to those given in Table 5 for other safety relevant radionuclides using a similar method. Nevertheless such data are required.

Given this situation we are forced to adopt a different procedure. Consider the data given in Table 6, taken from GREENFIELD et al. (1992). Here the solubility limits for five actinides, including Pu, and Tc are given for experiments in which the measurements were made in solutions with the same levels of cellulose degradation products.

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1) Note that the solubilty enhancement factor has the same value as the sorption reduction factor, see equation (17).

The Pu solubility limit, in the presence of cellulose degradation products, is given as ~10^{-5} M and from Table 5 this corresponds to an iso-saccharinic acid concentration of ~10^{-3} M. This iso-saccharinic acid concentration is taken as a point of comparison between Pu and the other radionuclides. Solubility enhancement factors are calculated for each radionuclide at 10^{-3} M iso-saccharinic acid from the data given in Table 6. The respective solubility enhancement factors are then expressed as a ratio with respect to the value for Pu, column 3, Table 7.

Note that GREENFIELD et al. (1992) assign valence states to the actinides and Tc (Table 6). This implies, that the redox conditions were either measured/known in their experiments or that the conditions were sufficiently reducing to produce the valence states given. From the level of experimental detail provided, we could not make any judgements as to whether the assigned valence states were likely or not. We therefore reproduce their data "as given".

Table 6: Actinide and Tc solubility data taken from GREENFIELD et al. (1992), Table 2.

Radionuclide	Radionuclide Solubility Limit (M)	
	Cellulose	None
Plutonium (IV)	10^{-5}	$5 \cdot 10^{-10}$
Americium (III)	10^{-6}	10^{-10}
Thorium (IV)	10^{-5}	$< 8 \cdot 10^{-10}$
Uranium (VI)	$5 \cdot 10^{-4}$	$5 \cdot 10^{-6}$
Neptunium (IV)	10^{-6}	10^{-8}
Technetium (IV)	10^{-6}	10^{-7}

Table 7: Solubility enhancement factors and their ratios with respect to the value for Pu (10^{-3} M iso-saccharinic acid, valence states as given in GREENFIELD et al. 1992).

Radionuclide	Solubility enhancement factors (from Table 6)	Solubility enhancement factors compared with Pu
Plutonium (IV)	$2 \cdot 10^{4}$	-
Americium (III)	10^{4}	~1
Thorium (IV)	$\sim 2 \cdot 10^{4}$	~1
Uranium (VI)	10^{2}	$\sim 5 \cdot 10^{-3}$
Neptunium (IV)	10^{2}	$\sim 5 \cdot 10^{-3}$
Technetium (IV)	10	$\sim 5 \cdot 10^{-4}$

In Table 7 the ratio of solubility enhancement factors with respect to Pu are given for an iso-saccharinic acid concentration of 10^{-3} M. In order to widen this comparison to other concentrations so as to enable the distribution ratios given in Table 4 to be modified as a function of iso-saccharinic acid concentration in a similar way given previously for Pu (Table 5), a further assumption is required:-

Assumption 8

We assume that most radionuclides (see later) behave in an analogous manner to Pu with respect to solubility enhancement as a function of iso-saccharinic acid concentration but the curves are displaced from one another by the factors given in column 3, Table 7. We further assume that the solubility enhancement factors calculated for Pu are the same for oxidising and reducing conditions.

Solubility limit enhancement factors for Pu can be deduced from Figure 3 and are given in column 2 Table 8 as a function of iso-saccharinic acid concentration. Equivalent factors for the other radioelements in Table 8 are calculated by multiplying the value for Pu by the factor given in column 3, Table 7.

Table 8: Calculated solubility enhancement factors as a function of iso-saccharinic acid concentration (valence states of actinides and Tc as given in GREENFIELD et al. 1992).

Iso-saccharinic acid concentration (M)	Solubility enhancement factors					
	Pu(IV)	Am(III)	Th(IV)	U(VI)	Np(IV)	Tc(IV)
10^{-6}	1	1	1	1	1	1
10^{-5}	20	20	20	1	1	1
10^{-4}	500	500	500	~2	~2	1
10^{-3}	$2 \cdot 10^4$	$2 \cdot 10^4$	$2 \cdot 10^4$	$\sim 10^2$	$\sim 10^2$	~10
10^{-2}	10^6	10^6	10^6	$\sim 5 \cdot 10^3$	$\sim 5 \cdot 10^3$	$\sim 5 \cdot 10^2$

As an illustration, consider a waste canister containing cellulose, which, when fully degraded, leads to an equivalent iso-saccharinic acid concentration of 10^{-2} M.

From Table 5, column 3, the solubility enhancement factor for Pu at 10^{-2} M iso-saccharinic acid is ~10^6. For U, the enhancement factor is $5 \cdot 10^{-3}$ times that of Pu, (column 3, Table 7). Therefore, at 10^{-2} M iso-saccharinic acid the solubility enhancement factor for U is, $10^6 \cdot 5 \cdot 10^{-3} \approx 5 \cdot 10^3$, i.e.

$$\frac{[U(org)]_{S.L.}}{[U]_{S.L.}} \approx 5 \cdot 10^{+3} \quad \text{at } 10^{-2} \text{ M iso-saccharinic acid.}$$

Equation (17) states:

$$R_d'(\text{Rn, organics}) = \frac{R_d(Rn)}{\frac{[Rn(org)]_{S.L.}}{[Rn]_{S.L.}}}$$

where Rn = radionuclide.

Let us assume that we are interested in region II under reducing conditions. From Table 4, the "undisturbed" distribution ratio for U under the above conditions is given as 5 $m^3 kg^{-1}$.

If these conditions are disturbed in a particular canister by the presence of cellulose degradation products equivalent to 10^{-2} M iso-saccharinic acid, then from the preceding discussion and equation (17),

$$R_d'(U,\ \text{organics}) = \frac{R_d(U)}{\frac{[U(org)]_{s.l.}}{[U]_{s.l.}}}$$

$$= \frac{5\ m^3 kg^{-1}}{5 \cdot 10^{+3}} = 10^{-3}\ \ m^3 kg^{-1}$$

i.e. low sorption for U would be expected provided assumptions 1 - 8 hold.

6.2.4 Comparison of Predictions with Experimental Sorption Data

EWART et al. (1991) make the remark that ".....solubility is a far more sensitive indicator to the presence of organic degradation products than sorption" which implies that solubilities are influenced to a greater extent than sorption properties. In the same report (Table 11) Pu solubility enhancement factors in the range 10^5 to 10^6 for cellulose degradation products appear to result in reductions in Pu sorption by factors of 200 to 10^3 in their experiments. (No organic concentrations given).

On the basis of the above observation from batch tests, the arguments put forward here leading to an inversely proportional relationship between the increase in solubility in the presence of organics and sorption (equation (17)) may appear to be very pessimistic. In fact we believe that the batch sorption results for Pu sorption in the presence of organics may yield overly optimistic results. The essential difference between the two cases is that we have taken the situation in which the cellulose inventory is sufficiently large to fix the level of organic complexant in solution, whereas in the batch tests the organic complexant is inventory limited i.e. the input organic concentration is fixed and the final concentration is not. The final concentration of organics in these experiments will depend on their sorption properties with respect to the cement (see section 6.2.2) and it is this final organic concentration, and not the initial concentration, which will determine the ratio,

$$\frac{[\text{Pu organic complexes}]}{[\text{Pu}]_{sol.}}$$

for the sorption of Pu in the presence of organics as expressed for example, in equation (17).

On the basis of the data presented in Table 11, in EWART et al. (1991), the solubility limit of Pu was measured to be $1.9 \cdot 10^{-4}$ M in a leachate from a cement containing 10 wt-% cellulose. From the arguments presented previously and Figure 3, this Pu concentration corresponds to an equivalent iso-saccharinic acid concentration of $\sim 5 \cdot 10^{-3}$ M. At this organic concentration we would predict virtually no sorption for Pu (Table 5) whereas the measured value is 0.06 $m^3 kg^{-1}$ compared with 45 $m^3 kg^{-1}$ in the absence of organics (Table 11 in EWART et al. 1991). The experiments were carried out at a liquid to solid ratio of 50:1 (l:kg) and if we assume an R_d(organics) of $\sim 2 \cdot 10^3$ l kg^{-1} as calculated in section 6.2.2, we can estimate the final concentration of organics, at equilibrium, from the mass balance equation:

Moles of organics sorbed + moles of organics in solution = initial inventory of organics, i.e.

$$m \cdot R_d(\text{organics}) \cdot C_{org.}(\text{eqbm}) + V \cdot C_{org.}(\text{eqbm}) = Q$$

m	= mass of cement present (kg)
R_d(organics)	= distribution coefficient for organics (l kg^{-1})
$C_{org.}$(eqbm)	= Equilibrium concentration of organics (M)
V	= Volume of solution (l)
Q	= Moles of organics present ($V \cdot C_{org.}$(initial))

$$1 \cdot 2 \cdot 10^3 \cdot C_{org.}(\text{eqbm}) + 50 \cdot C_{org.}(\text{eqbm}) = 50 \cdot 5 \cdot 10^{-3}$$

Thus $C_{org.}$(equilibrium) $\sim 1.25 \cdot 10^{-4}$ M

and therefore from Figure 3,

$$\frac{[\text{Pu(org)}]_{S.L.}}{[\text{Pu}]_{S.L.}} \approx 900$$

Substituting the above value together with the R_d(Pu) in the absence of organics (experimental value given as 45 $m^3 kg^{-1}$) into equation (17) yields ~0.05 $m^3 kg^{-1}$.

The calculated value of 0.05 $m^3 kg^{-1}$ is close to the measured value of 0.06 $m^3 kg^{-1}$. Of course, the agreement in this one case might be fortuitous. If a slightly different approach had been taken, and the conservative cement capacity for iso-saccharinic acid had been used i.e. 10^{-1} mol kg^{-1} (section 6.2.2) then the organic concentration calculated after sorption would have been ~25 times greater, and the estimated R_d value about the same factor lower than the measured value i.e. poor agreement.

The processes occurring in such tests may be far more complex than sorption/complexation of Pu coupled with the sorption of organics. Only a more thorough understanding of the processes and mechanisms combined with better defined and characterised experiments can sort out the actual situation.

One process which has been ignored here, for example, is that the radionuclide-organic complexes could themselves sorb. If the organic ligands can sorb then why not the complexes? This could be an alternative explanation for the relatively weak reduction for Pu sorption in the presence of organics measured by EWART et al. (1991). Another, is the competitive effect of Ca complexation, particularly in the sorption tests, where cement is present.

6.2.5 The Influence of Cellulose Degradation Products on Sorption: General Summary

We believe that the sorption of alkali and alkali earth cations will not be significantly influenced by cellulose degradation products. Cs will probably not form complexes at all. Cations such as Sr and Ra (at low concentrations) will not be influenced because they form weaker complexes than Ca and this, coupled with the high Ca concentrations will cause Ca to be extremely competitive. To a first approximation we assume there to be little or no effect on the sorption of Sr and Ra.

The weak sorption of monovalent silver is not expected to be influenced by cellulose since any tendency to form complexes would be blocked by competitive effects from the high concentrations of Na and K present.

For the actinides, it appears from the limited data available that Pu, Am and Th behave similarly with respect to cellulose degradation products, as do Np and U, Table 6. These groupings are not entirely understandable on the basis of the respective chemistries of the actinides within each group.

Because of the arguments given in section 5.2.2 we assume that Zr and Cm belong to the plutonium group.

Since we have taken the behaviour of Pa to be similar to that of Np (section 5.2.1.2), the sorption reduction factors calculated for Np are taken to apply to Pa also.

We assume that there is no effect on radionuclides which exist in solution primarily as negative species i.e. carbonate, iodide, chloride, pertechnetate, selenite/selenide and molybdate.

PILKINGTON & STONE (1990) report increases in Ni solubility of ~10 in leachates similar to those used in the Pu studies. i.e. 10 wt-% cellulose loading, 80°C, leaching time ~750 days. In the same leachates Ni sorption was reduced by up to an order of magnitude. Comparison with Pu measurements leads us to propose that the influence of cellulose degradation products on Ni sorption is a factor of $\sim 5 \cdot 10^{-4}$ times that for Pu. Because of chemical similarity we take the same reduction factor for Mn. No data were found for Pb. We propose the same value as for Ni.

Nothing at all is known for Pd and Sn, but because they form stronger hydroxy complexes than Ni at high pH, the influence of cellulose degradation products may be weaker than for Ni. A rough conservative estimate is that the effect is also a factor of $\sim 5 \cdot 10^{-4}$ times that for Pu. On the basis of the data given in Table 6, the same factor is taken for Tc(IV). Nb is treated similarly.

The above factors have been estimated with respect to Pu for the simple reason that the solubility enhancement factors with respect to cellulose degradation products are only "known" for Pu as a function of ligand concentration. A summary of estimated sorption reduction factors for cellulose containing waste is given in Table 9.

We wish to point out once more that **the sorption reduction factors in this table are based on an extremely pessimistic treatment** of the influence of cellulose degradation products on sorption. Indeed, it is difficult to think of any

additional assumptions which could make the situation worse! The values given in Table 9 should be viewed as resulting from an absolute worse case analysis. In reality, the influence of cellulose degradation products is, in all probability, considerably less severe. How less severe we cannot say, since, in our view, our understanding of the cellulose degradation process at high pH is poor, the products remain unidentified and it is uncertain what the end products are. An apparent effect on radionuclide solubilities of cellulose degradation products has been demonstrated but what exactly is happening in such experiments with respect to processes and mechanisms is very poorly understood.

Table 9: Reduction factors* for the sorption on cement in the presence of cellulose degradation products. The elements are listed according to increasing atomic number.

Element	Oxidising	Reducing
H (HTO)	1	1
CO_3^{2-}	1	1
Cl	1	1
Mn	$5 \cdot 10^{-4}$·Pu	$5 \cdot 10^{-4}$·Pu
Ni	$5 \cdot 10^{-4}$·Pu	$5 \cdot 10^{-4}$·Pu
Se	1	1
Sr	1	1
Zr	Pu	Pu
Nb	$5 \cdot 10^{-4}$·Pu	$5 \cdot 10^{-4}$·Pu
Mo	1	1
Tc	1	$5 \cdot 10^{-4}$·Pu
Pd	$5 \cdot 10^{-4}$·Pu	$5 \cdot 10^{-4}$·Pu
Ag	1	1
Sn	$5 \cdot 10^{-4}$·Pu	$5 \cdot 10^{-4}$·Pu
I	1	1
Cs	1	1
Pb	$5 \cdot 10^{-4}$·Pu	$5 \cdot 10^{-4}$·Pu
Ra	1	1
Th	Pu	Pu
Pa	$5 \cdot 10^{-3}$·Pu	$5 \cdot 10^{-3}$·Pu
U	$5 \cdot 10^{-3}$·Pu	$5 \cdot 10^{-3}$·Pu
Np	$5 \cdot 10^{-3}$·Pu	$5 \cdot 10^{-3}$·Pu
Pu	see Table 5	see Table 5
Am	Pu	Pu
Cm	Pu	Pu

* All sorption reduction factors are given with respect to Pu. Therefore the nomenclature "5.10^{-3}·Pu", means that the reduction factor is $5 \cdot 10^{-3}$ times that for Pu. Note that a calculated sorption reduction factor of <1 has no physical meaning, and in such cases the factor is unity. Pu sorption reduction factors have the same magnitude as a function of iso-saccharinic acid as the solubility enhancement factors given in Table 5.

6.2.6 Estimates of Uncertainties

The results of the procedures described in sections 6.1. to 6.2.5 for determining the influence of the degradation products of cellulose on radionuclide sorption on cement are summarised in Table 9 as sorption reduction factors. As can be seen from this table and Table 5, the calculated reduction factors are, in most cases, large, implying severely reduced distribution ratios for cementitious materials. Low distribution ratios for the near-field can have very important consequences in safety studies. For this reason, we believe it to be only right and proper that we attempt to place some uncertainty levels on the values listed in Tables 5 and 9.

At appropriate points in the text we have tried to indicate where the data are limited, where the data used may have been of uncertain quality and, in particular, where we were forced to make assumptions, due to lack of data/ understanding, in order to derive a required result. We will now try to summarise these "uncertainties" in this section.

Practically the only source of data on this topic was AEA at Harwell and the main thrust of this work was concerned with the influence of cellulose degradation products on solubility limits and **not** sorption, though limited sorption data sets are available. Increases in solubility of several orders of magnitude were reported for Pu, the most studied radionuclide in these investigations. The interpretation given by AEA at Harwell was, that complexation with an unidentified degradation product, "ingredient X", was solely responsible for the enormous increases in solubilities reported. In our view, this is by no means proven. The rôle played by experimental method, and other factors briefly discussed in section 6.2.1, is not clear. Nevertheless we took the interpretation and data of AEA at Harwell as being valid. (A conservative view of the system is implicit in this).

Although some "point sorption measurements" for a limited number of radionuclides in the presence of cellulose degradation products were available, we saw no way in which we could justifiably extrapolate these isolated sorption data to different conditions and other radionuclides. Consequently we were forced to derive quantitative relationships between organic ligand concentrations, complexation and sorption on the basis of solubility limit data. This procedure is described in Chapter 6 and Appendix B. Many assumptions to critical and open questions were required in order to derive the sorption reduction factors listed in Table 9. Because answers to open questions were not known in the majority of cases, many conservative assumptions were made. For example that all the

cellulose present degrades fully to a single product which complexes strongly with virtually all radionuclides, that this degradation product is stable for all time at high pH, that the redox conditions have no influence on degradation products, and that any complexes formed do not sorb. Indeed, it is difficult to envisage another set of assumptions which are more conservative and which would lead to higher sorption reduction factors than those given in Table 9. A direct consequence of this approach is that the system becomes extremely sensitive even to low cellulose contents. Above ~1.5 wt-% cellulose, the sorption of many radionuclides tends rapidly to zero (it almost comes to the point where one A4 piece of paper determines the radionuclide distribution ratios within a 200 l container!). It must not be forgotten that the approach taken and in particular the assumptions made determine this situation. Slightly different assumptions could radically revise the sorption reduction factors downwards. From an experimental viewpoint (see EWART et al. 1991), measurements indicate that sorption reduction factors are 10^2 to 10^3 times less than the corresponding solubility enhancement factors. (For the treatment described in Chapter 6, these two factors have the same value.)

In summary we would say that the influence of cellulose degradation products is, in all probability, less severe than presented here. How less severe is difficult to say since our understanding of the cellulose-cement-radionuclide system is very poor. The limited and relatively poorly defined sorption tests indicate that we could have overestimated sorption reduction factors by as much as two to three orders of magnitude. The answers to key questions remain unresolved and further research in this critical area is clearly required. A programme of work has begun at PSI and it is anticipated that a revision of the data in a positive sense for sorption is a likely outcome of the research.

7 INFLUENCE OF ORGANIC MATERIALS DIFFERENT FROM CELLULOSE ON SORPTION IN CEMENT

7.1 Introduction

The intention in this chapter is to suggest general procedures whereby the influence on radionuclide sorption of organic materials different from cellulose might be estimated. Topics such as degradation processes (chemical and radiolytic), degradation products and thermodynamic properties of organic complexants have been discussed in, for example ALLARD & PERSSON (1985), ALLARD et al. (1987), PILLAY (1986), ALLARD & ANDERSSON (1987), GUEST (1987), DUDDRIDGE (1987), WILKINS (1987), WOLF (1989), VAN LOON & KOPAJTIC (1991), EWART et al. (1991), ALLARD & BORÉN (1991), HUMMEL (1992), HUMMEL (1993) and will only be referred to here where necessary.

For convenience, we will divide the organic materials into two broad categories: "low" molecular weight organics and "high" molecular weight organics.

7.2 "Low" Molecular Weight Organics

The types of organic compounds included here are NTA, EDTA, DTPA; oxalic, citric and tartaric acids; alkyl sulphonic acids and substituted phenols.

Formation constants for actinide complexes with many of the above organic ligands have been listed by ALLARD & PERSSON (1985). For those fission and activation products where the constants have not been measured, the approach described by HUMMEL (1992) provides a potentially powerful tool for deriving defensible estimated constants.

The effect of even very powerful complexing ligands such as EDTA and DTPA can be severely reduced through competition between the organic ligand and major inorganic complexing ions (OH^-) and the competition between the trace concentrations of radionuclides and Ca^{2+}. The source of OH^- and Ca^{2+} ions in the cement system is effectively infinite and their free concentrations will remain constant and be determined by the solubility of "$Ca(OH)_2$" in region II (see for example the calculations reported by BERNER & BRADBURY 1991; HUMMEL 1992 and the experimental results for Am sorption on cement in the presence of EDTA and DTPA, ALLARD et al. 1987).

Provided that the appropriate complexation constants have been measured or can be estimated, speciation calculations for specific radionuclides under the specific conditions appropriate to individual waste canisters in the presence of organic ligands can be performed. Following the argument presented in section 6.2.3, the influence of specific organics on sorption can be calculated using relations similar to that given in equation (14).

HUMMEL (1993) studied the influence of the organic ligands EDTA, NTA, citrate and oxalate on the speciation of Cs, Sr, Ra, Ag, Mn, Ni, Pb, Pd, Tc, Sn, Zr, Th, U, Np, Pu, Am and Cm in cement pore waters. Chemical equilibria were computed within the range of pH 11 to 13 and a range of Ca concentrations from 0.001 M to 0.1 M. EDTA complexes predominate only in the cases of Mn, Ni and Pb. In all other cases Ca-organic or metal-hydroxo complexes successfully prevent any significant influence of EDTA, NTA, citrate or oxalate on the speciation of radionuclides.

The consequences of Hummel's work for radionuclide sorption are expressed as sorption reduction parameters for each radionuclide. These data are summarised in Table 10. For Ni, Mn and Pb sorption reduction factors as a function of EDTA concentration are given separately in Table 11.

Table 10: Sorption reduction factors for radionuclides in the presence of oxalate, citrate, NTA and EDTA at concentrations ≤ 0.1 M. The elements are listed according to increasing atomic number.

Element	Oxalate	Citrate	NTA	EDTA
H (HTO)	1	1	1	1
CO_3^{2-}	1	1	1	1
Cl	1	1	1	1
Mn	1	$2 \cdot 10^{-2}$ EDTA**	$3 \cdot 10^{-2}$ EDTA**	Table 11
Ni	1	$1 \cdot 10^{-2}$ EDTA**	$5 \cdot 10^{-2}$ EDTA**	Table 11
Se	1	1	1	1
Sr	1	1	1	1
Zr	1	1	1	1
Nb	(1)*	(1)*	(1)*	(1)*
Mo	(1)*	(1)*	(1)*	(1)*
Tc	(1)*	(1)*	(1)*	(1)*
Pd	1	1	1	1
Ag	1	1	1	1
Sn	1	1	1	1
I	1	1	1	1
Cs	1	1	1	1
Pb	1	$1 \cdot 10^{-1}$ EDTA**	$2 \cdot 10^{-1}$ EDTA**	Table 11
Ra	1	1	1	1
Th	1	1	1	1
Pa	(1)*	(1)*	(1)*	(1)*
U	1	1	1	1
Np	1	1	1	1
Pu	1	1	1	1
Am	1	1	1	1
Cm	1	1	1	1

* No thermodynamic calculations performed. Values based on chemical analogy.

** The sorption reduction factors for Mn, Ni and Pb in presence of NTA or citrate are calculated by multiplying the reduction factors in the presence of EDTA (Table 11) by the values given here. Example: At a NTA concentration of 0.1 M the reduction factor for nickel is $100 \cdot 5 \cdot 10^{-2} = 5$. Calculated sorption reduction factors <1 have no physical meaning and are set equal to unity.

Table 11: Sorption reduction factors for Ni, Mn and Pb in presence of EDTA.

Total concentration of EDTA [M]	Reduction factor		
	Ni	Mn	Pb
10^{-7}	1	1	1
10^{-6}	1	1	1
10^{-5}	1	1	1
10^{-4}	1	1	1
10^{-3}	2	3	1
10^{-2}	10	20	2
10^{-1}	100	200	10

7.3 "High" Molecular Weight Organics

7.3.1 Polymers

In this category we are mainly considering the degradation products of organic polymers such as polyethylene, neoprene, nylon, polyurethane etc.

As with cellulose material, the only source of data for the above classes of organic compounds comes from AEA at Harwell. Summaries of the main results from this work can be found in BROWNSWORD et al. (1992), GREENFIELD et al. (1992) and EWART et al. (1991). Accelerated leaching tests (80°C) were performed on a variety of cement matrices containing (mainly) 10 wt-% loadings of the various polymers for times of up to 500 days, considered to be equivalent to 50-100 years under repository conditions. Solubilities of Pu were measured in aliquots of the leachates taken at various time intervals.

In general, the effect of the degradation products from polymers on Pu solubility limits was orders of magnitude less than in the case of cellulose. Chemical de-

gradation appeared to be the dominant effect since the additional imposition of α and γ radiation fields had no significant influence on the results.

For any of the polymers tested, the largest Pu solubility limit measured in the leachate was ~10^{-7} M (an isolated value). In most cases Pu solubilities of $\leq 10^{-8}$ M were measured in the presence of polymer degradation products. EWART et al. (1991) consider a "best value" of 10^{-8} M in their treatment. According to the discussion in section 6.2.2, an increase in Pu solubility to 10^{-8} M from $5 \cdot 10^{-10}$ M implies a reduction in sorption of:

$$\frac{10^{-8}}{5 \cdot 10^{-10}} \approx 20 \qquad \text{(see equation 17)}$$

If we take a sorption reduction factor for Pu of 50 to apply whenever polymers are present above the ~1 wt-% level then this should be conservative since the experiments were carried out at loadings of 10 wt-% for times which simulated repository time scales of 50 to 100 years. At values below 1 wt-% we would suggest a sorption reduction factor for Pu of the order unity. It should be remembered that in mixtures containing cellulose material, the effect of cellulose degradation products will dominate.

The sorption reduction factors for Am, Zr, Np, Th, U, Cm and Pa are taken to be the same as for Pu.

In leachates from various cement mixes containing ~10 wt-% loadings of different plastics (degradation time and temperature 750 days and 80°C respectively) PILKINGTON & STONE (1990) measured increases in Ni solubilities of approximately one order of magnitude and corresponding decreases in sorption. Consequently a sorption reduction factor of 10 is taken for Ni. The same value is assumed for Mn, Nb, Tc, Pd, Sn and Pb (reducing conditions). For all other radionuclides listed in the summary Table 12, no effect of degradation products from plastics on sorption is expected.

Table 12: Sorption reduction factors for radionuclides in waste canisters containing polymers (loadings between 1 and 10 wt-%).

Element	Oxidising	Reducing
H (HTO)	1	1
CO_3^{2-}	1	1
Cl	1	1
Mn	10	10
Ni	10	10
Se	1	1
Sr	1	1
Zr	Pu	Pu
Nb	10	10
Mo	1	1
Tc	1	10
Pd	10	10
Sn	10	10
I	1	1
Cs	1	1
Pb	10	10
Ra	1	1
Th	Pu	Pu
Pa	Pu	Pu
U	Pu	Pu
Np	Pu	Pu
Pu	50	50
Am	Pu	Pu
Cm	Pu	Pu

7.3.2 Bitumen

VAN LOON & KOPAJTIC (1991) have investigated the radiolytic degradation of bitumen at pH~12.5. They found that the major degradation products in solution were monocarboxylic acids (acetic, formic, myristic, stearic acids etc.), dicarboxylic acids (oxalic, phthalic acids) and carbonates. Experimentally derived complexation constants with Cu^{2+}, Ni^{2+} and UO_2^{2+} at pH values less that 7 strongly indicated that oxalic acid was determining the complexation behaviour of the bitumen degradation products. At high pH two factors severely limit the ability of oxalic acid to complex with radionuclides:

(i) the competitive effect of OH^--ligands

(ii) the maximum concentration of free oxalate in solution is set by the solubility of calcium oxalate to ~10^{-5} M

These considerations led VAN LOON & KOPAJTIC (1991) to conclude that the radiolytic degradation products of bitumen will have no influence on radionuclide speciation in a cementitious repository. As a direct consequence of this, there will also be no influence on radionuclide sorption (see also Table 10).

7.3.3 Ion Exchange Resins

Cation and anion exchange resins, comprising of cross linked polystyrene with sulphonic acid and quaternary ammonium functional groups respectively, will undergo gradual degradation in the high pH environment of the near-field. Since exchange resins will also accumulate a significant radiation dose, radiolytic as well as chemical degradation processes will be occurring.

Recently, VAN LOON et al. (1992) subjected cation exchange resins to a dose of ~1.7 MGy accrued over several days in a solution at pH~12.5 and 50°C. Subsequent analysis of the solutions showed that the major degradation product was oxalate. The comments previously made for bitumen therefore also apply to cation exchange resins with respect to this degradation product i.e. its concentration will be limited to ~10^{-5} M by the solubility limit of calcium oxalate, and this, coupled with weak radionuclide complexation constants, means that oxalates will have no significant influence on sorption. However, in contrast to bitumen, a second unidentified degradation product was present at concentrations approximately one hundredth that of oxalate but with complexation constants (measured for Ni) three orders of magnitude greater (pH = 5 to 9).

VAN LOON et al. (1992). conclude from a modelling study analogous to that performed for oxalate, citrate, NTA and EDTA (HUMMEL 1993), that ligand X has no influence on speciation (and therefore sorption) in cement pore water for those elements listed in Table 1. However, a condition on this conclusion is that the concentration of ligand X should not exceed 10^{-5} M (worse case scenario, low CaX complex stability) or 10^{-4} M ("realistic" scenario, mean CaX complex stability).

In similar studies on anion exchange resins (VAN LOON & HUMMEL 1995) the most important radiolytic degradation products observed were amines such as ammonia, methylamine, dimethylamine and trimethylamine.

Mono-, di- and trimethylamines and related compounds do not form stable complexes with metals. However, although NH_3 is known to form complexes with metal cations such as Ni^{2+}, Cu^{2+} and Pd^{2+}, they are positively charged and may be expected to adsorb.

On the basis of the available evidence we would conclude that the degradation products from ion exchange resins do not significantly influence the sorption of radionuclides on cementitious materials.

7.3.4 Cement Additives

Compounds such as naphthalene formaldehyde, melamine formaldehyde, sodium lignosulphonate and sodium gluconate are commonly added to cement mixtures as plasticisers and water content reducers. Again, little quantitative information exists on the influence of these additives on radionuclide speciation, solubilities and sorption.

EWART et al. (1991) report Pu solubility enhancement factors for 1% additive loadings of ~10 for naphthalene formaldehyde, ~10^3 for sodium lignosulphonate, and ~10^4 for melamine formaldehyde and sodium gluconate. (Note that these effects may not be due to the compounds themselves but possibly to their degradation products). In the same paper a Pu solubility enhancement factor of 400 is given for solutions containing 10^{-3} M glucose at pH~12.

In contrast to this, Pu sorption measurements performed in leachates from different cement mixtures containing 0.5 - 1% additives appear to indicate that cement additives have no effect on the magnitude of Pu distribution ratios and,

indeed, in many cases the distribution ratios increased in their presence (EWART et al. 1991).

Again, as was the case for cellulose degradation products (see section 6), we have apparently contradictory observations. A compound which increases Pu solubilities by many orders of magnitude, presumably because of the formation of very strong organic complexes, has a considerably less effect or no effect on sorption. **As stated previously, our understanding in this area is very poor.**

Given our low level of understanding of the processes occurring here, all we can do is make very general and conservative estimates. For naphthalene formaldehyde we would suggest that there is no effect on sorption for loadings up to ~1 wt-%. For sodium lignosulphonate, melamine formaldehyde and sodium gluconate with 1% loadings, taking into account the apparently contradictory observations on increases in solubility limit and little or no effect on sorption, we would suggest an overall reduction factor for Pu in the maximum of 500. The corresponding reduction factors for other radioelements can be estimated following the arguments given in section 6.

8 INFLUENCE OF INORGANIC WASTE COMPONENTS ON SORPTION IN CEMENT

As shown in Table A-1 (Appendix A) radioactive waste may contain a plurality of inorganic materials such as metals, salts, ashes and glasses. Of these 4 groups the inorganic salts are of primary concern since they can dissolve in the cement pore water and potentially form complexes with radionuclides thereby influencing sorption. The discussion here will therefore be restricted to such salts.

The major ligands entering the pore water fluid which need to be considered are: CO_3^{2-}, NO_3^{2-}, SO_4^{2-}, S^{2-}, PO_4^{3-}, CN^-, $B(OH)_4^-$ and the halogens F^-, Cl^-, Br^- and I^-. The extent to which radionuclides will form complexes with the above ligands will depend on the radionuclide itself, the free ligand concentration and the respective complexation constants.

In regions I and II (section 3.3) the pH of the pore water is ≥ 12.5, hence radionuclide-hydroxy complex formation will be strongly competitive to all other complexation reactions. Since thermodynamic data are available for virtually all the ligands listed (PEARSON et al. 1992 , SMITH & MARTELL 1976), together with inventory data for the various waste streams (ALDER & McGINNES 1994), realistic speciation calculations can be performed. The methodolgy and calculations are analogous to those described in HUMMEL (1993). These calculations indicate that under the conditions existing in regions I and II only cyanide complexes are likely to be of any significance. The influence of ligands such as CO_3^{2-}, PO_4^{3-} and $B(OH)_4^-$, which can form strong complexes, is limited since their free concentrations in solutions are determined by low solubility solid phases, i.e. calcite, calcium hydroxo phosphate (apatite) and calcium metaborate.

The formation of cyanide complexes is not equally important for all radionuclides. BUFFLE (1988) states that cyanide has a much greater tendency to form complexes with ("soft") cations such as Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ag^{2+}, Cd^{2+}, Hg^{2+} rather than ("hard") cations, such as the actinides. Even at the high pH existing in the repository, the cations Ag^+, Ni^{2+}, Mn^{2+} and Pb^{2+} (see Table 4) are expected to complex with CN^-.

As an example, the complexation behaviour of Ni^{2+} with different CN^- concentrations in the presence of $Ni(OH)_2$ solid phase in a cement pore water has been calculated. The thermodynamic data for the Ni-cyanide complexes was

taken from SMITH & MARTELL (1976) and all other thermodynamic data from PEARSON et al. (1992). The results of these calculations are summarised in Table 13 as sorption reduction factors as a function of total CN^- concentration obtained using equation (17).

Table 13: Reduction factors for the sorption of Ni on cement in the presence of CN^- (HUMMEL, unpublished results).

Total CN^- concentration [M]	Sorption reduction factor
10^{-8}	1
10^{-7}	1
10^{-6}	1
10^{-5}	1
10^{-4}	~2
10^{-3}	~10
10^{-2}	~100

9 RECRYSTALLISATION OF CSH-GEL

The main and most important product formed during the hydration of cement is the calcium-silicate-hydrate gel (CSH-gel) which can be represented by the general formula $(CaO)_x \cdot SiO_2 \cdot y\, H_2O$ ($1.4 < x \leq 1.8$, $y \geq x$). The CSH-gel is very poorly crystalline and its importance lies in the fact that it (and portlandite) determine the pH of the pore water solution for most of the lifetime of the hardened cement paste (BERNER 1990). Also its large surface area (~250 $m^2 g^{-1}$, EWART et al. 1991) is mainly responsible for the good radionuclide sorption properties of cementitious materials. This gel is generally viewed as being meta-stable, and on the very long time scales considered for radioactive waste repositories, the possibility exists that it could gradually transform to a more stable crystalline phase with a resulting change in properties, particularly with respect to sorption (reduction in surface area) and pH. ATKINSON et al. (1988a) contacted ~0.25 g quantities of seven **natural crystalline** calcium-silicate-hydrates with ~2 ml of demineralised water at 25°C in the absence of CO_2 and monitored the evolution of pH in these systems over a 51 day period. The pH values measured were between 7.8 and 9.6 whereas pH's between 10 and 12.5 would have been expected for corresponding amorphous CSH-gels, depending on the Ca/Si ratio. This work appears to imply that **highly crystalline** CSH compounds do not readily produce the high pH values associated with their poorly crystalline counterparts. However, it should be remembered that these solids were highly crystalline natural materials and that the experimental time scales were relatively short. ATKINSON et al. (1988a) admit themselves that they had no evidence to conclude that equilibrium had been reached. Also, the question as to whether such highly crystalline phases with similar properties to the natural materials investigated will ever form in cementitious materials under repository conditions is completely open. Although numerous crystalline silicate hydrates can form in cements, this has usually been observed only during hydrothermal treatment (ATKINSON et al. 1988a). In natural systems, CSH minerals have been found in both the crystalline and gelatinous forms and the latter are similar in form to the CSH-gels found in cement, albeit with a lower Ca/Si ratio of ~0.8 (McCONNELL 1955). In a recent review article on ancient analogues of cement based materials, THOMASSIN & RASSINEUX (1992) provide evidence from many sources that CSH type hydrates have existed for 1'700-1'800 years in cements of Roman origin.

From the information available we would suggest that part re-crystallisation of the CSH-gel appears to be a possibility over very long periods of time but that

the consequences for pH are not likely to be as severe as the data from ATKINSON et al. (1988a) might indicate. Reductions of pH down to as low as ~10 could be tolerated without any significant adverse effects on sorption.

EWART et al. (1991) have published sorption measurements for Pu and Am on a number of synthetic compounds prepared to represent those considered to be present in a mature concrete. Amongst these were crystalline calcium silicate minerals (analogous to re-crystallised CSH-gels). The distribution ratios given are, if anything, slightly higher than those for fresh cement. It is unfortunate that no data on water chemistry and pH were reported for these tests other than to say that saturated solutions were prepared for each of the phases.

The available (limited) evidence leads us to conclude that even if (part) re-crystallisation of the CSH-gel occurs, the consequences for the pH of the pore water and sorption will not be significant. This is particularly so in the case of sorption where a gradual re-crystallisation process, though it may lead to a reduction in the surface area for sorption, will not lead to any sorption site saturation effects due to the generally very low concentrations of radionuclides present. Indeed, re-crystallisation could have positive consequences in that sorbed radionuclides could be incorporated within the re-crystallised structure. There are indications of this in the work of EWART et al. (1991).

10 CARBONATION

When a carbonate containing groundwater, such as that present in marl formations, contacts cementitious material, $CaCO_3$ will tend to precipitate. BERNER (1990), on the basis of an equilibrium mixing tank model, predicts that ~80% of the original "$Ca(OH)_2$" present will eventually be transformed to calcite. He states that "this transformation approximately halves the "lifetime" of the CSH-gel (compared to the dissolution in pure water) and therefore the CO_3^{2-} concentration is a very important parameter". On this basis carbonation would appear to have a rather negative long-term effect on the performance of the repository in general and on sorption in particular since the main sorbing phase, the CSH-gel, is gradually converted to calcite, which could adversely influence the sorption for some radionuclides. However, BERNER (1990) modelled the system from the point of view of thermodynamic equilibrium, and this is certainly not the whole story. Transport processes will also play an important rôle but coupled codes of the required sophistication with acceptable CPU times are not available.

Recently, SAROTT et al. (1992), for example have shown that the effect of carbonation on diffusion rates and permeabilities can be quite dramatic and rapid. Even though the amounts of $CaCO_3$ formed are too low to be quantified, they can be detected by XRD. In disc specimens ~1 cm thick, diffusion rates decreased by approximately 3 orders of magnitude in ~3'000 hour tests and permeabilities fell by ~2 orders of magnitude in ~1'000 hours. The data suggest that the diffusion rates and hydraulic conductivities were still falling when the experiments were terminated. The results were simply interpreted in terms of $CaCO_3$ precipitation within the pore space in the near surface region of the specimens. There is no reason to believe that a similar effect should not occur within a repository. The result would be a gradual "sealing up" of the repository through the pore space becoming progressively more and more blocked. The degree of carbonation need only be slight, since transport through a pore would cease once the pore became blocked at one point along its length. Pore sealing would reduce the transport rates of groundwater into, and radionuclides out of, the repository through the bulk concrete. As far as we can see this would have a predominantly positive effect on repository performance. The rate at which cement degrades would be reduced since the mass transport of groundwater into the cement and the migration of cement pore water components out of the repository into the far-field would be reduced in accordance with the decrease in diffusion rates / hydraulic conductivities. Likewise, the transport rate of radio-

nuclides out of the repository would be decreased without any effect on sorption since the quantities of "$Ca(OH)_2$" converted to $CaCO_3$ would be relatively small. It is entirely conceivable that the repository could become effectively sealed off from the far-field before any of the canisters failed.

If an interconnected crack network were to be generated within the repository providing preferential flow paths connecting to the far-field, then the same process of pore blocking by calcite formation is likely to occur on the crack surfaces. Fine networks of cracks may not be permanent features since these could also heal through the precipitation of calcite (GUPPY 1988). If large cracks form which 1/ cannot heal, 2/ intersect one or more canisters, 3/ are filled with water and 4/ provide a connection to the far-field, then the carbonation of the surfaces of such cracks may have a negative influence. The radionuclides released to the aqueous phase directly from breached canisters into the cracks will have reduced access, via diffusion, to the bulk concrete sorption sites because of pore blocking by calcite. The only sorption sites then available are those on the crack surfaces, and these may also be reduced by $CaCO_3$ formation.

The formation of ettringite, which is one mechanism by which cracking in cement/concrete could be induced, would also become less probable through calcite blocking of the pore space since the transport of SO_4^{2-} ions from the groundwater into the cement would be impeded.

11 STEEL CORROSION PRODUCTS

According to the data compiled for PROJEKT GEWÄHR (1985) with respect to the material composition in a low- and intermediate-level radioactive waste repository, steel, in one form or another, comprises well over 10% of the total mass. The steel is present as waste containers, constituents of the waste and as construction components. For comparison, the total quantity of cement (hardened cement paste) present is ~20% of the total mass. Corrosion of the steel will occur throughout the lifetime of the repository producing iron hydroxide and oxide products e.g. magnetite (Fe_3O_4), haematite (Fe_2O_3). Such products, because of their large surface areas and surface structures will have a significant sorption capacity for radionuclides which has not been taken into consideration in the compilation of the sorption data base given earlier. At high pH, iron oxides are particularly effective sinks for actinides and transition metals. For example, GARDINER et al. (1990), report distribution ratios for Pu and Am on Fe_2O_3 and Fe_3O_4 of $\geq 10^2\ m^3\ kg^{-1}$ i.e. values which are orders of magnitude greater than those given in Table 4.

Corrosion products are only briefly mentioned here to indicate that there are compounds present within the repository which, in the long term, may be equally important sinks for radionuclides as the cementitious materials. No credit has been taken for their potentially significant contribution to radionuclide retention which makes the generally conservative distribution ratios chosen in Table 4 even more conservative.

12 COLLOIDS IN THE NEAR-FIELD

It has often been argued that the transport of radionuclides sorbed on colloidal material(s) could have a significant impact on the near-field source term and on the subsequent migration in the far-field. In order for colloids to influence significantly the source term i.e. the temporal release rates of radionuclides from the near-field to the far-field, implies that a number of conditions need to be fulfilled. First and foremost, colloidal particles would have to form **within the pore space** of the bulk cement/concrete.

In most laboratory experiments, whether batch sorption experiments on crushed cement or leaching experiments from small blocks of cement, colloids appear to form readily. However, virtually all of such tests are carried out on weak, incompletely hydrated cements, where "free" cement surfaces are available. The colloids are likely to be generated at these "free surfaces" which are in contact with relatively large volumes of solution with which they may not, at least initially, be in equilibrium i.e. degradation effects may be playing a rôle at the free surfaces. In tests where agitation of some sort is applied, mechanical effects may be a major contributing factor to colloid generation. Within bulk cement, free surfaces and mechanical effects, in the same sense as mentioned above, do not exist in the confined pore volumes. We know of no evidence which shows that colloids, of the type seen in laboratory experiments, can form within the pore space of fully hydrated bulk cement.

Generally, in order to increase the total concentration of radionuclides in the aqueous phase over and above that which it would have been in the absence of colloids, a sufficient mass of colloids would have to be present in solution having distribution ratios similar to or greater than the solid phase. In cement systems it is reasonable to assume that the sorption properties of the colloids and the solid phase would be similar since in both cases the CSH-gel is the major component (see RAMSAY et al. 1991). As a simple illustration, consider 1 kg of bulk cement which has a distribution ratio of R_d (l kg^{-1}) at an equilibrium radionuclide concentration (in "true solution") of C mol l^{-1}. 1 kg of cement has a volume of ~0.5 l (assuming a bulk density of 2 kg l^{-1}) and a pore volume, V_{pore}, of ~0.1 l (assuming of porosity of 20%). If we now set up a mass balance for the system with a mass m_c kg of colloids present in suspension with sorption properties similar to the bulk then:

$$R_d \cdot 1 \cdot C + R_d \cdot m_c \cdot C + C \cdot V_{pore} = Q \qquad (34)$$

where $R_d \cdot 1 \cdot C$ is the number of moles of radionuclide sorbed on the solid phase

$R_d \cdot m_c \cdot C$ is the number of moles of radionuclide sorbed on to the colloidal phase

$V_{pore} \cdot C$ is the number of moles of radionuclide in solution

Q is the total number of moles of radionuclide in the system at equilibrium

For the colloids to have an impact on the total quantity of radionuclides in "solution" (radionuclides in "true solution" plus those attached to colloids) then:

$$R_d \cdot m_c \cdot C > V_{pore} \cdot C \qquad (35)$$

or $$m_c > \frac{V_{pore}}{R_d}$$

Consider a highly sorbing radionuclide with R_d ~10^3 l kg^{-1}. Since V_{pore} = 0.1 l, then m_c must be greater than ~10^{-4} kg i.e. in this case a colloid concentration of > 10^{-3} kg l^{-1} (> 1 g l^{-1}) is implied.

If the colloids increase the **total** quantity of radionuclide in solution by an order of magnitude then m_c is ~10^{-3} kg corresponding to a colloid concentration in the pore volume of ~10^{-2} kg l^{-1} (~10 g l^{-1}).

Even if R_d (colloids) were to be an order of magnitude greater than R_d (solid) this would still imply a colloid concentration of ~1g l^{-1} **in the pore volume.** Thus, for colloidal material to have a significant influence, it must be present at relatively high concentrations in the pore water and/or exhibit much stronger sorption than the solid phase.

Even if the above conditions are met, the colloids, with their sorbed radionuclides, must diffuse out of the cement through the connected porosity. The majority of the pores in partially hydrated fresh cement, as used in laboratory experiments, have radii < 100 nm (see for example ROWAN et al. 1988) and pore size decreases as a function of the degree of hydration. This implies that even if colloids can form in the restricted pore space available they would have to be significantly smaller than the pore diameters to have any chance of being

able to diffuse. Also the pores are not smooth sided tubes of constant diameter, but are rough (on the scale of the diameters), highly tortuous and contain constrictions. There is then a considerable potential for colloids in bulk cement to be "filtered out" by the cement itself, even when they are in principle mobile. Finally, colloids with their sorbed radionuclides, may eventually diffuse ahead of the retarded radionuclides with which they were initially in equilibrium and enter regions where the radionuclide concentrations are smaller. Desorption processes will then take place together with competitive sorption effects from the solid phase which will result in ever decreasing radionuclide loadings on mobile colloids. (There is no evidence of which we are aware that radionuclides are irreversibly sorbed on "cement colloids").

GARDINER et al. (1990) produced colloidal suspensions of magnetite and haematite with mean particle diameters of 450 nm and 130 nm respectively as iron corrosion product simulants. These colloidal suspensions were carefully laid on the surface of solution saturated beds of crushed concrete (0.5-1 mm) held in a column and eluted periodically over ~15 days with a total of ~20 column void volumes of solution. Even in such experiments with high column porosities and exceedingly large void sizes compared to bulk cement, GARDINER et al. (1990) conclude "....only a small fraction of (colloidal) oxide is potentially mobile and that this is probably transported via a few large voids in the column".

Although the transport of colloids involves complex processes and will undoubtedly be a continuing topic for research, we are of the opinion, based on the arguments and evidence given above, that the diffusional transport of radionuclides sorbed onto "cement colloids" through intact bulk concrete will not make any significant contribution to the repository source term. We state this view since we believe that in the confined, tortuous and constricted pore space existing in intact cement, "cement colloids" (if they form at all) will not be mobile and may even have a positive influence on radionuclide retardation.

At the boundaries of the repository where "free cement surfaces" may be in contact with flowing groundwater "cement colloids" may well form, but these will not effect the source term. Rather, they may have an influence on radionuclide migration in the far-field if such colloids are stable. The only circumstances under which we can envisage a potential influence is when cracking occurs in the cement and radionuclides reach the solution filled cracks after diffusion through the bulk cement matrix. Colloids may form in the solution within these cracks

(again "free cement surfaces" are involved) and radionuclides may sorb on these colloids and be transported through the crack network by them.

The above applies predominantly to high density cements and concretes used as binding material for the waste itself, and in the manufacture of container walls and tunnel linings. For the "monokorn" cement, envisaged as an extremely porous backfill, the situation may be quite different. The "pore size" in this material is of the order of mm, and hence a colloid filtration effect is not expected. The pore surfaces in pores of this size may behave similarly to a free surface, and, on the basis of the above discussion, colloids may be generated here.

Radionuclide transport by colloids in the "monokorn" cement backfill is certainly possible, but its influence on the source term is impossible to estimate at this time.

APPENDIX A: Material Inventory in the L/ILW Repository

Table A-1: Summary of the masses of materials arising in the L/ILW repository on a waste group basis (from ALDER & McGINNES 1994).

Material	OW [1] [kg]	RW [2] [kg]	DW [3] [kg]	RPW [4] [kg]	MIR [5] [kg]	Total [kg]
Metals	$3.21 \cdot 10^6$	$2.67 \cdot 10^5$	$4.59 \cdot 10^7$	$5.92 \cdot 10^6$	$4.18 \cdot 10^6$	$6.19 \cdot 10^7$
Steels	$3.15 \cdot 10^6$	$1.75 \cdot 10^6$	$4.30 \cdot 10^7$	$5.83 \cdot 10^6$	$3.89 \cdot 10^6$	$5.77 \cdot 10^7$
Al/Zn	$4.78 \cdot 10^4$	$8.64 \cdot 10^1$	$1.40 \cdot 10^5$	$3.90 \cdot 10^4$	$1.62 \cdot 10^5$	$3.89 \cdot 10^5$
Inconel	-	$1.32 \cdot 10^3$	$1.71 \cdot 10^6$	-	-	$1.72 \cdot 10^6$
Zircalloy	-	$3.24 \cdot 10^5$	-	-	-	$3.24 \cdot 10^5$
Other	$9.68 \cdot 10^3$	$5.98 \cdot 10^5$	$1.02 \cdot 10^6$	$5.32 \cdot 10^4$	$1.30 \cdot 10^5$	$1.81 \cdot 10^6$
Inorganics	$1.21 \cdot 10^7$	$3.44 \cdot 10^6$	$1.27 \cdot 10^8$	$2.42 \cdot 10^7$	$1.19 \cdot 10^7$	$1.78 \cdot 10^8$
Salts	$1.37 \cdot 10^5$	$6.17 \cdot 10^1$	$1.84 \cdot 10^3$	$8.32 \cdot 10^4$	-	$2.22 \cdot 10^5$
Ashes	$9.48 \cdot 10^4$	-	$2.99 \cdot 10^4$	-	$2.68 \cdot 10^5$	$3.93 \cdot 10^5$
Glass	$4.62 \cdot 10^5$	$8.40 \cdot 10^2$	$8.65 \cdot 10^4$	$5.63 \cdot 10^5$	$4.97 \cdot 10^5$	$1.61 \cdot 10^6$
Concrete/ cement	$1.13 \cdot 10^7$	$3.43 \cdot 10^6$	$1.25 \cdot 10^8$	$2.35 \cdot 10^7$	$1.12 \cdot 10^7$	$1.74 \cdot 10^8$
Other	$3.22 \cdot 10^4$	$4.62 \cdot 10^3$	$1.89 \cdot 10^6$	$2.91 \cdot 10^3$	$1.75 \cdot 10^2$	$1.93 \cdot 10^6$
Organics	$2.08 \cdot 10^6$	$1.90 \cdot 10^3$	$9.41 \cdot 10^5$	$8.06 \cdot 10^6$	$1.42 \cdot 10^6$	$1.25 \cdot 10^7$
High Mwt [6]						
subtotal	$2.07 \cdot 10^6$	$1.90 \cdot 10^3$	$9.14 \cdot 10^5$	$8.06 \cdot 10^6$	$1.38 \cdot 10^6$	$1.24 \cdot 10^7$
Bitumen	$3.36 \cdot 10^5$	-	-	-	-	$3.36 \cdot 10^5$
Ix [7] resins	$1.37 \cdot 10^6$	-	$3.34 \cdot 10^5$	-	$2.84 \cdot 10^5$	$2.00 \cdot 10^6$
Cellulose	$2.78 \cdot 10^4$	-	-	$5.62 \cdot 10^6$	$1.29 \cdot 10^5$	$5.77 \cdot 10^6$
Other	$3.38 \cdot 10^5$	$1.90 \cdot 10^3$	$5.71 \cdot 10^5$	$2.44 \cdot 10^6$	$9.66 \cdot 10^5$	$4.32 \cdot 10^6$
Low Mwt [6]						
subtotal	$5.28 \cdot 10^3$	-	$2.74 \cdot 10^4$	-	$4.31 \cdot 10^4$	$7.57 \cdot 10^4$
Detergents	$1.32 \cdot 10^3$	-	-	-	$4.25 \cdot 10^4$	$4.38 \cdot 10^4$
Flocculants	$6.35 \cdot 10^{-1}$	-	-	-	$5.68 \cdot 10^2$	$5.69 \cdot 10^2$
Complexing agents	$2.89 \cdot 10^3$	-	$2.74 \cdot 10^4$	-	-	$3.03 \cdot 10^4$
Other	$1.07 \cdot 10^3$	-	-	-	-	$1.07 \cdot 10^3$
Not specified	$1.48 \cdot 10^5$	-	-	-	$4.15 \cdot 10^6$	$4.29 \cdot 10^6$
Total	$1.75 \cdot 10^7$	$6.11 \cdot 10^6$	$1.74 \cdot 10^8$	$3.82 \cdot 10^7$	$2.17 \cdot 10^7$	$2.57 \cdot 10^8$

1) Operational waste 2) Reactor waste 3) Decommissioning waste

4) Reprocessing waste 5) Waste from medicine, industry and research

6) Molecular weight 7) Ion exchange

APPENDIX B: Derivation of the Sorption Reduction Factor

We make the assumption that, at the low concentrations of radionuclides expected in individual waste canisters the sorption is independent of concentration, i.e. linear.

The distribution ratio, $R_d(B)$, is given by:

$$R_d(B) = \frac{\text{Quantity of B sorbed per unit mass of solid}}{\text{Equilibrium concentration of B in solution}} \quad (1\text{-B})$$

$$= \frac{B_{sorb.}}{[B]_{sol.}} \quad (2\text{-B})$$

The term $[B]_{sol.}$ is the sum of all inorganic B species existing in solution.

Consider the sorption of B in the presence of an organic ligand, L, which forms complexes of the form B_nL_m. The concentration of such complexes in solution at equilibrium after sorption is simply:

$$\sum_{n=1}^{N}\sum_{m=1}^{M}[B_nL_m] \quad (3\text{-B})$$

Since each B_nL_m complex contains "n" B atoms the concentration of B existing as B_nL_m organic complexes is

$$\sum_{n=1}^{N}\sum_{m=1}^{M} n\cdot[B_nL_m] \quad (4\text{-B})$$

From the definition of the distribution ratio, equation (1-B), the sorption of B in the presence of organics, $R'_d(B)$ is:

$$R'_d(B) = \frac{B'_{sorb.}}{\text{Equilibrium concentration of B in solution}} \quad (5\text{-B})$$

$$= \frac{B'_{sorb.}}{[B]'_{sol.} + \sum_{n=1}^{N}\sum_{m=1}^{M} n\cdot[B_nL_m]} \quad (6\text{-B})$$

$B'_{sorb.}$ and $[B]'_{sol.}$, respectively, are the amounts of B sorbed and the sum of all inorganic B species in solution in the presence of a complexing organic ligand at equilibrium.

Equation (6-B) can be re-expressed as:

$$R'_d(B) = \frac{\frac{B'_{sorb.}}{[B]'_{sol.}}}{1+\frac{\sum_{n=1}^{N}\sum_{m=1}^{M} n \cdot [B_nL_m]}{[B]'_{sol.}}} \qquad (7\text{-B})$$

If we assume that the complexes B_nL_m do not sorb, and therefore make no contribution to $B'_{sorb.}$, then only the inorganic B species are involved in sorption.

Since only the inorganic species of B are involved in sorption processes and since sorption is linear then:

$$R_d(B) = \frac{B_{sorb.}}{[B]_{sol.}} = \frac{B'_{sorb.}}{[B]'_{sol.}} \qquad (8\text{-B})$$

and hence equation (7-B) becomes:

$$R'_d(B) = \frac{R_d(B)}{1+\frac{\sum_{n=1}^{N}\sum_{m=1}^{M} n \cdot [B_nL_m]}{[B]'_{sol.}}} \qquad (9\text{-B})$$

The above is not new, and similar relations have been presented many times before in the literature, e.g. MAES et al. (1988), and appear in a wide variety of forms of varying complexity. Indeed, a similar relation is the basis for an ion exchange method for determining stability constants for complexes (SCHUBERT 1948).

In essence, for the example given here, equation (9-B) states that the sorption measured in the presence of organic complexing ligands is the distribution ratio measured in their absence reduced by a factor of unity plus the ratio of the radionuclide concentration existing as organic complexes to the sum of the concentrations of inorganic radionuclide species.

For a general organic complexation reaction of the form:

$$nB + mL \rightleftarrows B_nL_m \tag{10-B}$$

we can write:

$$K_{nm} = \frac{[B_nL_m]}{[B]^n[L]^m} \tag{11-B}$$

and hence the sum over all organic complexes is:

$$\sum_{n=1}^{N}\sum_{m=1}^{M} n \cdot [B_nL_m] = \sum_{n=1}^{N}\sum_{m=1}^{M} n \cdot K_{nm} \cdot [B]^n[L]^m \tag{12a-B}$$

i.e. $$\sum[\text{organic complexes}] = \sum_{n=1}^{N}\sum_{m=1}^{M} n \cdot K_{nm} \cdot [B]^n[L]^m \tag{12b-B}$$

In equation (9-B), $[B]'_{sol.}$ represents the sum of the concentrations of all inorganic radionuclide species existing in solution. To a first approximation, metals do not form inorganic complexes in aqueous solutions which contain more than one metal ion.

In a similar manner to the organic ligand L, we can write a general complexation reaction for an inorganic ligand, J.

$$pB + qJ \rightleftarrows B_pJ_q \tag{13-B}$$

$$^{J}K_{pq} = \frac{[B_pJ_q]}{[B]^p[J]^q} \tag{14-B}$$

For all possible inorganic ligands, J, i.e. OH^-, CO_3^{2-}, etc., which can form inorganic complexes with B, we can write:

$$\sum_{J}\sum_{p=1}^{P}\sum_{q=1}^{Q} p \cdot [B_pJ_q] = \sum_{J}\sum_{p=1}^{P}\sum_{q=1}^{Q} p \cdot {}^{J}K_{pq} \cdot [B]^p[J]^q \tag{15-B}$$

$$[B]'_{sol.} = [B] + \sum_{J}\sum_{p=1}^{P}\sum_{q=1}^{Q} p \cdot {}^{J}K_{pq} \cdot [B]^p[J]^q \tag{16-B}$$

The total concentration of B in solution, $[B]_{Tot.Aqu.}$, is

$$[B]_{Tot.Aqu.} = [B]'_{sol.} + \sum[\text{organic complexes}] \qquad (17\text{-B})$$

$$\frac{[B]_{Tot.Aqu.}}{[B]'_{sol.}} = 1 + \frac{\sum[\text{organic complexes}]}{[B]'_{sol.}} \qquad (18\text{-B})$$

or, substituting the expressions for Σ [organic complexes] and $[B]'_{sol.}$ from equations (12b-B) and (16-B) respectively:

$$\frac{[B]_{Tot.Aqu.}}{[B]'_{sol.}} = 1 + \frac{\sum_{n=1}^{N}\sum_{m=1}^{M} n \cdot K_{nm} \cdot [B]^n [L]^m}{[B] + \sum_{J}\sum_{p=1}^{P}\sum_{q=1}^{Q} p \cdot {}^{J}K_{pq} \cdot [B]^p [J]^q} \qquad (19\text{-B})$$

$$= 1 + \frac{\sum_{n=1}^{N}\sum_{m=1}^{M} n \cdot K_{nm} \cdot [B]^{n-1} [L]^m}{1 + \sum_{J}\sum_{p=1}^{P}\sum_{q=1}^{Q} p \cdot {}^{J}K_{pq} \cdot [B]^{p-1} [J]^q} \qquad (20\text{-B})$$

If the term $\sum_{n=1}^{N}\sum_{m=1}^{M} n \cdot K_{nm} \cdot [B]^{n-1}[L]^m$ is expanded, we have:

$$\sum_{m=1}^{M} 1 \cdot K_{1m} \cdot [L]^m + \sum_{m=1}^{M} 2 \cdot K_{2m} \cdot [B][L]^m + \sum_{m=1}^{M} 3 \cdot K_{3m} \cdot [B]^2 [L]^m \quad \text{etc.} \qquad (21\text{-B})$$

and see that the first term in the expansion i.e., $\sum_{m=1}^{M} 1 \cdot K_{1m} \cdot [L]^m$, is

independent of [B]. The second, third, fourth, etc. terms are a function of [B], $[B]^2$, $[B]^3$, etc. respectively.

If we take plutonium as an example, its solubility limit, in the absence of organics in a cement pore water at pH~12.5, is ~5×10^{-10} M. The concentration of free Pu in solution, [Pu], is certainly much less than the above value. This implies that in order for the second, third, etc. terms in equation (21-B) to be comparable with the first, the complexation constants K_{2m}, K_{3m}, etc. must be at least ~10^{10}, 10^{20}, etc. times greater than K_{1m}. Though this is theoretically possible,

we consider it to be unlikely and therefore conclude that 1:m complexes will dominate.

A similar treatment can be applied to the expression for the sum of the inorganic complexes, i.e. the denominator in equation (20-B), to reach the same conclusion as above.

Equation (20-B) then becomes:

$$\frac{[B]_{Tot.Aqu.}}{[B]'_{sol.}} = 1 + \frac{\sum_{m=1}^{M} K_{1m} \cdot [L]^m}{1 + \sum_{J} \sum_{q=1}^{Q} {}^{J}K_{1q} \cdot [J]^q} \qquad (22\text{-B})$$

Thus, in any system having the same water chemistry and the same organic ligand concentration, [L], the ratio $[B]_{Tot.Aqu.}/[B]'_{sol.}$ is constant and independent of the free radionuclide concentration [B]. Equation (22-B) sets no condition on the magnitude of [B]. Therefore $[B]_{Tot.Aqu.}/[B]'_{sol}$ has the same value (for constant [L]) irrespective of whether [B] is very small or whether it has its maximum possible value when the solubility controlling solid phase is present and the value of $[B]'_{sol.}$ equals the solubility limit of B under the prevailing water chemistry conditions. From Figure 3 the ratio $[B]_{Tot.Aqu.}/[B]'_{sol}$ is known for plutonium as a function of [L] at the solubility limit $[Pu]_{S.L.}$, i.e. in the presence of a solid Pu containing phase. Equation (22-B) indicates that the value of this ratio applies to all $[Pu]_{sol.}$ concentrations (for the same [L]) given the assumptions and simplifications made.

The significance of this is that the denominator in equation (9-B), which relates R_d values in the presence and absence of complexing organic ligands, is nothing other than $[B]_{Tot.Aqu.}/[B]'_{sol}$ (see equation (18-B)). Hence, the influence of Plutonium complexation with iso-saccharinic acid (taken as being equivalent to "organic molecule X" from the degradation of cellulose) on its sorption properties as a function of iso-saccharinic acid concentration can be calculated with the aid of Figure 3.

Thus, if the sorption of Pu in the absence of organics is R_d(Pu), and we know that a free organic ligand concentration of [L] increases the Pu solubility limit from $Pu_{S.L.}$ to $Pu(org.)_{S.L.}$ then the sorption of Pu in the presence of this organic ligand concentration, [L], is given by

$$R_d'(\text{Pu, organics}) = \frac{R_d(\text{Pu})}{\frac{[\text{Pu(org)}]_{S\perp}}{[\text{Pu}]_{S\perp}}} \qquad (23\text{-B})$$

$$[\text{Pu(org)}]_{S\perp} \gg [\text{Pu}]_{S\perp}$$

$[Pu(org)]_{S\perp}/[Pu]_{S\perp}$ is defined as the solubility enhancement factor for Pu at a given free organic ligand concentration, [L].

The sorption reduction factor, R_f, is then simply given by the ratio of the distribution ratios in the absence and presence of an organic complexing ligand, i.e. from equation (23-B)

$$R_f = \frac{R_d(\text{Pu})}{R_d'(\text{Pu, organics})} = \frac{[\text{Pu(org)}]_{S\perp}}{[\text{Pu}]_{S\perp}} \qquad (24\text{-B})$$

The sorption reduction factor is numerically equal to the solubility enhancement factor.

Consider now a situation in which the individual sorption reduction factors $R_{f,1}$, $R_{f,2}$, $R_{f,3}$ ... $R_{f,z}$ are known for the organic ligands $(org)_1$, $(org)_2$, $(org)_3$ ... $(org)_z$ and we wish to know the total reduction factor in the presence of all of these organic ligands.

Following equation (24-B) the overall sorption reduction factor is equal to the total concentration of B in solution in the presence of complexing organic ligands divided by the concentration of B in solution in the absence of organic ligands under the same chemical conditions, i.e.

$$R_{f,\text{Tot.}} \approx \frac{\sum_z [\text{Pu(org)}_z]_{S\perp}}{[\text{Pu}]_{S\perp}} \qquad (25\text{-B})$$

$$\approx \frac{[\text{Pu(org)}_1]_{S\perp}}{[\text{Pu}]_{S\perp}} + \frac{[\text{Pu(org)}_2]_{S\perp}}{[\text{Pu}]_{S\perp}} + \cdots + \frac{[\text{Pu(org)}_z]_{S\perp}}{[\text{Pu}]_{S\perp}} \qquad (26\text{-B})$$

But each of the terms on the right hand side of equation (26-B) is the individual reduction factor for each of the organic molecules, i.e.

$$R_{f,Tot.} \approx R_{f,1} + R_{f,2} + R_{f,3} + \cdots + R_{f,z}$$

Thus the overall sorption reduction factor for a radionuclide in the presence of a mixture of organic ligands, with which it forms complexes, is the sum of the individual reduction factors for each organic ligand.

However, it is important to note that this conclusion is only valid under the assumptions and approximations used to derive equation (23-B).

APPENDIX C: Radionuclide Concentrations in the Cement Pore Water of the L/ILW Repository

Table C-1 gives the maximum concentrations of safety relevant radionuclides in the cement pore fluid of a L/ILW repository calculated within 10^6 years after closure. The concentrations are sums over all radioactive isotopes. Contributions from stable isotopes were not included.

The calculations were performed as follows. The maximum concentration of each radioactive isotope was calculated for the first 10^6 years after repository closure using the decay chain programme RAPIDE and the inventory data of ALDER & McGINNES (1994). For each element, the maximum individual radioactive isotope concentrations were summed to yield the maximum concentration. (Note that this is a conservative calculation since the maximum concentrations for each radioactive isotope occur at different times.) For these calculations an average cement porosity of 20 volume-% was assumed. Finally, to calculate the concentrations given in Table C-1, linear sorption was assumed. The distribution ratios used depended on which of the 4 regions of the repository, SMA-1 to SMA-4, was being considered. The variation is from region SMA-1, which contains no components which adversely effect radionuclide sorption (sorption data given in Table 4), to SMA-4 where the sorption of many radionuclides is set to zero because of the presence of large quantities of cellulose. The characteristics of regions SMA-1 to SMA-4 and the distribution ratios used in each of this regions are given in NAGRA (1993).

Table C-1: Maximum concentrations of safety relevant radionuclides in the cement pore water of a L/ILW repository calculated within 10^6 years for four different repository.

Element	Maximum radionuclide concentration [M]			
	SMA-1	SMA-2	SMA-3	SMA-4
H (HTO)	$1.6 \cdot 10^{-15}$	$7.6 \cdot 10^{-14}$	$2.3 \cdot 10^{-18}$	$9.0 \cdot 10^{-17}$
C	$3.1 \cdot 10^{-10}$	$1.6 \cdot 10^{-10}$	$8.0 \cdot 10^{-15}$	$6.8 \cdot 10^{-10}$
Cl	$2.9 \cdot 10^{-9}$	$2.9 \cdot 10^{-10}$	$1.8 \cdot 10^{-13}$	$2.5 \cdot 10^{-9}$
Mn	$1.7 \cdot 10^{-8}$	-	$2.0 \cdot 10^{-13}$	$8.5 \cdot 10^{-10}$
Ni	$3.8 \cdot 10^{-7}$	$8.1 \cdot 10^{-11}$	$4.0 \cdot 10^{-11}$	$3.3 \cdot 10^{-8}$
Se	$5.9 \cdot 10^{-10}$	-	$6.5 \cdot 10^{-11}$	$8.0 \cdot 10^{-12}$
Sr	$5.4 \cdot 10^{-13}$	$7.8 \cdot 10^{-14}$	$7.2 \cdot 10^{-13}$	$1.2 \cdot 10^{-13}$
Zr	$1.1 \cdot 10^{-9}$	$1.1 \cdot 10^{-12}$	$2.3 \cdot 10^{-10}$	$2.4 \cdot 10^{-10}$
Nb	$4.1 \cdot 10^{-9}$	$3.4 \cdot 10^{-13}$	$9.5 \cdot 10^{-12}$	$3.7 \cdot 10^{-11}$
Mo	$2.6 \cdot 10^{-7}$	$8.8 \cdot 10^{-11}$	$1.5 \cdot 10^{-13}$	$1.8 \cdot 10^{-11}$
Tc	$3.5 \cdot 10^{-11}$	$4.2 \cdot 10^{-10}$	$1.3 \cdot 10^{-11}$	$2.0 \cdot 10^{-9}$
Pd	$3.6 \cdot 10^{-9}$	-	$3.4 \cdot 10^{-11}$	$1.5 \cdot 10^{-12}$
Ag	$7.1 \cdot 10^{-8}$	-	$2.9 \cdot 10^{-11}$	$6.1 \cdot 10^{-14}$
Sn	$5.9 \cdot 10^{-13}$	-	$3.4 \cdot 10^{-11}$	$5.8 \cdot 10^{-12}$
I	$1.7 \cdot 10^{-8}$	$4.7 \cdot 10^{-12}$	$2.1 \cdot 10^{-10}$	$7.9 \cdot 10^{-11}$
Cs	$1.1 \cdot 10^{-9}$	$2.0 \cdot 10^{-10}$	$3.7 \cdot 10^{-10}$	$1.3 \cdot 10^{-10}$
Pb	$2.9 \cdot 10^{-12}$	$1.3 \cdot 10^{-11}$	$5.2 \cdot 10^{-12}$	$4.9 \cdot 10^{-10}$
Ra	$2.3 \cdot 10^{-11}$	$1.7 \cdot 10^{-12}$	$1.7 \cdot 10^{-14}$	$1.6 \cdot 10^{-12}$
Th	$3.1 \cdot 10^{-14}$	$1.1 \cdot 10^{-12}$	$1.6 \cdot 10^{-11}$	$4.3 \cdot 10^{-10}$
Pa	$6.4 \cdot 10^{-17}$	$1.2 \cdot 10^{-14}$	$4.8 \cdot 10^{-14}$	$8.4 \cdot 10^{-13}$
U	$2.4 \cdot 10^{-10}$	$5.8 \cdot 10^{-8}$	$6.7 \cdot 10^{-8}$	$1.2 \cdot 10^{-6}$
Np	$1.4 \cdot 10^{-14}$	$2.5 \cdot 10^{-12}$	$1.1 \cdot 10^{-10}$	$7.0 \cdot 10^{-8}$
Pu	$3.3 \cdot 10^{-13}$	$2.5 \cdot 10^{-11}$	$5.3 \cdot 10^{-10}$	$8.2 \cdot 10^{-9}$
Am	$9.7 \cdot 10^{-14}$	$1.4 \cdot 10^{-12}$	$5.7 \cdot 10^{-11}$	$4.3 \cdot 10^{-8}$
Cm	$6.0 \cdot 10^{-20}$	$1.0 \cdot 10^{-19}$	$4.3 \cdot 10^{-14}$	$8.8 \cdot 10^{-13}$

The elements are listed according to increasing atomic number.

APPENDIX D: Sorption Values for the Low Priority Elements

No relevant literature data for sorption on cement of the low priority elements listed in Table 2 was found. The estimated distribution ratios given below are based on chemical analogy.

Beryllium

Be sorption will be similar to that exhibited by the alkali-earth metals. These elements have sorption intensities increasing in the order Be, Mg, Ca, Sr, Ba and Ra. In Table 4 a value of 10^{-3} m^3 kg^{-1} was selected for Sr. Be will sorb more weakly. Consequently we assign a conservative value of zero. (Note that we have not considered here that the alkali earths may well sorb by a similar mechanism to Ca).

Sodium and Potassium

K (but not Na) might sorb in a similar manner to Cs, but less strongly. Thus there may be some weak sorption for K particularly in regions II and III. Nevertheless, we conservatively set the distribution ratios for these two elements at zero over the whole range of conditions anticipated within the repository.

Calcium

Since Ca is normally grouped together with Mg, Sr, Ra and Ba, its distribution ratio might be anticipated to be in the range given for Sr and Ra (see section 5.2.5). However, we would contend that when $Ca(OH)_2$ and $CaCO_3$ are present in the cement, an argument similar to that given for CO_3^{2-} might be more appropriate i.e. radioactive Ca would be removed from solution by isotopic exchange with the calcium in portlandite and calcite (see section 5.2.7). For this reason the "sorption" value for Ca will also be system dependent.

Iron and Cobalt

In Figure 1, Fe and Co appear on the graph grouped closely together with Cu, Zn, Ni and Mn. For this reason we assign the same distribution ratios given for Ni to Fe and Co (see section 5.2.3).

Samarium, Europium and Holmium

The sorption behaviour of these trivalent rare-earth elements has been taken to be analogous to Am (see section 5.2.1).

Polonium

We have taken Pb as a chemical analogue for Po and hence assign the same distribution ratios (see section 5.2.13).

Actinium

The sorption behaviour of Ac has been taken to be analogous to Am.

APPENDIX E: Sorption Reduction Factors for Plutonium as a Function of Cellulose Content in Cement

In Chapter 6 a relationship between the total concentration of iso-saccharinic acid (ISA) in the cement pore fluid and the sorption of plutonium in cement was derived. For performance assessment a relationship between the **cellulose content** in cement and its influence on sorption is more convenient. This relationship is derived in the following for low loadings of cellulose under the assumption that the cellulose degrades completely to iso-saccharinic acid.

If the concentration of iso-saccharinic acid in the cement pore fluid is C_{ISA} (mol l^{-1}) and the corresponding distribution ratio is R_d (ISA), then the following expression gives the total mass of cellulose in the system (m_{cell}, kg) when it has all degraded to iso-saccharinic acid:

$$m_{cell} = \{V_{cem} \cdot \varepsilon \cdot C_{ISA} \cdot MW + M_{cem} \cdot R_d(ISA) \cdot C_{ISA} \cdot MW\} \qquad (1\text{-E})$$

where
- V_{cem} = volume of cement (m^3)
- M_{cem} = mass of cement (kg)
- ε = cement porosity (0.2)
- MW = molecular weight of iso-saccharinic acid (165, g mol^{-1})
- R_d (ISA) = distribution ratio for iso-saccharinic acid (1 $m^3 kg^{-1}$)

Under the conditions that the sorption capacity of the cement is exceeded (see Chapter 6) equation (1-E) has to be replaced by

$$m_{cell} = \{V_{cem} \cdot \varepsilon \cdot C_{ISA} \cdot MW + M_{cem} \cdot S_{cem} \cdot MW\} \qquad (2\text{-E})$$

where S_{cem} = cement sorption capacity for iso-saccharinic acid (0.1 mol kg^{-1})

The sorption capacity of cement is attained at an iso-saccharinic acid concentration of 10^{-4} M.

It follows from (1-E) and (2-E) that

$$\frac{m_{cell}}{M_{cem}} = \frac{1}{\rho_{cem}} \cdot \varepsilon \cdot C_{ISA} \cdot MW + R_d(ISA) \cdot C_{ISA} \cdot MW \qquad C_{ISA} < 10^{-4}\ M \qquad (3\text{-E})$$

$$\frac{m_{cell}}{M_{cem}} = \frac{1}{\rho_{cem}} \cdot \varepsilon \cdot C_{ISA} \cdot MW + S_{cem} \cdot MW \cdot 10^{-3} \qquad C_{ISA} \geq 10^{-4}\ M \qquad (4\text{-E})$$

where $\rho_{cem} = \frac{M_{cem}}{V_{cem}} = 2250\ kg\,m^{-3}$

Substituting parameter values into equation (3-E) gives:

$$\frac{m_{cell}}{M_{cem}} = 1.47 \cdot 10^{-2}\,[M^{-1}] \cdot C_{ISA} + 165\,[M^{-1}] \cdot C_{ISA} \approx 165\,[M^{-1}] \cdot C_{ISA} \qquad (5\text{-E})$$

for all $C_{ISA} < 10^{-4}$ M.

Likewise, substituting parameter values into equation (4-E):

$$\frac{m_{cell}}{M_{cem}} = 1.47 \cdot 10^{-2}\,[M^{-1}] \cdot C_{ISA} + 1.65 \cdot 10^{-2} \qquad (6\text{-E})$$

In section 6.2.3, the sorption reduction factor (solubility enhancement factor) was defined as

$$R_f(Pu, C_{ISA}) = \frac{[Pu(org)]_{S.L.}}{[Pu]_{S.L.}} \qquad (7\text{-E})$$

where $[Pu(org)]_{S.L.}$ is the total concentration of Pu in solution at an iso-saccharinic acid concentration of C_{ISA}. $[Pu]_{S.L.}$ is the solubility limit of Pu in the absence of complexing organic ligands, ~$5 \cdot 10^{-10}$ M. (Note: The degradation products of cellulose are assumed to have a complexation behaviour similar to iso-saccharinic acid, see section 6.2.1).

Using the above expression for the sorption reduction factor and the data in Figure 3, the following relationship can easily be derived:

$$\log R_f(Pu, C_{ISA}) = 1.5 \log C_{ISA} + 8.8 \qquad (8\text{-E})$$

Equation (8-E) can then be combined with equations (5-E) and (6-E) to give expressions relating the content of cellulose in the waste (m_{cell}/M_{cem}) to the corresponding sorption reduction factor R_f, i.e.

$$\log R_f\,(Pu, m_{cell}/M_{cem}) = 1.5 \log \frac{m_{cell}}{M_{cem}} + 5.47 \qquad C_{ISA} < 10^{-4}\ M \qquad (9\text{-E})$$

$$\log R_f\,(Pu, m_{cell}/M_{cem}) = 1.5 \log\left(68 \cdot \frac{m_{cell}}{M_{cem}} - 1.12\right) + 8.8 \qquad C_{ISA} \geq 10^{-4}\ M \qquad (10\text{-E})$$

Table E-1: Sorption reduction factors for plutonium as function of the cellulose content in cement.

Cellulose content in cement paste		Total concentration of ISA in the pore fluid of cement paste after complete degradation of cellulose	Sorption reduction factor for plutonium	Sorption reduction factor for plutonium for performance assessment
	(%)	(M)	(-)	(-)
Equation (9-E)	0.01	$6.06 \cdot 10^{-7}$	1	-
	0.025	$1.51 \cdot 10^{-6}$	1.2	1
	0.05	$3.03 \cdot 10^{-6}$	3.3	-
	0.075	$4.55 \cdot 10^{-6}$	6.1	-
	0.1	$6.06 \cdot 10^{-6}$	9.3	-
	0.25	$1.52 \cdot 10^{-5}$	36.9	50
	0.5	$3.03 \cdot 10^{-5}$	104	-
	0.75	$4.55 \cdot 10^{-5}$	192	-
	1	$6.06 \cdot 10^{-5}$	295	-
	1.25	$7.58 \cdot 10^{-5}$	412	-
	1.5	$9.09 \cdot 10^{-5}$	542	500
Equation (10-E)	1.75	$6.8 \cdot 10^{-2}$	$(1.2 \cdot 10^{7})$	∞
	2	$2.38 \cdot 10^{-1}$	$(7.4 \cdot 10^{7})$	∞

APPENDIX F: Sorption of Carbonate in Cement

In section 5.2.7, (equation (7)), an expression was derived for the distribution ratio of ^{14}C (as carbonate) based on isotope exchange between $^{14}CO_3^{2-}$ and inactive carbonate in the liquid and solid phases, i.e.

$$R_d(^{14}CO_3^{2-}) = \frac{Z}{S} \quad l\,kg^{-1} \qquad (1\text{-}F)$$

where Z is the quantity of inactive carbonate in a cementitious mix (in mol kg^{-1}) and S the concentration of CO_3^{2-} in the pore water (in mol l^{-1}).

In a repository the value of the above quotient is time dependent, on the one hand because the carbonate in the infiltrating groundwater is continuously precipitating out in the cement pore space, and on the other, because the solubility of carbonates in the cement pore water is decreasing with decreasing pH as the cement degrades. In order to quantify these effects $^{14}CO_3^{2-}$ distribution ratios were calculated from equation (1-F) using the results from some recent cement degradation calculations (NEALL 1994).

In the above study, HTS cement was taken as the reference material and cement degradation in both $NaHCO_3$ and NaCl type groundwaters from Wellenberg was calculated. Distribution ratios are presented for cases where 10% and 100% of the solid carbonate are available.

The results are given in Tables (F-1) and (F-2) for $NaHCO_3$ and NaCl type infiltrating fluids respectively. A (water exchange) cycle in these tables is defined as the time during which one volume of pore solution is removed from the system and replaced by a fresh volume of groundwater. On the basis that one cycle lasts for ~10^4 years (NEALL 1994), the time dependent variation of the distribution ratio of $^{14}CO_3^{2-}$ over ~10^7 years is shown in Figures (F-1) and (F-2). For both cases, the trends are similar.

Table F-1: Distribution ratios for $^{14}CO_3^{2-}$ as a function of pH calculated for the degradation of HTS cement in $NaHCO_3$ groundwater. The data in the first four columns are taken from NEALL (1994).

pH	Cycle number	Carbonate concentration in solution	Carbonate concentration in solid phase (1)	Distribution ratio for $^{14}CO_3^{2-}$ (2)	Distribution ratio for $^{14}CO_3^{2-}$ (3)
		(mol l^{-1})	(mol kg^{-1})	(m^3 kg^{-1})	(m^3 kg^{-1})
13.5	1	$6.1\ 10^{-4}$	$4.2\ 10^{-2}$	$6.9\ 10^{-2}$	$6.9\ 10^{-3}$
13.3	3	$1.8\ 10^{-4}$	$4.6\ 10^{-2}$	$2.6\ 10^{-1}$	$2.6\ 10^{-2}$
13.1	5	$6.0\ 10^{-5}$	$5.1\ 10^{-2}$	$8.5\ 10^{-1}$	$8.5\ 10^{-2}$
12.9	7	$2.5\ 10^{-5}$	$5.4\ 10^{-2}$	2.2	$2.2\ 10^{-1}$
12.8	9	$1.4\ 10^{-5}$	$5.9\ 10^{-2}$	4.2	$4.2\ 10^{-1}$
12.5	25	$8.0\ 10^{-6}$	$9.2\ 10^{-2}$	11	1.1
12.4	314	$8.0\ 10^{-6}$	0.75	93	9.3
11.7	1046	$3.3\ 10^{-5}$	2.6	79	7.9

(1) These data include an initial level of $CaCO_3$ in HTS cement of 0.04 mol kg^{-1}.

(2) 100% of the carbonate in the solid phase is accessible.

(3) 10% of the carbonate in the solid phase is accessible.

Table F-2: Distribution ratios for $^{14}CO_3^{2-}$ as a function of pH calculated for the degradation of HTS cement in NaCl groundwater. The data in the first four columns are taken from NEALL (1994).

pH	Cycle number	Carbonate concentration in solution	Carbonate concentration in solid phase (1)	Distribution ratio for $^{14}CO_3^{2-}$ (2)	Distribution ratio for $^{14}CO_3^{2-}$ (3)
		(mol l^{-1})	(mol kg^{-1})	(m^3 kg^{-1})	(m^3 kg^{-1})
13.4	1	$8.8\ 10^{-4}$	$4.0\ 10^{-2}$	$4.6\ 10^{-2}$	$4.6\ 10^{-3}$
13.2	3	$2.7\ 10^{-4}$	$4.1\ 10^{-2}$	$1.5 \cdot 10^{-1}$	$1.5 \cdot 10^{-2}$
12.9	5	$8.8\ 10^{-5}$	$5.1\ 10^{-2}$	$4.8\ 10^{-1}$	$4.8\ 10^{-2}$
12.7	7	$3.6\ 10^{-5}$	$4.3\ 10^{-2}$	1.2	$1.2\ 10^{-1}$
12.6	9	$2.1\ 10^{-5}$	$4.4\ 10^{-2}$	2.1	$2.1\ 10^{-1}$
12.4	25	$1.3\ 10^{-5}$	$5.1\ 10^{-2}$	3.9	$3.9\ 10^{-1}$
12.2	409	$1.5\ 10^{-5}$	0.25	17	1.7
11.2	1089	$2.5\ 10^{-5}$	0.69	28	2.8

(1) These data include an initial level of $CaCO_3$ in HTS cement of 0.04 mol kg^{-1}.

(2) 100% of the carbonate in the solid phase is accessible.

(3) 10% of the carbonate in the solid phase is accessible.

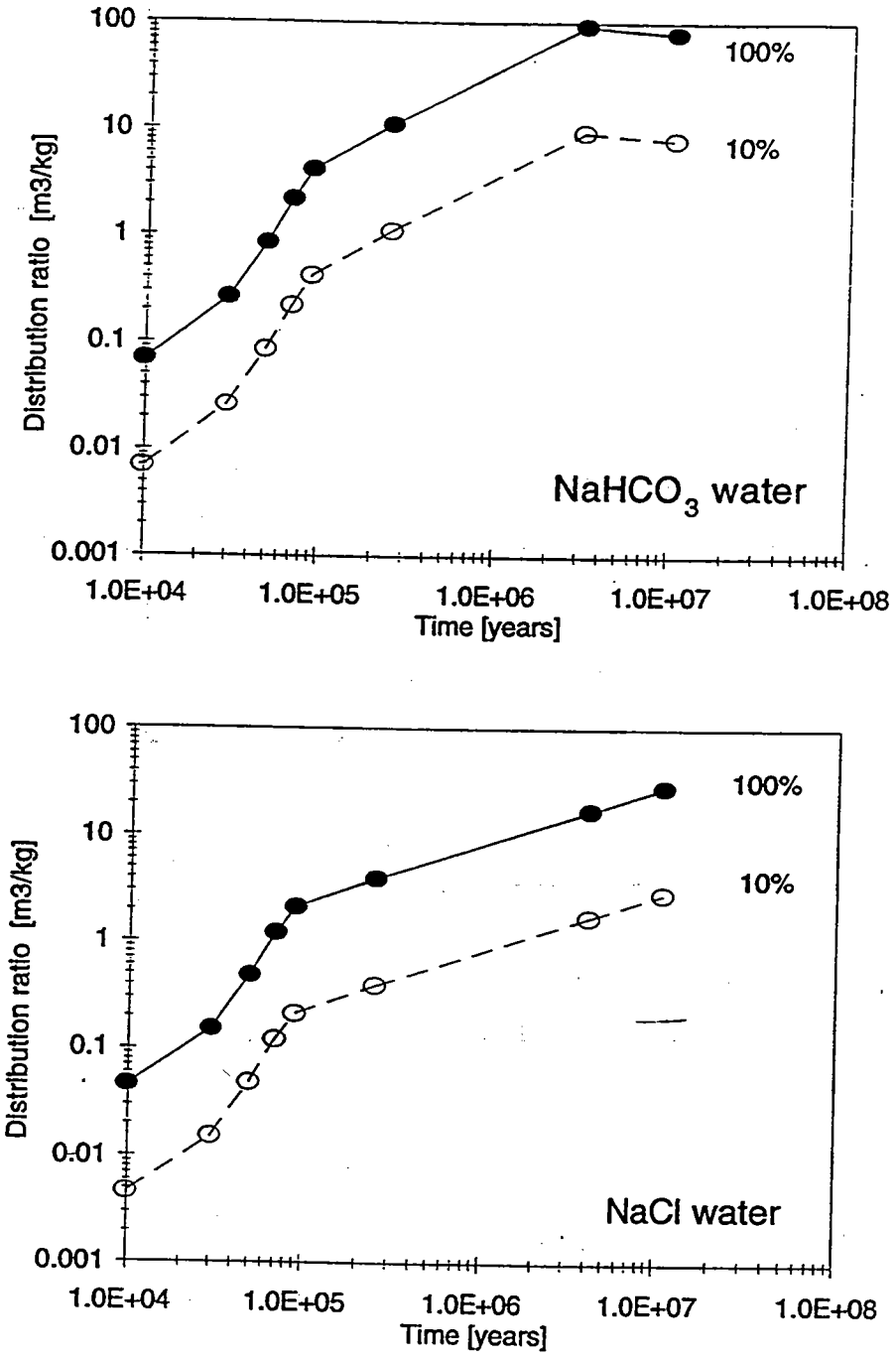

Fig. F-1: Calculated distribution ratios of $^{14}CO_3^{2-}$ as a function of time for HTS cement degradation in two types of groundwater. The calculated values are presented for two extreme cases: a) 100% of the solid carbonate phase in the cement is accessible (full symbols) and b) 10% of the carbonate is accessible (open symbols).

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