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MARTIN MARIETTA

Determination of Metabolic Data Appropriate for HLW Dosimetry (ICRP-30), I.

K. F. Eckerman
R. W. Leggett
R. Meyer
G. D. O'Kelley

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DETERMINATION OF METABOLIC DATA APPROPRIATE FOR HLW DOSIMETRY (ICRP-30), I.

K. F. Eckerman, R. W. Leggett, R. Meyer,* and G. D. O'Kelley,*

*Chemistry Division

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1. INTRODUCTION

The purpose of this report is to provide an initial evaluation of the dependence on chemical forms of estimates of health effects from radionuclides in high-level waste (HLW). It is assumed that the organ dose is a suitable index for health effects from exposure to radionuclides, and our discussion is usually directed toward the metabolism and dosimetry of various chemical forms of a radionuclide rather than toward health effects per se.

This study is needed because the chemical species of radioelements released to the environment from a high-level waste repository may not be adequately described by the metabolic and dosimetric models of Publication 30 of the International Commission on Radiological Protection (ICRP 30). Discussion is limited to a review of studies that may be useful in identifying (a) those chemical forms of radionuclides which are likely to reach humans after migration from a waste repository and (b) differences in metabolism and organ doses that result from intake of various chemical forms of these radionuclides; we also attempt to identify research needs in these two areas. Since a survey covering all radionuclides in high-level waste would be prohibitive, discussion is limited mainly to four radionuclides of critical importance in high-level waste management: plutonium, americium, neptunium, and strontium. Because the metabolism of curium is often discussed in the literature along with that of the physiologically similar element americium, we include curium in our discussion of the metabolism of different compounds.

There has been a great deal of work on the development of data concerning complexing, hydrolysis, and precipitation reactions of Pu, Am, Np, and Sr. With the assumption that the nuclides are present at equilibrium with the environment, these data may be used to predict speciation in the environment. There are, however, substantial uncertainties associated with such predictions. In particular, the data were derived for relatively high concentrations of the nuclides, and verification for low environmental levels is an extremely difficult task. Also, the assumption that the nuclides are at equilibrium with the environment is often inaccurate. Thus, despite the relatively large body of information related to the speciation of nuclides in the

environment, a great deal of research is still needed for the purpose of verifying predicted speciation under realistic environmental conditions.

There have also been several studies concerning the metabolism and dosimetry of various chemical and physical forms of these elements, particularly Pu. Unfortunately, the chemical forms studied in laboratory experiments often are not those of interest for evaluation of environmental exposures. Rather, the various chemical forms often are chosen for convenience in experimentation or because of their interest in occupational exposures. For this reason there may be sufficient data available (such as in the case of Pu) to study the sensitivity of uptake, metabolism, and organ doses to chemical form in a general sense, although few conclusions can be drawn concerning specific chemical forms that may be encountered in the environment.

Thus, in addition to providing a limited review of the literature that may be pertinent to estimating doses to humans from radionuclides in high-level wastes, this report identifies some of the problems involved in determining speciation of these radionuclides in the environment and provides a general picture of the potential errors that may be involved in applying models assumed to be independent of chemical form to estimate metabolism and dose from exposure to different chemical species of a radionuclide. The report is divided into two main parts. In Section 2 we discuss speciation of Pu, Am, Np, and Sr in the environment. Section 3 deals with the behavior of various chemical forms of these elements (and Cm) after they are inhaled or ingested. Identification of further research needs is made at the end of each of these sections.

2. CHEMICAL SPECIES IN THE ENVIRONMENT

The task of determining the chemical form of radionuclides in the environment at trace concentrations is by no means a simple matter of laboratory investigation of appropriate samples with well-established procedures. Although certain procedures tend to be used regularly, there is always uncertainty in application of these experimental techniques to the positive identification of speciation. There is, in effect, a sort of uncertainty principle in these measurements when applied to trace concentrations of radionuclides in that it is always possible that the measurement itself may disturb the speciation of the nuclide. There is also a basic assumption in the literature concerning speciation of trace nuclides which states that chemistry observed at macro concentrations is applicable to tracer concentrations. This assumption appears justified for many cases, even for chemical properties measured with only a few atoms. Thus, determination of standard redox potentials for nobelium, element 102, falls in line with potentials measured for larger concentrations of other comparable elements.[1-3] These experiments were performed on cyclotron produced nobelium in which only 100 to 500 atoms were produced in a given run, and data were taken in repeated runs, each producing only a few hundred atoms. In the application of this assumption, it is important to keep in mind that at low concentrations the relative proportion of various species of a given element may be quite different from the proportions at high concentrations.[4] In particular, sparingly soluble neutral species can exist in relatively high proportions at low total concentrations of nuclides; at high total concentrations, solubility will often limit the concentrations of these neutral species so that these neutral species will be only a small fraction of the total concentration.

In light of the difficulties of experimental determination of chemical speciation, it is not surprising that different approaches have been taken. A great deal of effort has been given to the construction of potential-pH diagrams and concentration-pH curves.[5,6] However, there has also been over the years a considerable literature on experimental determination of speciation. A truly sceptical chemist would have difficulty accepting either approach exclusively, but faced with the task

of giving best estimates of speciation in the environment, an approach must be adopted. We will therefore start with the results of equilibrium calculations, but we will point out, whenever appropriate, when experiments and other considerations may alter conclusions from these diagrams. There are a number of non-equilibrium effects such as formation of pseudocolloids and biological phenomena that would very likely alter these conclusions, and these effects cannot be ignored. We emphasize that the results of equilibrium calculations are always just a beginning; without experiments to support the conclusions, there can be little confidence in predicting speciation from these diagrams.

Because of the radioactivity of the nuclides, it is usually easy to determine their concentrations in the environment provided, of course, that their concentrations are high enough. However, determinations of the concentrations of the nuclides by radiometric means give no direct information on their speciation (that is, their existing or potential chemical forms). A frustrating aspect of this task was to find that by far most of the literature on the subject of nuclides in the environment dealt only in detecting the presence and concentrations of the nuclides, and by far most of these investigations did not consider the chemical form of the nuclides. However, there has recently been an encouraging trend to try to determine the valence states of polyvalent nuclides in groundwaters, but the volume of this literature is much smaller than the literature dealing solely with concentration.

Before proceeding with the discussions of speciation, we will give a brief review of the environmental parameters that may affect speciation and the methods used to estimate or to determine experimentally the chemical form of nuclides.

RELEVANT ENVIRONMENTAL PARAMETERS

Speciation will depend to a greater or less degree on a number of parameters. We will discuss the most important parameters in this section and also present a brief assessment of methods of determination of these parameters.

The elements Pu, Sr, Am, and Np are included in this report. Of these, Sr and Am are expected to exist in a single valence state in the environment, and Np and Pu can exist in several. Therefore, the oxidizing or reducing conditions of the groundwater and the geological formations will affect the valence state of Np and Pu. In the geochemical literature, redox conditions are often described by a single parameter, Eh[7] which refers to an oxidation reduction potential. However, as has been clearly stated,[7,8] this parameter applies only to conditions where there is complete equilibrium between all redox couples in the natural system. Actually, complete equilibrium is rarely achieved in natural systems, and potentials measured on indicator electrodes will generally be mixed potentials which are related to kinetic effects.[7-10] Measurements on an indicator electrode can be related to oxygen content of the groundwater,[8] but the relationship may be complicated. There is often no correlation between redox potentials calculated from analyses of redox couples and measurements made on indicator electrodes.[11] Pertinent parameters are the dissolved oxygen content of the groundwaters and the concentrations of other electroactive species, such as iron and sulfur containing species. The reducing or oxidizing abilities of the solids in the flowpaths of the nuclides must also be considered, because reactions altering the valence state of the nuclides could be heterogeneous, i.e., take place by reaction with species on the surface of the solids. The concentrations of groundwater species can often be estimated with considerable precision by standard analytical techniques. It is much more difficult to characterize the redox properties of the solids, especially at normal formation-groundwater conditions of temperature and pressure where kinetic considerations are usually so important.

The pH of groundwaters is of considerable importance for those species which tend to hydrolyse strongly in the pH range of natural groundwaters. The pH was originally defined as the negative logarithm (base 10) of the hydrogen ion concentration. In many textbooks and references, pH is defined as the negative logarithm of the hydrogen ion activity, a definition which is not practical because single ion activities cannot be determined experimentally.[12-14] This definition therefore cannot be used to devise a practical laboratory pH scale. In order to overcome this difficulty, an operational definition is used in which

pH refers to measurements, either with a hydrogen or glass electrode, using a series of reference buffer solutions specified by the National Bureau of Standards.[12,14] Measurement of pH in pure solutions is a relatively simple laboratory procedure and can be done with considerable precision; measurements in the field are complicated by the presence of unknown materials which can limit the reliability of the measurement.

The chemical composition of the groundwater will also be very important, and the pH will affect the relative amounts of possible complexing ligands such as carbonate ion. The concentrations of carbonate and bicarbonate ion will strongly affect the transport and final speciation of those elements which form negatively charged carbonate complexes. Titration methods are commonly used to determine carbonate and bicarbonate contents with considerable precision.

The particulate content of the groundwater could be quite important with respect to formation of pseudocolloids, a term which is now often used to describe colloidal particles on which the nuclides are sorbed. The presence of colloids and other particulates is often determined either by filtration or ultra-centrifugation.

REVIEW OF ANALYTICAL METHODS

In the previous section, we briefly mentioned methods for determination of the environmental parameters affecting the speciation of the nuclides. In this section, we review methods used either to estimate the speciation if the pertinent environmental parameters are known or methods used in attempts to determine the speciation directly by experiment.

For the determination of species in an aqueous solution, chemists would prefer spectrophotometric methods. However, ordinary spectrophotometric methods are generally not sensitive enough for determination of speciation at trace concentrations. In practice, a lower limit of roughly 1E-4 to 1E-6 molar eliminates this method for trace constituents. The lower limit for a particular species will, of course, depend on the extinction coefficient of the species.

A great deal of effort therefore has gone into attempts to predict speciation at trace levels from data gathered for macro-concentrations of the species. Frequently, this takes the form of potential-pH diagrams[5] or Eh-pH diagrams, as they are usually called in the geochemical literature. Closely allied to these diagrams are so-called "spaghetti" diagrams, which for certain assumptions, present lines of concentration vs pH for all of the species in equilibrium. In the construction of these concentration-pH diagrams some assumption must be made regarding variation of the concentration of the nuclide. This often takes the form of species in equilibrium with a solid phase. In applying these diagrams to trace constituents, one must assume that the system is at complete thermodynamic equilibrium, that the data base for the system is complete and accurate, i.e. that nothing has been overlooked, and that conditions applicable to high concentrations of the nuclides may be applied without change to very low concentrations. The validity of all of these assumption is by no means obvious or certain. In its most elaborate form, this method uses complex mathematical codes which are solved by computer techniques.[15,16] In applying these diagrams and codes to specific situations, certain information must be known. The valence states of the nuclides, the pH, the identity of the solids in contact with the groundwater, the redox properties of the system, and groundwater composition all must be specified. It is evident that a host rock groundwater system is quite complicated, and it is certainly debatable whether these methods could be applied to these complex systems. However, investigators in the field believe that equilibrium methods are beginnings to the prediction of speciation. By no means can estimates of speciation taken from these codes or diagrams be taken as sufficient for prediction of speciation.

Experimentally, the methods used to determine speciation are difficult and almost invariably rely upon use of radiotracers. Coprecipitation and solvent extraction are widely used to determine the valence states of species. However, in the use of these methods, generally one must adjust conditions of the solution prior to the solvent extraction or precipitation. It is possible that these operations may change the speciation. One must therefore perform a number of experiments under

known oxidizing and reducing conditions in order to accumulate evidence that the valence state determination is reasonably justified.

Migration methods are commonly used in attempts to determine speciation at trace levels. For example, measurements of diffusion rates as a function of solution composition, particularly as a function of pH, are often used for estimation of radii of migrating species.[17] Electrophoretic methods are also used, and ideally this technique gives mobility and charge of the species.[18] From these parameters, it is possible to obtain estimates of speciation of nuclides by experiments in which solution parameters are changed. In each of these methods, radiotracers are usually employed to detect the movement of the species. Various forms of chromatography may be used to detect the presence of relatively high molecular weight substances. Gel chromatography has been used to determine the forms of heavy metals in lake water, and the results indicate that probably the metals are associated with humic substances.[19]

Ion exchange and adsorption reactions are often used to deduce speciation, but again use of these methods requires many assumptions. In a common form, the ion exchange method consists of passing solution through cation and anion exchangers, either columns or membranes. It is assumed that species adsorbed on the cation exchanger are cationic and species adsorbed on anion exchangers are anionic. Unfortunately, this is often not the case, and different results are sometimes obtained in experiments of this type if the order of passage through the anion and cation exchangers is reversed. More elaborate techniques must therefore be applied in which the solution compositions are varied. However, with care, considerable information can be obtained from studies of this type.[20,21] Adsorption methods are also used where adsorption is studied as a function of solution composition on materials such as glass and silica.[22] However, evidence of speciation obtained from this method is quite indirect, and results must be judged carefully.

Electrochemical techniques, such as polarography and electrodeposition, have also been used.[23] Again, evidence obtained this way is quite often indirect.

One of the main problems in these methods is that at very low concentrations, certain factors enter that are not significant at high concentrations. Among these, are sorption of the species on the walls of the container, formation of colloids and pseudocolloids, and the

presence of trace amounts of organic materials that may interact chemically by forming complexes or causing redox reactions. The formation of pseudocolloids, i.e., colloidal particles of usually unknown composition which sorb the nuclide in question, is particularly troublesome. In order to detect them and true colloids, ultrafiltration and high-speed centrifugation are often used. However, the information so obtained is usually difficult to interpret.[24]

Because methods of determination of speciation at trace concentrations are difficult and rely on considerable judgement concerning the interpretation of the data, determinations of information such as the charge and size of species should always be verified by one or two other methods, if possible.

Although the experimental methods we describe are difficult, they have been used extensively. At times, the results of these experiments are consistent with predictions from data at high concentrations, but quite often there are conflicts, probably due to the effects mentioned above, which begin to become important at trace concentration levels. Therefore, considerable caution must be exercised in the use of Eh-pH and concentration-pH diagrams for prediction of speciation at trace concentration levels.

FACTORS WHICH CHANGE SPECIATION DURING TRANSPORT

If the chemical species were always at equilibrium with the groundwater, then it would only be necessary to consider the final accessible environment in order to predict or determine experimentally the final chemical form of nuclides that might be released from a high level waste repository. We cannot make this assumption, and therefore some consideration must be given to the path that could be taken. If a HLW repository in basalt is considered, it is likely that conditions in the basalt environment will be reducing and those elements like Pu and Np that can exist in several valence states will be reduced to a lower state. In the absence of ligands that might form complexes and at the pH range of about 8-10 of the basalt groundwaters, the solubility product of the hydroxides of the lower valence states of these elements could be exceeded. Several possibilities now exist: (1) The hydroxides

could form as separate discrete phases in the repository on the surface of minerals. (2) The lower valent species of the nuclides could adsorb on the surfaces of the minerals before they could form discrete particles of hydroxide or oxide. (3) As the solubility product of the hydroxide is exceeded, stable colloids of the hydroxide could be formed. (4) The lower valent species could adsorb on stable colloids of other materials and form psuedocolloids.

If the nuclides are in the form of colloids or pseudocolloids, then the question is whether or not these forms can be transported to the accessible environment. The transport of fine particulates has recently been reviewed and discussed by Apps et al.,[79] and a number of experimental studies have been reported.[24,80] However, there is really very little research on this subject, and if we must take a conservative approach, there is little that can be said with certainty concerning the transport properties of fine particulates. It is well known that colloidal solutions can be stable for long periods of time, but whether they would be stable in a long flowpath is not known. Further, it is possible to envision a mechanism by which colloids are trapped or adsorbed by the formations but then become redispersed again. Alternatively, the nuclides could be redissolved into the groundwater and again be sorbed on colloids. Thus, there would be a process of continuous formation and redispersal of colloidal material. Further investigation into the transport of charged colloidal particles and sensitivity studies of the relative importance of colloidal diffusional transport are recommended by Apps et al.[79]

Another possibility that must be considered during transport is biological alteration of the chemical speciation of the nuclide. Although we have not found evidence of any such effects with the four nuclides covered in this work, Behrens has reported evidence of such an effect with iodide ion.[25] He reported that iodide ion is oxidized enzymatically and then incorporated into large organic molecules, possibly proteins. Such a mechanism would cause retardation of migration in soils, but it is possible that these materials could appear in waters that are accessible to human consumption.

Colloid formation and biological action are two examples of processes that complicate the prediction of speciation from equilibrium type arguments. But probably the most important effects that cause deviations from equilibrium are kinetic effects.

EXPECTED SPECIATION OF THE NUCLIDES

Strontium

The primary isotope of concern to waste migration is Sr-90 with a half-life of 29 y. Other nuclides are produced but their half-lives are too short to be of significance. Of these, Sr-85, with a half-life of 65 d, is often used as a tracer in laboratory studies. The only valence state which can exist in the environment is Sr(II).

Several reviews which deal with chemical speciation of nuclides in the environment give the result that the most probable specie of strontium is Sr^{2+}.[26-28] These reviews present equilibrium calculations using constants taken from some of the standard references for formation of complexes and hydrolytic species.[29,30] Strontium does not in general form strong complexes with either organic or inorganic ligands, and, unless ligands are present in unusually high concentration, complexation is not expected to alter the conclusion that Sr(II) will be present principally as the divalent ion. However, data bases for equilibrium distributions of species never take into account such nonequilibrium types of reactions as formation of pseudocolloids or the presence of biological phenomena. Thus, the fact that these equilibrium calculations predict Sr^{2+} must be taken as only a beginning.

Most of the literature concerning strontium in the environment deals with sorption on various minerals and natural materials. With respect to sorption reactions, strontium is probably the most studied nuclide. In one of the larger environmental reviews,[26] dated August, 1978, over two hundred references are listed for soil and rock interactions with Sr. Many of these references simply give results in terms of Kd (amount of the nuclide per unit weight of sorbent divided by concentration of the nuclide in the groundwater) without specifying completely the conditions and parameters of the experiment. Because Kd is a parameter that can be sensitive to solution concentrations of other ions, loading of the sorbent, pH, and various parameters describing the solid, Kd values without specification of the pertinent parameters are of little value, and not much can be learned concerning speciation of strontium. Fairly complete studies of strontium sorption have been reported for clay minerals,[31-33] and it is clear from these laboratory studies

that Sr exists as Sr^{2+} in these solutions. However the solutions used were generally various types of laboratory solutions that have been equilibrated with laboratory samples (often purified) of clay minerals.

Strontium adsorption on minerals is generally a reversible ion exchange process. Thus, migration of strontium may proceed readily if Kd values are low. For adsorption of strontium on hydrous oxides, values of Kd increase sharply with pH;[34,35] for adsorption on clay minerals, values of Kd generally remain constant or increase moderately with pH.[31] Because many geological formations contain iron and aluminum hydroxy compounds, the adsorption properties of such formations at high pH may therefore be dominated by these hydrous materials. If these hydroxides exist as colloidal particles, then at higher pH values, it is quite likely that Sr^{2+} could be adsorbed on them. If these colloidal particles can be easily transported, then the final form of Sr in the accessible environment could be Sr adsorbed on very fine colloids of hydrous oxides. Pseudocolloids of Sr have been reported.[36] It is of some interest that studies of chemically similar radium at trace concentrations show that a large amount of the radium has a very low electrophoretic mobility,[37] an observation that suggests that a significant portion of the radium may be present as organic complexes or colloids. If strontium is adsorbed on colloidal hydroxides at high pH, then, since the process is probably reversible, any lowering of the pH would probably release Sr^{2+}. A study[38] using columns of soils from the Hanford site showed that some Sr-90 apparently passed through the column as colloidal material. Evidence for particulates was obtained from centrifugation experiments.

Studies of chemical speciation of Sr from Maxey Flats sump water show that a variety of organic acids and other water soluble, polar organic compounds co-eluted with Sr-90 in chromatographic studies.[39] Another study[40] with silty clay also gave evidence that strontium could be present in the form of low-molecular weight organic complexes. Dialysis and gel filtration techniques were used in this study.

In summary, it appears that in general Sr(II) would be expected to exist as the divalent ion Sr^{2+}. There are two other possibilities, however. If the strontium passes through certain types of soils, there is the possibility of formation of negatively charged low molecular weight

organic complexes. In addition, there is the possibility of transport by colloidal particles of soils.

Americium

The americium nuclides of interest to nuclear waste are Am-241 with a half-life of 432 y and Am-243 with a half-life of 7380 y. Like the other actinides, it can exist in the valence state III, IV, V, and VI. However, in the environment, only the III state is expected to be important, because strong oxidizing agents are required to convert Am(III) to the higher oxidation states.

Thermodynamic data concerning hydrolysis and complexation of Am(III) have been somewhat sparse and contradictory. There have recently been a number of careful investigations of hydrolysis of Am(III) in aqueous solutions.[41,42] In an earlier report,[43] values were given for the logarithm of the first hydrolysis constant of -5.9 at an ionic strength of 0.1 and -6.2 at ionic strength 1.0. In Ref. 41, a value of -7.2 is given (ionic strength = 1) and in Ref. 42, the most recent reference, a value of -7.7 at zero ionic strength is suggested. Thus it appears that there is some disagreement. If we take the most recent values, then we can say that in acidic solutions in the absence of complexing agents the primary species of Am(III) will be Am^{3+}, and hydrolysis will be almost negligible at pH values below 7. Above pH 7, hydrolytic species will begin to be formed, presumably beginning with $Am(OH)^{2+}$. In Ref. 42 the constants were inferred from a careful study of the solubility of crystalline americium hydroxide. The presence or absence of these hydrolytic products could not be demonstrated from this study or the other studies; rather, they were inferred from the general behavior of tripositive ions. The solubility of americium trihydroxide in aqueous solutions which do not have complexing agents begins to limit americium concentrations significantly above pH 7, and at pH 9 the concentration of americium decreases to a lower limit of about 5mM. If sufficient carbonate is present, a solid carbonate of americium could be formed which would further decrease the concentration.[81] In more alkaline solutions, the solubility would probably rise due to formation of negatively charged hydrolytic species. Also, if sufficient carbonate is

present, formation of carbonate complexes may occur.[41] Complexes could also occur with other ligands if present in sufficient quantity, in particular, fluoride ion and sulfate ion.[26]

The interaction of humic compounds with Am(III) has also been carefully studied recently. Cleveland and Rees[45] conclude that in natural groundwaters, there would be little solubilization of Am (and Pu) by humic substances for the particular samples of humic compounds and experimental conditions that they tested. However, they urge caution in extrapolating these results to other conditions. On the other hand, the formation constants for humic ligands with Am(III) and Eu(III) were found to be high,[46] suggesting rather strong interaction with humic substances.

One of the uncertainties of Am(III) chemistry is the possibility of the presence of Am in colloidal particles, either as true colloids or pseudocolloids. There are a number of reports on this subject,[4,47-49] and in Ref. 26 there is an extensive review and discussion of the interaction of Am with particulate materials. Because of the experimental difficulties in investigating low concentrations of colloidal materials, it is difficult to predict from this literature the nature of the species. It seems certain, however, that in the pH range of interest in natural waters, pH 6 to 10, Am(III) has a strong tendency to exist in the colloidal state. Oloffson[47] found that a significant fraction of Am can be centrifuged in this pH range for the conditions that they studied. They suggest that this fraction of Am may exist in psuedocolloids, perhaps on colloidal particles of oxides or hydroxides of other metals. They also found, as have other investigators who have worked with tripositive ions of Am and lanthanides, that Am(III) tends to adsorb on many surfaces from solutions at these intermediate pH values. Because of this tendency of Am to adsorb on many types of surfaces, it is quite possible that the primary form of Am in natural waters is Am(III) adsorbed on colloidal particles. In more acidic solutions, the tripositive americium ion, Am^{3+}, is to be expected.

Recently, Cleveland _et al._[50] have investigated the speciation of Am in groundwaters of the type associated with various types of rocks which have been proposed as hosts for HLW repositories. Americium was added to the groundwaters at trace concentrations (10 pM). After a 27-day

equilibration period at 25°C and 75°C, all of the americium that was introduced remained in the granite groundwater. For experiments with shale groundwater, most of the added americium was removed from the water after 27 days. For other groundwaters, roughly half of the Am was removed. Am(III) was the only oxidation state detected. All solutions were filtered through a 0.05 micron filter before counting. Thus americium must have been present either as a very fine colloid or as a true solution species.

Fried et al. reported migration experiments with solutions in contact with basalt, tuff, and limestone.[51] They reported electromigration experiments with Am which suggested that it is present in the form of neutral species. Similar results from migration experiments were reported by Oloffson.[47]

In summary, therefore, it appears that in acid solutions Am(III) exists as Am^{3+}. In neutral to basic solutions it will very probably not exist as Am(III) but as some form of neutral species, perhaps as very fine colloids or as true neutral species. It is evident that exact speciation is not known for Am in the neutral to basic region.

Neptunium

The only Np isotope of interest to nuclear waste is Np-237 which has a half life of 2.14E6 y. The valence states of interest to nuclear waste are Np(IV) and Np(V). Np in aqueous solutions can also exist as Np(III), Np(VI), and Np(VII). Unlike the other actinides, the (V) state is stable over a wide range of conditions. In acid and neutral solutions, there is little doubt that Np(V) exists as the large, singly charged ion, NpO_2^+. Because of its unit charge and large size, it is often thought to be only weakly adsorbed by most sorbents. However, recent results show that it is strongly adsorbed by some hydrous oxides at pH values above 4 to 5.[8]

Also because of its large size and single charge, it is thought to be relatively weakly complexed by most of the common complexing agents. Of critical importance to the prediction of its speciation is an estimate of the extent to which NpO_2^+ undergoes hydrolysis and complexation with carbonate ion. These reactions are likely to occur above about pH 6 or 7 as the solution becomes more alkaline.

The first reported measurement of the hydrolysis constant of Np(V) gives a value of 1.26E-9 for the reaction $NpO_2^+ + H_2O = NpO_2(OH) + H^+$.[52] Because a later reference, Ref. 53, reported a value much smaller than this, the hydrolysis constant was redetermined.[54] It is interesting that these authors reported hydrolysis constants of 1.22E-9 and 1.28E-9, as determined by two different methods. Thus, these authors confirmed the earliest constant. The implication of these values is that there is a significant fraction of the hydrolyzed form of Np(V) only above about pH 8; at pH < 8 most of the Np(V) is present as NpO_2^+ in the absence of complexing agents.

Formerly, there was no way to determine accurately the formation constants of carbonate species of Np(V). Recently, Maya[55] investigated the formation of carbonate complexes, and his investigations show that at a carbon dioxide partial pressure of 1E-2 atm (a reasonable estimate for environmental carbon dioxide) carbonate complexation is substantial above pH 7. Thus at pH < 7, Np(V) exists as the NpO_2^+ ion; but above pH 7, Np(V) will exist in several forms, depending on the solution conditions. Between pH 7.5 and 8, the complex $NpO_2CO_3^-$ will predominate, and at higher pH values the di- and tricarbonate complexes will progressively tend to form. Because these are negatively charged complexes, they will tend to migrate easily and not be adsorbed.

If nuclear waste is buried in host rocks that are reducing (e.g., basalt), then the most likely valence state of Np will be Np(IV). Experiments with Np(IV) have shown that it is adsorbed readily by almost any surface.[8] Np(IV) is expected to hydrolyze strongly in solution and form a number of species such as $Np(OH)_3^+$ and $Np(OH)_4$. These hydrolytic species will adsorb strongly on finely divided particulates, and it is possible that these particulates might be transported for considerable distances. If these particulates are transported to a substantial degree to the environment, then speciation in the environment might be forms of Np(IV) adsorbed on particulate matter.

In summary, it is not difficult to say what the speciation might be if Np is in the V valence state. It will exist either as NpO_2^+ in more acid solutions and probably as carbonate complexes in carbonate containing neutral and basic solutions. If the Np were present as Np(IV) at

some time in its transport to the environment it would probably be adsorbed and particulate transport would be the only mechanism by which it could reach the environment. Thus, it is possible that particulate forms of Np(IV) could be present.

Plutonium

Isotopes of plutonium with all the mass numbers from 232 through 246 have been discovered.[56,57] The light plutonium isotopes are produced mainly in accelerator-induced reactions and so are not of importance to nuclear waste chemistry. The plutonium isotopes of possible concern to waste disposal are listed in Table 2.1. Those tabulated are all products of neutron reactions and so may be present at various concentrations in reactor fuel reprocessing wastes. The long-lived isotopes of highest yield and, therefore, of most concern to waste considerations are Pu-239 and Pu-240. Since long irradiation times and intense neutron fluxes are required to produce Pu-242 and Pu-244 by multiple neutron capture, these nuclides will be present in very small amounts in power reactor processing wastes.

Table 2.1. Decay Properties of Plutonium Isotopes[57]

Isotope	Half-Life, y	Decay Mode
Pu-238	8.78E1	alpha
Pu-239	2.41E4	alpha
Pu-240	6.57E3	alpha
Pu-241	1.44E1	beta
Pu-242	3.76E5	alpha
Pu-244	8.27E7	alpha

The complexity of the environmental chemistry of plutonium is due, in part, to the large number of oxidation states possible. In aqueous solutions five oxidation states are known:[8] Pu(III), Pu(IV), Pu(V), Pu(VI), and Pu(VII). The heptavalent aquo ion, believed to occur as PuO_5^{3-}, is unstable and is readily reduced by water.[58] Thus, the first four oxidation states are of most environmental interest and are present

in aqueous solution as the hydrated ions Pu^{3+}, Pu^{4+}, PuO_2^{+}, and PuO_2^{2+}.[58-60] Pu(IV) and Pu(V) are both unstable with respect to disproportionation into higher and lower oxidation states,[58,59] and all oxidation states from Pu(III) through Pu(VI) can be present simultaneously in a thermodynamically stable solution.[58] It is important to recognize that disproportionation reactions may be involved in oxidation-reduction reactions between plutonium and other reagents. In such cases, disproportionation might occur first, followed by direct oxidation or reduction of the appropriate product.[59,60]

The large number of plutonium oxidation states, together with the closely-spaced values of reduction potentials for these states, leads to the obvious conclusion that the concentrations of plutonium ions in the possible oxidation states will be very sensitive to the redox conditions of an aqueous system. Although the reduction potentials for the four principal valence states are well known in standard, noncomplexing media, it should be borne in mind that these well-determined potentials can change in the strongly complexing media of some groundwaters. A number of authors have attempted to predict the species of plutonium expected under specific redox conditions, assuming equilibrium between the solids and the aqueous solution.[26,27,44,63-65] These efforts have been met with only indifferent success to date, because of large uncertainties in much of the thermodynamic data employed and because of a paucity of experimental data for verifying the models. Many of the calculations predict that in natural waters under oxic conditions and for the pH range 6-10, Pu(V) would be the dominant oxidation state under these conditions, and Pu(V) would dominate only above pH 8-9, in solutions with high carbonate concentrations.[44] Bondietti and Trabalka[66] reported evidence for Pu(V) in an alkaline, freshwater pond, and Rai, Serne, and Swanson inferred the presence of Pu(V) in solutions contacting PuO_2 or $Pu(OH)_4$. In contrast, Allard et al.[67] concluded from sorption and diffusion measurements that plutonium under oxic conditions at low carbonate concentration exists predominantly as Pu(IV). It is difficult to assess these experimental differences in terms of the models used to generate the results described, since the thermodynamic data needed as input are rather uncertain, especially for Pu(IV). Under reducing conditions, it seems generally agreed that species containing Pu(III) will predominate

in the environmental range of pH, although other oxidation states would, of course, be present.

Groundwaters contain low concentrations of a number of inorganic complexing agents such as carbonate, phosphate, sulfate, and fluoride ions, and organic ligands derived from substances such as humic and fulvic acids.[44,68-70] In nonsaline waters, these ligands are present at levels of a few mmol/L or less, although concentrations in equilibrium with particular host rocks may be higher in special cases.[69] The first step in analyzing solubility and speciation of the actinides is to describe the composition of systems at equilibrium, using thermodynamic data. For accurate results kinetic information should be included, since many groundwater systems of interest are not at equilibrium; however, because the needed kinetic factors are either known poorly or not at all, the oxidation state/speciation calculations already discussed are of the equilibrium thermodynamic type.[25,27,44,63-65] To calculate the concentrations of plutonium complexes requires a great deal of thermodynamic data, but the stability constants for inorganic complexes of plutonium are, in general, not well known. Several authors have assembled data bases which are useful in this connection.[29,30,61,71-75] In cases where measured stability constants of plutonium complexes are not known, the approach has been to extrapolate values from systematics or to obtain rough estimates by comparisons with analogous ions (e.g., La^{3+} for Pu^{3+}, Th^{4+} for Pu^{4+}, NpO_2^+ for PuO_2^+, UO_2^{2+} for PuO_2^{2+}). Although values obtained in this way often must be employed, the inherent uncertainties must be recognized.

Natural waters exhibit a considerable variation in the amount of dissolved organic matter which might be involved in complexation. Concentrations as low as 0.1 mg/L of dissolved organic matter are typical of unpolluted and nonproductive freshwater and sea water, while concentrations of 10 mg/L might be expected in polluted lakes, streams, and estuaries.[68] About half of the organic carbon may appear as humic or fulvic acids. These substances have high molecular weights and contain aromatic hydroxyl and carboxyl groups which can bind metal ions. Surface waters typically contain 5-10 mg/L of humic acids with an ion exchange capacity of 5-10 mmol/g, due mainly to carboxyl groups.[76] Classification of humic compounds is based chiefly upon solubility; humic

acid is the fraction soluble only in base, and the fraction which is soluble in both acid and base is known as fulvic acid. Allard and Rydberg[75] have made estimates of the complexation of plutonium by humic substances, based on typical concentrations and unpublished data on the value of the stability constant for the Th^{4+} complex as an analog for that of the Pu^{4+}. The result is that humic complexes of Pu^{4+} should be negligible in natural waters of pH ~6, but these complexes might become very important in solubilizing plutonium at values of pH below 4 or 5. These calculations are consistent with results of experiments by Cleveland and Rees,[45] who found that solubilization of plutonium by fulvic acid was slight at environmental values of pH. The resulting solutions of plutonium were unstable and the plutonium eventually precipitated, apparently either by flocculation of colloids or by slow hydrolysis reactions.

At the near-neutral or basic conditions characteristic of many natural aqueous systems, hydrolysis plays a major role in determining the nature of the species in solution. Hydrolysis may be viewed as a complexation process with OH^- as the ligand, and so it is easy to understand that the extent of hydrolysis quite generally increases with pH, i.e., with increasing concentration of OH^- ions. In natural waters the species which limits the solubility may be a product of hydrolysis, such as PuO_2. Solubilities of plutonium at near-neutral pH have been measured (c.f., Ref. 65), but the results are difficult to interpret. Polynuclear hydrolytic species of plutonium form slowly, and solubility results are often obscured by kinetic effects. The precipitates which form through hydrolysis are generally amorphous, and so their structures are not well defined.[26] Data bases containing hydrolysis constants from experiments and from the kind of analog extrapolation procedure described earlier for stability constants of plutonium complexes have been compiled by several authors for use in modeling the speciation in groundwater systems.[29,30,61,71-75]

A further aspect of hydrolysis is that polynuclear species, particularly of Pu(IV), tend to form polymers of high molecular weight which disperse readily as colloids.[58,59,62] These aggregates may become so polynuclear that it may become practically impossible to find their exact composition.[77,78] The colloidal particles carry a low, residual positive

charge at low values of pH, but a negative charge dominates at pH above 7. As a result of its low charge, the Pu(IV) polymer does not sorb on cation exchange resins as the free ions would do, but sorbs strongly onto surfaces.

Thus, the formation of colloids by hydrolysis may provide a mechanism whereby nuclides are mobilized under conditions for which precipitation would have been expected. Further, the colloidal particles can deposit readily on minerals or other surfaces, or they may sorb on the surfaces of colloidal particles of clay, silica, or metal hydroxides to form pseudocolloids.[4] The slow kinetics for polymer formation and the wide range of polymer properties under various conditions make it impossible to predict with much confidence the behavior of plutonium species at a given site.

In summary, the speciation of plutonium depends mainly upon the redox conditions, which determine the oxidation state present; the groundwater composition, which determines the nature of the complexation; the pH, which exerts a powerful influence through hydrolysis reactions; and the temperature, which affects the values of the equilibrium constants involved. As discussed earlier, a number of authors have attempted to estimate the concentrations of plutonium species present under representative oxic and anoxic conditions, usually in the form of stability fields on an Eh-pH diagram. Some of the authors omitted hydrolysis and complexation reactions of Pu(IV) on the grounds that the necessary equilibrium constants were poorly known, e.g., Refs. 26, 61, 63, 65. Below we summarize the conclusions of Allard[44] and of Allard and Rydberg,[75] who evaluated all available data, estimated and extrapolated some values, and, most importantly, considered all relevant species.

Under oxic conditions and for groundwaters of average composition,[44,75] the solubility of plutonium is limited by $PuO_2(s)$, with $Pu(OH)_4$ as the dominant species in solution in the range of pH 6-9. Below pH 5-6, the pentavalent PuO_2^+ would dominate, and below that Pu^{3+} would be the major species. High carbonate concentrations would stabilize the pentavalent state under conditions of high alkalinity, so that species like $PuO_2(CO_3)_3^{5-}$ would dominate at values of pH above 8-9. Hexavalent species would not be expected to contribute significantly.

Under reducing conditions, the solubility would still be limited by $PuO_2(s)$ at pH values above 7-8 but by $Pu_2(CO_3)_3(s)$ in the low range of pH. The trivalent aqueous species such as $Pu(CO_3)^+$, $Pu(OH)^{2+}$, and $Pu(CO_3)_2^-$ would dominate in the range of pH 7-9, but tetravalent species like $Pu(OH)_4$ or $Pu(OH)_5^-$ would become important above pH 9-10. These results suggest that, in the presence of carbonate, the solubility of plutonium would be higher under reducing conditions than under oxidizing conditions. Any of the oxidation states (III), (IV), or (V) would be expected.

To investigate the strong effect of groundwater compositions on speciation, Cleveland, Rees, and Nash[69] studied the oxidation states and solubility of plutonium (III), (IV), and (V)/(VI) in groundwaters from tuff, granite, basalt, and shale formations. Plutonium was surprisingly soluble in the basalt water, which was not a typical basalt groundwater in that it contained a high concentration of fluoride ions (52 mg/L); this high concentration of fluoride ions was presumed to stabilize soluble fluoro-complexes, primarily of Pu(IV). On the other hand, the plutonium was very insoluble in the shale groundwater, which contained the highest concentration of sulfate ions (2000 mg/L). The insoluble plutonium was present predominantly as Pu(IV). Stoichiometry suggested that the insoluble species was not a simple sulfate but that Pu(IV) polymeric species were involved.

FURTHER RESEARCH NEEDS

In summary, there has been a great deal of work on data bases consisting of equilibrium constants for complexing, hydrolysis, and precipitation reactions. With the assumption that the nuclides are present at equilibrium with the environment, it is relatively easy to predict the speciation of the form from these data. There are still data that need to be clarified, particularly with respect to carbonate complexation of the actinide elements included in this report but there are at present a number of groups actively studying these problems.

Although it is not difficult to predict speciation from data bases, it is not at all easy to verify these predictions. The direct determination of speciation at tracer levels is an extremely difficult field of

research both for relatively pure solutions prepared in the laboratory and for solutions in the field. The latter is made more difficult by the fact that the species must first be concentrated since they will generally be present in solutions too dilute to detect.

We recommend, therefore, that increased attention should be given to research in the laboratory for the direct determination of speciation of nuclides at tracer levels. We feel that sufficient attention has been given to data base generation and computer codes to generate speciation diagrams. Of course, for cases where thermodynamic data are needed or existing data verified, there should be continued experimental work; our first recommendation below deals with one of these needs.

Specifically, we recommend the following:

1. Experimental determination of formation constants for actinide complexes, especially carbonate complexes, in the pH region 5-10 of natural waters. Verification of existing data which have not been duplicated by several investigators.

2. A critical review and examination of experimental methods of determining speciation in the laboratory and in the field.

3. Increased attention to experimental determination of the presence and, if present, the composition of colloidal particles in groundwaters.

4. Increased attention to the determination of possible biological reactions such as oxidation or reduction of nuclides and the incorporation of nuclides in large organic molecules.

5. A review of existing data on migration of colloids, and an experimental study of migration of colloids.

6. Finally, reviews of speciation should be updated at regular intervals, particularly because investigators now are beginning to give increased attention to this subject.

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3. DEPENDENCE OF METABOLISM ON CHEMICAL FORM

BIOPHYSICAL AND BIOCHEMICAL PROPERTIES OF Pu, Am, Cm, Np, AND Sr

Some of the physical and chemical properties of the radionuclides discussed in the following paragraphs have already been mentioned in the preceding section. Despite the repetition, however, we think it is worthwhile to collect and summarize those properties which are important in understanding the metabolism of these radionuclides.

The terms "monomeric" and "polymeric" are often used in metabolic studies to describe the physical state of chemical compounds. Generally, "monomeric" refers to laboratory preparations in which any particulates formed are below about 0.01 μm in diameter, while "polymeric" particles are those of diameter 0.01 μm or greater.[1]

Plutonium

Plutonium can exist in solution mainly in four valence states: Pu(III), Pu(IV), Pu(V), and Pu(VI). The tendency to react with water (hydrolyze) decreases in the order Pu(IV) > Pu(VI) > Pu(III) > Pu(V).[2,3] Biological evidence and chemical properties of Pu suggest that most systemic Pu would be in the (IV) state. Hydrolysis of Pu(IV) may result in a change from the monomeric form to an insoluble polymeric form of Pu. In high concentrations, Pu may begin to polymerize at pH values as low as pH 1. In fairly dilute solutions such as those that might be expected in body fluids in typical exposure situations, pseudocolloidal formation begins at pH 2.8, and genuine aggregates form above about pH 7.5.[2,3] In the human body, the pH of pure gastric juice is about 1.0, of intracellular fluid of muscle is about 6.8, and of blood is usually about 7.4, although the pH of blood can exceed 7.5 in some cases.[4]

A large fraction of Pu(IV) introduced into the bloodstream in monomeric form is quickly bound to the iron-transport protein transferrin and is eventually carried to the bone marrow, the liver, and other iron depots.[5-14] Pu(IV) may transfer from transferrin to ferritin, the major iron storage protein in the liver, *in vivo* at physiological pH.[15] The ferritin-Pu(IV) complex may be more stable than the transferrin-Pu(IV) complex.[15]

It appears from experimental results for laboratory animals that Pu injected in particulate or colloidal form is cleared very rapidly from blood and is deposited in cells of the reticulo-endothelial (RE) system.[11,16,17] In fact, colloidal particles of any composition are rapidly taken up by RE cells.[2] These cells are found in all tissues but are most concentrated in liver, spleen, lymph nodes, erythropoietic marrow, and lung tissues.[2]

Americium and Curium

Biophysical and biochemical properties of Am and Cm have been described by D. M. Taylor.[18] Am(III) is the common oxidation state of Am in solution. Cm(III) is the only stable oxidation state in solution which is known. The smaller ionic potential of Am and Cm compared with Pu, resulting from the lower ionic charge and larger ionic radius, indicates that these trivalent ions will hydrolyze much less readily than Pu(IV) ions. However, as with Pu(IV), hydrolytic reactions and complex formation are still important to the solution chemistry of Am and Cm. Am(III) may be present in ionic form from pH 1 to pH 4.5, but above pH 4.5 some hydrolysis occurs, and genuine colloids of Am are formed above pH 7. It has also been observed that the formation of large polymeric species of Cm(III) occurs above pH 4.5.

Am(III) and Cm(III) become bound in plasma to transferrin, albumin, and other proteins.[7,18] However, they appear to form only weak complexes with serum proteins. Am and Pu also are known to bind strongly to ferritin in the liver.[18-23] Rapid association of Am and Cm with ferritin in the cytoplasm of hepatocytes is very different from Pu, whose association was not observed until about 3 days after injection.[22] It is not clear whether this more rapid association is due to a higher affinity of Am and Cm than Pu to ferritin or a lower affinity of Am and Cm to the proteins that transport these elements to the cell membrane (cf. Poppelwell *et al.*).[23] In general, it appears that differences in deposition and retention of actinides in the liver and other tissues may be related to differences in chemical binding and solubility of these elements and their compounds. As we shall discuss later, compounds and

colloids of Am and Cm are generally much more easily dissolved than those of Pu. This could lead to greater and more rapid transportability of Am and Cm than Pu into blood from the respiratory and gastrointestinal tracts, for example.

Neptunium

Compared with Pu, Am, and Cm, there is relatively little information on the biophysical and biochemical properties of Np. The following information is gleaned from Refs. 24 and 25 and an unpublished summary by D. M. Taylor.

In aqueous solutions, Np can exist in oxidation states 3^+, 4^+, 5^+, 6'sup+,and7sup+,withtheoxidationstates4sup+,4'sup+, and 6^+ being the most stable and the ones most frequently used in experiments. In solutions of neptunium free from complexing anions the Np(V) oxidation state appears to predominate at pH values up to about 7. The oxidation state of neptunium under physiological conditions is not known, but Np(V) probably predominates. The tendency of Np ions toward reactions of complex formation decreases in the sequence $Np^{4+} > Np^{3+} > NpO_2^{2+} > NpO_2^{+}$, that is, in accordance with decreasing ionization potentials. The more stable the complex compound, the more hydrolysis of Np ions is suppressed. It is known that NpO_2^{+} shows virtually no tendency to hydrolyze below about pH 7. Thus it might be expected that NpO_2^{+}, and perhaps other forms of Np, would tend toward polymerization inside the body less than most compounds of Pu, Am, and Cm.

Strontium

Strontium is chemically similar to calcium and appears to behave similarly to calcium in the body, although there is some discrimination against Sr at membranes.[26-28] Thus it is expected that Sr, like calcium, will be carried in body fluids both in ionic and complexed form. In normal human plasma, about half of the calcium exists as free ions, while most of the rest is bound to protein (mainly albumin).[29] The remainder is carried as $CaHPO_4$ and calcium citrate, and as unidentified complexes.[29] The extent of complexing of Sr is probably similar. Strontium chloride, for example, is probably very soluble in the lungs or

gastrointestinal tract,[30] while strontium titanate ($SrTiO_3$) is probably relatively insoluble in these regions.[31,32]

ABSORPTION FROM THE LUNGS TO BLOOD

In the most recent version of the model of the respiratory system approved by the ICRP[33,34] the respiratory system is considered to be divided into four regions: nasal-pharynx (NP), tracheobronchial region (TB), pulmonary region (P), and lymphatic tissue (L). The fraction of material entering the body which deposits in each of the NP, TB, and P regions depends on the size (activity median aerodynamic diameter or AMAD) of the particle carrying the radionuclide. The NP, TB, and P regions are divided into compartments corresponding to clearance routes. Biological half-times for clearance as well as fractions cleared along various routes are classified according to the time particles are retained in the pulmonary region. Only three clearance (solubility) classes are defined: D (days), W (weeks), and Y (years). According to this model, 12% of deposited class W particles of size 1 μ will eventually reach blood, compared with 5% for class Y compounds of the same size.

Thus, according to the ICRP model, the chemical form of inhaled activity influences the time course of the clearance of activity from the lungs to blood, as well as the total amount eventually cleared to blood. Translocation is viewed largely as a property of particle disaggregation or dissolution, although biological clearance processes such as mucociliary clearance and phagocytosis by macrophages are implicitly incorporated into the model through the clearance rate constants for the three compartments. More soluble or more easily disaggregated chemical forms are expected to have shorter residence times in the lungs than more rigid complexes, and a larger fraction of easily decomposed compounds is expected to eventually reach blood.

In the following paragraphs we shall discuss the importance of chemical form on the clearance of Pu, Am, Cm, Np, and Sr from the lungs. Experimental data for these elements are, for the most part, in agreement with the ICRP lung model. However, as we shall discuss later, there are some compounds whose behaviors do not conform to the ICRP model.

Plutonium

There are numerous experimental results concerning retention of various chemical forms of Pu in the lungs. Retention half-times of inhaled citrate, other organic complexes, and nitrates in the pulmonary region of the lung are on the order of 30 to 300 days in rats and dogs.[35] Pulmonary retention of plutonium dioxide, a less soluble compound, varies from 150 to 500 days in rats and from 200 to 1250 days in dogs.[35,36]

Results of experiments with rats and dogs indicate that Pu citrate is transported from the lung more rapidly than Pu nitrate, probably because Pu nitrate hydrolyzes more rapidly at physiological pH and forms relatively insoluble polymers.[36] As indicated in Table 3.1, there is little retention of Pu citrate or nitrate in the thoracic lymph nodes (TBLN). This is in contrast to the less soluble compound, Pu dioxide; approximately 30% of the pulmonary deposit of Pu dioxide (Pu-239) was found in the lymph nodes of beagles 5 years after exposure, and about 40% was found in the lymph nodes after 11 years.[37] Lyubchanskii[38] found that Pu citrate, Pu nitrate, Pu chloride, sodium plutonyltriacetate, and ammonium plutonium pentacarbonate all behave as relatively soluble forms of Pu after inhalation by rats. However, inhaled Pu fluoride was transported only slowly from the lungs of dogs, and there was a relatively large deposit in the tracheobronchial lymph nodes.[39]

As indicated in Table 3.2, the temperature of formation of inhaled plutonium particles affects the retention of plutonium in the lungs.[40] In general, higher temperatures of production lead to longer retention times. These changes in retention are probably due to differences in solubility of the aerosol caused by differences in chemical form produced by heat treatment.[36,40] At lower temperatures the aerosol particles consist of a mixture of plutonium chloride, oxychloride, and plutonium dioxide, while at higher temperatures production of plutonium dioxide would be increased.[36,40] As suggested by data in Table 3.2, particle size will also influence retention; for various sized particles calcined at similar temperatures, retention half-times are generally less for aerosols with a smaller particle size distribution (see also Bair *et al.*, 1963[41]).

Table 3.1. Distribution of plutonium after inhalation as nitrate or citrate[35]

Compound	Species	Time (days)	% Administered Plutonium			
			Lung	Thoracic lymph nodes	Liver	Skeleton plus other soft tissues
Plutonium-239 citrate[a]	Dog	1	74	0.05	1.4	6
		30	37	0.20	5.3	38
		100	29	0.40	16	38
Plutonium-239 citrate[b]	Rat	1	27	–	9.5	45
		28	9	–	4.3	59
		182	1.8	–	2.5	58
Plutonium-239 nitrate[a]	Dog	1	88	0.06	0.32	1.8
		30	32	0.4	9	43
		100	41	0.6	10	28
Plutonium-239 nitrate[c]	Rat	1	78	–	1.8	3.2
		30	40	–	1.0	7.7
		90	15	–	0.3	4.4
Plutonium-238 nitrate[c]	Rat	1	96	–	0.6	1.9
		30	53	–	2.2	18.1
Plutonium-239 nitrate[d]	Rat	30	32	–	1.5	11
		100	12	–	0.5	9
		200	4	–	0.4	12
Plutonium-238 nitrate[d]	Rat	30	18	–	2.2	18
		100	9	–	1.8	12
		200	3	–	0.6	21

[a]Percent inhaled activity less faecal activity in first 6 days

[b]Administered by pulmonary intubation

[c]Percent inhaled activity less faecal activity in first 3 days

[d]Percent initial lung burden

Table 3.2. Summary of solubility of aerosol samples and long-term retention half-times in lung of beagle dog for aerosols of Pu-239 and Pu-238

Radionuclide	Particle size AMAD (μ)	Size distribution	Production temperature	Per cent of activity dissolved in 2 hours in saline	Lung retention half-times in days (long-term component)
Pu-239	1.9	Poly	326	0.82	180
	1.9	Poly	600	0.10	340
	1.9	Poly	900	0.01	>500
	1.9	Poly	1150	0.001	>500
Pu-238	0.8	Mono	1150	0.60	450
	1.9	Mono	1150	0.15	>500
	3.0	Bimodal	1150	7.4	200
	1.3	Poly	1150	2.2	250

The residence time of Pu in the lungs may depend on the particular isotope inhaled. In animals exposed to aerosols of Pu-238 or Pu-239 dioxide with similar particle size characteristics, there was more rapid translocation of Pu-238 than Pu-239 from the lung to systemic organs.[36,42] Similar results were found using Pu-238 and Pu-239 in the nitrate form.[36,43,44] The increased transportability may be the result of higher specific activity of particles containing Pu-238; this higher specific activity may cause more rapid breakdown and solubilization of the particles.[36]

Plutonium may have different clearance characteristics when mixed with oxides of other metals. A series of studies of rodents exposed to mixed aerosols of Pu and Na oxides have shown that with an excess of Na the transportable fraction of Pu may be increased to values characteristic of soluble forms of Pu.[36,45-47]

Inhaled activity may leave the lungs through the bloodstream, in macrophages which may be cleared from the tracheobronchial region and swallowed, or via lymphatics to lymph nodes.[36] As indicated by the experimental data discussed to this point, the rate of transport from the lung by these routes depends on the solubility and hence the chemical form of the particles as well as on their size. There is information on the distribution of some nuclides after they reach the bloodstream, and for the most part it would appear that the distribution to internal organs is independent of the physico-chemical form deposited in the lungs (although, as discussed later, there is some evidence that particulate Pu, which would deposit primarily in the liver, may reach blood from the lungs). This is illustrated in Table 3.3 for the case of pulmonary intubation of various chemical forms of Pu in rats.[36,47,48] Although the total amount reaching blood varied considerably with chemical form at one week after intubation, the amount in liver, for example, was between 13.1 and 17.4 percent of the total non-pulmonary tissue deposit for all chemical forms considered.

Table 3.3. Tissue distribution of Pu-239 in rats one week after pulmonary intubation in various chemical forms[36,47,48]

Compound	% Administered activity				
	Lung	Liver	Skeleton and other soft tissues	Total tissue deposit (T)	$\frac{\text{Liver}}{T} \times 100$ (%)
Plutonium dioxide[a]	59.2	3.5	18.6	22.1	15.8
Plutonium dioxide[a]	43.5	4.2	27.8	32.0	13.1
Plutonium nitrate	52.2	6.5	30.8	37.3	17.4
Plutonium citrate	15.9	11.2	58.4	69.6	16.1
Plutonium dioxide + sodium oxide[a,b]	54.9	3.1	15.5	18.6	16.7
Plutonium citrate[c]	0.16	12.9	69.2	82.1	15.7

[a]Filtered aerosol suspension

[b]Atomic ratio of plutonium and sodium in mixed aerosol 1:19.2

[c]Administered by intravenous injection

Americium and curium

Americium and curium compounds appear to behave somewhat similarly (but not identically) in the respiratory systems of laboratory animals. These elements will be discussed together, and some differences will be noted.

Although Am and Cm are metabolically similar to Pu in many respects,[1,7,49-53] clearance of Am and Cm compounds from the lungs appears to be much more rapid than clearance of analogous Pu compounds.[36] This may result from the lesser tendency of Am and Cm to form polymers than Pu and a greater rate of solubility of any polymers that are formed.[36]

Results of animal experiments indicate that oxides of Am and Cm behave as relatively soluble material in the lungs.[54,55] In beagle dogs about 45% of the body burden of Am-241 oxide and about 80% of the burden of Cm-244 oxide at 30 days after inhalation was in tissues other than the lungs.[55] Generally, Cm-244 oxide appears to be more soluble than Am-241 oxide, perhaps because of the smaller particle size and greater specific activity of the Cm-244 compared with Am-241.[36]

The nitrate and citrate forms of Am or Cm are also cleared rapidly from the lungs of experimental animals.[51,56] Following pulmonary administration of Am citrate to rats, about 80% of the administered activity had translocated to extrapulmonary tissue after one week.[56]

These results suggest that there may be minor differences in the retention of different chemical forms of Am or Cm in the lungs. However, these differences appear to be much less important than the differences exhibited by different forms of Pu, since all forms of Am and Cm appear to leave the lungs fairly rapidly.

Neptunium

The biological and environmental literature on Np has been reviewed recently by Thompson[57] and also by Moskalev.[24] These authors found that data on the inhalation of Np was limited to one species, the rat.

Np-237 inhaled in the form of industrial dust was quickly eliminated by rats.[58] After three weeks, 93% of the initial burden of Np-237 was eliminated from the lungs, and about 11% had been absorbed to blood. The rapid elimination of fairly insoluble Np from the lungs of rats is apparently due to clearance by macrophages.[24]

By contrast, removal of a highly soluble Np citrate complex from the lungs of rats was relatively slow, with about 70% of the administered Np removed with a half-time of 133 days.[59,60] The long retention time of this soluble complex may have resulted from radiation damage to the pulmonary parenchyma.[24] Absorption of this form of Np to blood was about 2 to 3 times higher than for Np in industrial dust.[24]

Experimental data indicate that there are some differences in elimination of Np nitrate and oxalate from the lungs of rats. Less than 20% of Np nitrate was retained with a long half-time (~130 days), while nearly 40% of Np oxalate was retained with a similar half-time.[24] At 7 days after intratracheal introduction of Np oxalate or nitrate into rats, the skeleton showed about 10 times as much activity and the kidneys showed about 5 times as much activity in those rats receiving Np nitrate; the activity of Np in the liver was the same in both sets of rats.[24] In the first few days following administration, Np nitrate was distributed more diffusely than Np oxalate, but distribution was similar by the seventh day.[57] Apparently penetration of Np in the form of nitrate proceeds much more easily than penetration of Np in the oxalate form. This may result from differences in capabilities of oxalate of Np(IV) and nitrate of Np(V,VI) to enter into the reaction of hydrolysis and complex formation.[24] The oxalate of ^{237}Np(IV) in the lungs may be altered to form a poorly soluble hydroxide, or it may form stable complexes with proteins.[24] NpO_2^+ and NpO_2^{2+} are found largely in ionic form because of their low hydrolytic and complex-forming capabilities. Lyubchanskii and Levdik[61] found that about 25% of inhaled ^{237}Np(V,VI) nitrate was cleared from the lungs of rats with a half-time of about 15 days, and about 8% with a half-time of approximately 170 days; the remainder was lost very rapidly. Those authors found that, for the oxalate, about 45% was lost with a half-time of 22 days and 20-25% with a half-time of 150 days, with the rest lost very rapidly.

Strontium

Strontium is usually regarded as highly soluble in the lungs, particularly in the chloride form.[30] However, it has been found that $SrTiO_3$ is poorly soluble.[31,32] In one case of accidental inhalation and

ingestion of $SrTiO_3$ by a worker, it was estimated that only a small fraction of Sr was absorbed to blood.[33] In ICRP 30, soluble compounds of Sr such as $SrCl_2$ are assigned to inhalation class D, while $SrTiO_3$ is assigned to inhalation class Y.[34]

EFFECTS OF CHEMICAL FORM ON GASTROINTESTINAL ABSORPTION

There is strong evidence that, for some elements, the gastrointestinal absorption fraction (f_1) depends on the chemical form of the element. For example, in 1972 a Task Group of the ICRP recommended that absorption of plutonium should be taken as 0.0001% for insoluble compounds (oxides) and 0.003% for more soluble compounds (e.g., nitrate, halides).[1] In 1979 these values were revised to 0.001% for insoluble forms of plutonium and 0.01% for all other commonly occurring compounds.[34] Similarly, the f_1 values recommended in Publication 30 of the ICRP differ by a factor of 16 for certain chemical forms of selenium or molybdenum, by a factor of 30 for compounds of strontium, and by a factor of 25 for compounds of uranium.[34] In the following we shall summarize experimental data on f_1 values for different chemical forms of each of the elements Pu, Am, Cm, Np, and Sr.

Plutonium

There have been numerous experimental studies on the gastrointestinal absorption of plutonium. These studies are reviewed in a recent report by Harrison.[62] Data on the percentage of ingested plutonium absorbed from the gastrointestinal tract (from Tables 1, 2, 4, 5 of Harrison's report) are summarized in Fig. 3.1, which shows the range of the measured values as well as the median (circle) for each indicated chemical form.

Ranges and median values for all species combined are indicated at the top of Fig. 3.1, for oxides, nitrates, citrates, and organic complexes other than citrate. Since it seemed likely that there would be differences among species in gastrointestinal absorption, ranges and median values for a single species (rat) are shown at the bottom of Fig. 3.1. The rat was chosen because it is the only species for which there exist sufficient data for a meaningful analysis.

Although the data on which Fig. 3.1 is based were not derived in any uniform manner and do not represent random samples from any easily characterizable distribution, some general patterns emerge. The probability of gastrointestinal absorption appears to decrease in the order: organic complexes>nitrates>oxides. Values of f_1 for oxides range from

0.000003% to 0.02% in the various species. The large variation may reflect the solubility of the oxide preparation, which is affected by the temperature of production,[40] the proportion of small particles present,[47] and the specific activity of the plutonium isotope.[63] Absorption fractions for plutonium administered as the nitrate were usually between 0.001% and 0.01% but were as high as 0.2% in fasted mice. Typically higher absorption for the citrate complex than for the nitrate and other inorganic forms is thought to be due to reduced hydrolysis of plutonium in the intestine due to the stability of the citrate complex.[62] Gut uptake of less soluble forms of plutonium, such as the nitrate complex, may be increased by its incorporation into plant and animal tissues.[62]

Americium and curium

Studies on the gastrointestinal absorption of Am and Cm have been reviewed by Harrison;[62] f_1 values for adult experimental animals given in that report are listed in Table 3.4. These data suggest that Am and Cm have similar absorption fractions in the nitrate, chloride, or oxide form, except that the f_1 value for the oxide form may be slightly lower under some conditions. The highest value obtained in a single experiment was for Cm nitrate (0.4%). Most values for Am and Cm were fairly similar for the citrate, nitrate, chloride, and oxide forms. In contrast to Pu, there is some suggestion of reduced f_1 values for Am (and possibly Cm) in "biologically incorporated" forms, such as in liver or tumbleweed.

The absorption of Pu, Am, and Cm may be limited by hydrolysis of their ions in the alkaline conditions of the small intestine (~ pH 8) leading to the formation of polymers and insoluble hydroxides.[62] Since the predominant oxidation state of plutonium, Pu(IV), is more readily hydrolyzed than the trivalent Am and Cm ions, absorption from the small intestine may be restricted more for Pu than for Am and Cm.[62]

Neptunium

Ballou *et al.*[64] described gastrointestinal absorption of various forms of Np-237 in rats. The absorbed fraction was reported as 0.8% for an

Table 3.4. The gut uptake of various chemical forms of americium and curium in adult animals.[62]

Isotope/Chemical form	Animal species	No. of animals in study	Percent absorbed
^{241}Am nitrate	Rat	11	0.02
	"	7	0.03
	"	5	0.06
	Hamster	11	0.05
	Guinea pig	15	0.02
^{241}Am chloride	Rat	3	0.05-0.10
	"	?	0.07
	"	?	0.03
^{243}Am oxide	Rat	6	0.02
	"	5	0.009
	Hamster	5	0.006
^{244}Cm nitrate	Rat	14	0.06
	"	5	0.4
^{242}Cm chloride	"	3	0.05-0.10
^{244}Cm chloride	"	7	0.02
^{244}Cm oxide			
fresh	"	3	0.004
aged 4 days	"	5	0.05
aged 4 months	"	11	0.06
^{241}Am citrate	Rat	?	0.1
	Hamster	13	0.01
	Rabbit	4	0.02
^{241}Am in rat given nitrate gavage	Rat	6	0.04
^{241}Am in liver of hamster given i.p. citrate[a]	Hamster	6	0.003
^{241}Am - ferritin	"	5	0.01
^{241}Am in tumbleweed added as nitrate	Rat	5	0.006
^{241}Am in tumbleweed added as DTPA complex	"	5	0.004
^{241}Am mixed with tumbleweed as nitrate	"	5	0.004
^{241}Am mixed with tumbleweed as DTPA complex	"	5	0.03
^{244}Cm in tumbleweed added as nitrate	"	5	0.009
^{244}Cm in tumbleweed added as DTPA complex	"	5	0.02
^{244}Cm mixed with tumbleweed as nitrate	"	5	0.02
^{244}Cm mixed with tumbleweed as DTPA complex	"	5	0.05

[a] i.p. = intraperitoneal

industrial dust containing Np-237, 0.26% for Np-237 citrate, and 0.12% for Np-237 nitrate. Further studies reported in the same paper suggested that the absorption fraction for Np(V) may be 3-4 times higher than for Np(IV), and the fraction for Np(VI) may be 8 times higher than for Np(IV). Results of Mahlum et al.[65] from experiments with rats also suggest that the oxidation state may affect the absorption of Np-239 with higher-valent forms of Np-239 having the highest absorption. Comparison of results of Ballou et al.[64] with those of Mahlum et al.[65] suggest that the high-specific-activity isotope Np-239 is absorbed about 10 times more readily than Np-237.

For the most part, research on the absorption of Np from the gastrointestinal tract has been conducted with large quantities of nitrate or other forms that are not biologically incorporated. Thus these experimental results comparing various chemical forms of Np may not be indicative of the situation in which animals or humans ingest small amounts of Np in food. In fact, Sullivan and Crosby[66] found that animals which were fed biologically incorporated Np-237 absorbed 10-20 times less than when administered this isotope in the nitrate form.

Strontium

The fractional uptake of dietary Sr and of soluble salts of Sr from the gastrointestinal tract is usually in the range 0.2 to 0.5.[67,68] One form of Sr, $SrTiO_3$, has been found to be poorly absorbed;[31] an f_1 value of 0.01 for $SrTiO_3$ is recommended in ICRP 30.[34]

DISTRIBUTION AND RETENTION OF ACTIVITY REACHING THE BLOODSTREAM

There is some evidence that small particles containing radionuclides may pass directly from the lungs to the systemic circulation without being dissolved or otherwise disaggregated.[36] Also, depending on the solubility of the compound and the extent of vascular involvement at a wound site, part of the activity in a wound may be introduced directly into the bloodstream.[1] In this section we discuss the metabolism of various chemical forms of the same elements discussed earlier, after these compounds have reached blood.

Plutonium

Although it is conceivable that Pu in the body could exist in a wide distribution of solubility classes, we shall distinguish only two very general classes for Pu that has reached the bloodstream, namely, soluble Pu and particulate or colloidal Pu. In their review of the metabolism and toxicity of Pu, Nenot and Stather[36] concluded that the colloidal form of Pu is not a chemical form likely to be of importance in the majority of cases of human contamination. Also, it appears that the distribution of Pu in tissues is usually independent of the chemical form inhaled or ingested.[36] However, there is evidence that relatively insoluble forms of Pu can reach the bloodstream under some circumstances.[69,70] Thus it seems worthwhile to consider the differences in the metabolism of soluble and particulate Pu in blood.

Soluble Pu will partially trace the iron pathway, and a substantial fraction of systemic Pu is carried to the bone marrow and to the liver.[5-14] Pu injected in particulate or colloidal form is cleared much more rapidly than soluble Pu from blood and is deposited in cells of the reticulo-endothelial (RE) system, as are colloidal particles of any composition.[2,11,16,17]

Stevens and co-workers[16] compared the distribution and excretion of three chemical species of ^{239}Pu(IV) - the transferrin complex (Pu-Tf), Pu citrate (Pu-Cit), and particulate Pu in colloidal form (Pu-P) - after injection into beagles. At 14 days after injection the distribution of Pu-Tf and Pu-Cit were nearly indistinguishable, although a slightly larger percentage of Pu-Cit had been excreted during that time.

Deposition, microdistribution, and retention of particulate Pu differed greatly from those seen with Pu-Tf and Pu-Cit. Pu-Tf and Pu-Cit cleared slowly from blood, with approximately 30% depositing in liver, 50% in the skeleton, and 2% in other soft tissues. Pu-P left the bloodstream very rapidly, with approximately 70% depositing in soft tissue, 2% in the skeleton, and 24% in other soft tissue. Moreover, the fractions of Pu-Tf and Pu-Cit excreted during the first 14 days were several times larger than the fraction of Pu-P excreted. In the liver, Pu-Tf and Pu-Cit initially were distributed uniformly; Pu was associated with a soluble protein and was gradually transferred to subcellular liver particles. By contrast, the microdistribution of Pu-P in the liver was heterogeneous; most of the activity was in the reticuloendothelial cells and little was associated with soluble proteins. In the skeleton, Pu-Cit and Pu-Tf were deposited on bone surfaces, whereas the small quantity of Pu-P in the skeleton was located exclusively in the macrophages of the bone marrow.

Thus, initially there are large differences between the microdistribution as well as the macrodistribution of particulate and nonparticulate Pu. These differences could be important in cases where the exposure level is high enough that harmful doses are incurred during the first few years after exposure. For chronic, low-level exposures to Pu, these differences may be less important because of the large amount of recycling of Pu that occurs among the skeleton, liver, and other soft tissues over a period of several years. Experimental evidence suggests that originally particulate Pu is dissolved in the phagocytic cells of the body and, when released, Pu is translocated mainly as monomeric Pu regardless of its original form. For example, Bruenger _et al_.[71] injected particulate Pu into beagles and observed that activity eventually released from the phagocytic cells of the liver, spleen, lung, and bone marrow deposited on bone surfaces and diffusely in the liver in a pattern similar to soluble Pu. Also, in the mouse, which shows a very short retention time for Pu in the liver, the skeletal distribution of initially polymeric Pu closely approximated that of initially monomeric Pu after only 15 days (Table 3.5).[17] Thus secondary deposition of particulate Pu probably is similar to the primary deposition of soluble Pu.

Americium and curium

As indicated earlier, Am and Cm are less likely to form polymers in body fluids than is Pu, and most compounds of Am and Cm are much more soluble than analogous compounds of Pu. Thus it does not seem likely that the initial chemical form of Am or Cm inhaled or ingested would be a particularly important factor once the radioelement reaches blood. In Publication 19 of the ICRP[1] it was concluded on the basis of available data on the injection of different chemical forms of Am and Cm into laboratory animals that the tissue distribution is not influenced by the chemical form injected. An exception is when the element enters blood as a stable complex with a non-metabolizable chelating agent, as illustrated by Am-TTHA.[1] Most of the data in ICRP Publication 19 for injection of Am and Cm are for the chloride, nitrate, and citrate forms (citrate is a metabolizable complexing agent).

Mewhinney and Craig[72] reviewed studies of inhaled Am in laboratory animals and concluded that there is close similarity in lung retention, tissue distribution, and excretion for Am citrate, nitrate, and chloride. Those authors found that Am dioxide is much more soluble in the lung and that much larger fractions reach the bloodstream than Pu dioxide. It would appear that the ultimate concentrations in tissues of the dioxide form is not too different over the long term from that of the other forms of Am.

Neptunium

In recent reviews Thompson[57] and Moskalev[24] pointed out differences in the distributions of different chemical forms of Np injected into rats. The nitrate, presumably Np(V) or Np(VI), is cleared from blood more rapidly than the oxalate, presumable Np(IV). Retention half-times in rat bone differed markedly for different chemical forms of Np, but some of the data are for inhalation and are clouded considerably by differences in the time course of entry of the different forms into the bloodstream as well as the possibility of recycling of Np among internal organs. Readily soluble compounds of Np(V) -- citrate, chloride, and nitrate -- are distributed similarly in the skeleton. Np(VI) oxalate and citrate are selectively built up in the liver. Despite these

apparent differences, evidence is lacking concerning the chemical form in which inhaled or ingested Np compounds reach the bloodstream.[24,57]

Strontium

No information was found on the behavior of different chemical forms of Sr in blood. Because of the chemical similarity of Sr and Ca and the body's tight control over entry of Ca, we would conjecture that the form of Sr or Ca entering the bloodstream from the small intestine, at least, would be independent of the chemical form entering the stomach.

SUITABILITY OF ICRP-30 METHODS FOR TREATING METABOLISM OF DIFFERENT CHEMICAL FORMS

ICRP-30 models assume that the deposition of a radionuclide that has entered the bloodstream is independent of the chemical form of the radionuclide taken in, and that the chemical form of a radionuclide is not changed during its sojourn in the body.[34] Radioactive particles deposited in the lungs are assumed to belong to one of three solubility classes for purposes of classification of clearance from the lung. For uptake from the GI tract, usually only one value is given for the fraction absorbed into blood, although two values are given for plutonium, strontium, and a few other elements.[34]

Clearance of activity from the lungs

Results of animal studies have led some researchers to conclude that the lung model of the ICRP is not flexible enough to treat all chemical forms of some elements. For example, in a review of studies of Am in laboratory animals, Mewhinney and Craig[72] conclude that the behavior of $^{241}AmO_2$ in the lung is not adequately described by any of the classifications of the ICRP model. The retention curves for $^{241}AmO_2$ may resemble those of class W material, but the fractional uptake of ^{241}Am from the lung to the systemic circulation is substantially greater than the recommended value for a class W material. The assignment of $^{241}AmO_2$ to class W would probably produce predictions that underestimate the dose to the liver and skeleton.[72] As a second example, Mewhinney and Diel[73] found in their experiments that the class Y compound Pu-238 dioxide is absorbed much more readily from the lungs of animals than is indicated by the ICRP model.

Problems arising from the rigid structure of the ICRP lung model have been described in a general setting by Cuddihy and co-workers.[74,75] Those authors suggest an alternative clearance model which would facilitate the use of measurements of particle solubility in laboratory animals or *in vitro* chemical systems. Their approach is an empirical one that depends upon absorption rates derived separately for different radionuclides and different chemical forms of these radionuclides. Apparently, improvements can be achieved with their model in predicting

respiratory tract retention of particles having time-varying solubility and of radionuclides in particles composed of material with solubility greatly different from the simple radionuclide compounds commonly considered. In their model, clearance of deposited material is represented by simple competition between mechanical clearance processes and dissolution of particles with absorption into blood. The same regions of the lung as in the ICRP model are used, but all material in each region is available to both mechanical clearance and absorption to blood. For the most part, clearance rates are considered to be functions of time.

Absorption of activity from the GI tract to blood

The ICRP model for movement of material through the GI tract includes four compartments: stomach, small intestine, upper large intestine, and lower large intestine. Absorption to blood usually is assumed to occur through the small intestine, and a characteristic absorption fraction f_1 is assigned to each element. For a few elements, a second value for f_1 is assigned to certain chemical forms.[34]

It is apparent from the data discussed earlier on gastrointestinal absorption of plutonium and neptunium that one or even two f_1 values are not sufficient to characterize gastrointestinal absorption for some elements. For example, in adult rats the f_1 value for Pu varied by about four orders of magnitude for the different chemical forms. For Np the f_1 value also varied significantly with chemical form, oxidation state, and isotope.

These examples suggest that it would be worthwhile to derive f_1 values that depend not only on the element but also on the chemical form and possibly other factors such as oxidation state and isotope. An important first step in this direction would be the development of a detailed, mechanistic model of absorption from the small intestine to blood based on a thorough review of the basic physiological literature as well as the literature on absorption of radionuclides.

Retention and translocation of activity that has reached the bloodstream

As discussed earlier, there are some indications that different forms of a radionuclide may enter blood and that the form of a radionuclide may sometimes change after introduction of the nuclide into the bloodstream. For example, Pu may enter the blood in particulate or colloidal form or may quickly change to this form, in which case it is likely to be taken up by the phagocytic cells of the liver and other organs. Eventually the particle or colloid will be dissolved and may be released to the bloodstream in a form likely to be deposited in the skeleton. The effect on estimated dose of such change of chemical form and recycling must be estimated using metabolic models.

Unfortunately, the metabolic models given in ICRP 30 are not flexible enough to allow proper treatment of different chemical forms of a radionuclide, of change of chemical form of the nuclide, or of recycling of activity among organs. The primary purpose of these models was for use in estimating dose commitment to organs over long time periods. In their development, little attention was given to identifying realistically the dynamic behavior of radionuclides during their sojourn in the body. For proper analysis of the potentially different effects of different chemical forms of radionuclides, it is essential that metabolic models trace the movement of the preponderance of the activity at all times after exposure.

A physiologically-based metabolic model for Pu is described in Ref. 76. That model traces the deposition of Pu on bone surfaces, in the cells of the liver, and in other soft tissues; the burial or removal of Pu on the skeleton during bone remodeling; the movement of (originally soluble) Pu from the hepatocytes to the reticuloendothelial cells of the liver; the removal of Pu from the skeleton, liver, and other soft tissue to blood and the redistribution of Pu among the organs; and the removal of Pu from the body via the kidneys, bile, and intestines. In Ref. 76 model parameters are developed only for originally soluble Pu; however, with suitable parameters the model is applicable to originally particulate or colloidal Pu as well. The relative activities of originally soluble and originally colloidal Pu as a function of time in the skeleton and liver, as estimated using the model, are shown in Fig. 3.2. The assumption was made that the original deposition fractions of soluble Pu are 50% in skeleton, 30% in liver, and 20% in soft tissue plus

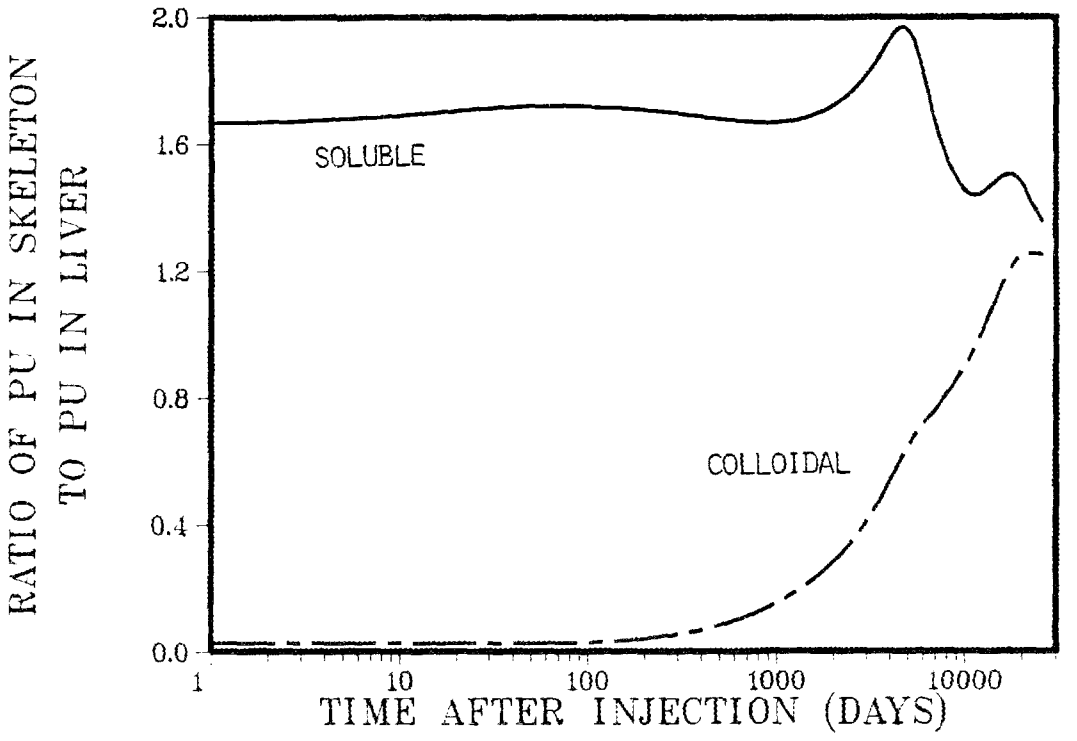

Fig. 3.2. Relative activities of originally soluble and originally colloidal Pu in the skeleton and liver, as a function of time, as estimated using a mechanistic model of Pu retention and translocation.[76]

rapid excretion, and the original deposition fractions of colloidal Pu are 2% in skeleton, 78% in liver, and the same as for soluble Pu in soft tissue and excretion (cf. Ref. 16). Further, Pu was assumed to be removed from each organ in soluble form. We have ignored the fact that soluble and colloidal Pu initially will have different distributions in the liver; this seems unimportant, however, since both forms will reside in RE cells during most of their sojourn in the liver, and both forms will probably be released from these cells in soluble form.

FURTHER RESEARCH NEEDS

The comparative uptake and metabolism of various radionuclides in high-level waste have been considered in several studies, although the chemical forms considered are often those of importance in occupational rather than environmental exposures, and experimental studies have often dealt with much higher concentrations of radionuclides than would be encountered in most environmental exposures. The trend in recent years has been toward studying the uptake and metabolism of lower concentrations of radionuclides and, as far as practical, of forms that may be encountered in the environment. If this trend continues, the magnitude of the uncertainties now present in evaluating the metabolism and dosimetry of chemical forms of radionuclides released from high-level wastes may soon be reduced.

For many radionuclides it appears that the greatest uncertainty now present in estimating organ doses from exposure to environmental contamination (assuming the level of contamination as well as the chemical form are known) is in the estimate of the fraction f_1 from the small intestine to blood.[1] The absorbed fraction has always been an empirically determined value, and further experimental studies using environmental forms of radionuclides are certainly needed. A more immediate need, however, is for the development of a mechanistic model of the movement of radionuclides through the gastrointestinal tract that deals in detail with absorption of material to blood. The development of such a model must be preceded by, and based on, a thorough review of the pertinent physiological literature as well as the literature on absorption of radionuclides. While such a literature review and model development would be a major task, this work may well lead to better estimates of absorption fractions of some radionuclides in the short term, and would certainly be valuable in guiding further experimental studies in the long term.

There are indications that the present ICRP model for the respiratory tract may not be very accurate for certain forms of various radionuclides. Alternative models have already been suggested by some researchers. Such models may represent a substantial improvement over the ICRP model for some chemical forms, although it would be surprising

if improved models frequently alter the predicted organ doses of the ICRP model by more than a factor of 5. Thus, although it is important to improve the ICRP lung model, the magnitude of the uncertainty in doses introduced by this model is small compared with that introduced by the estimate of f_1 for poorly absorbed radionuclides.

Work has begun on the development of mechanistic models that describe the retention and translocation of radionuclides that have reached blood. These models are needed for many reasons, one of which is to study the relative metabolism of different chemical forms of a radionuclide. Unfortunately, little is known concerning the form in which radionuclides reach blood. Thus application of mechanistic models to study the relative metabolism of different chemical forms will remain primarily a theoretical study in sensitivity until more information is gained on the form of radionuclides in blood.

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4. SUMMARY AND CONCLUSIONS

There has been a great deal of work on the development of data concerning complexing, hydrolysis, and precipitation reactions of Pu, Am, Np, and Sr. These data may be used to predict speciation in the environment under the assumption that the nuclides are present at equilibrium with the environment. Significant uncertainties arise, however, because the data were derived for much higher concentrations of the nuclides than would be expected in most environmental exposures, and because the nuclides often would not actually be at equilibrium with the environment.

Although there have been several studies concerning the metabolism of various chemical forms of these radioelements, the chemical forms considered often are not those of great interest in environmental exposures. The data are sufficient, however, to provide some understanding of the sensitivity of uptake, metabolism, and organ doses to variation in the chemical form of a radionuclide. There is a great deal of information concerning different chemical forms of Pu and there is adequate information on Am and Cm to draw general conclusions with some confidence. Several results on different forms of Np in rats have been published, but it is difficult to draw conclusions from these results with much confidence because the rats were usually administered large doses of Np. Data on Sr appear to be limited to soluble forms of Sr and one very insoluble form, $SrTiO_3$, which has been produced industrially.

Speciation of Pu in the environment depends mainly upon: the redox conditions, which determine the oxidation state present; the groundwater composition, which determines the nature of the complexation; the pH, which exerts a powerful influence through hydrolysis reactions; and the temperature, which affects the values of the equilibrium constants involved. In groundwater, Pu may exist as $PuO_2(s)$, $Pu(OH)_4$, or various other forms, depending on these factors. In the presence of carbonate, the solubility of Pu would be higher under reducing conditions than under oxidizing conditions, and any of the oxidation states (III), (IV), or (V) would be expected. Pu is relatively soluble in basalt water with a high concentration of fluoride ions, but is very insoluble in shale groundwater with a high concentration of sulfate ions. In the latter

case, insoluble Pu may be present predominantly as Pu(IV), and the insoluble species may involve polymeric Pu(IV).

The influence of chemical or physical form on the metabolism of Pu appears to be strong because there are large differences in the propensities of different forms of Pu to dissolve, hydrolyze, or form insoluble polymers. Pu dioxide is absorbed more poorly from the lungs and GI tract than other common forms of Pu and is transported mechanically from the lungs more slowly than other common forms of Pu. Thus we would expect higher doses to the respiratory tract following inhalation of Pu dioxide, and higher doses to liver and skeleton following inhalation or ingestion of Pu nitrate, citrate, or other common forms of Pu.

It appears that the absorption fraction from the gastrointestinal tract to blood may vary by 4 orders of magnitude for different chemical forms of Pu ingested by a single species (rat). Organic complexes, particularly citrate, may be the most easily absorbed form of Pu, while oxides constitute the least easily absorbed form. Even within oxides the absorption fraction may vary by 2-3 orders of magnitude as the solubility of the particles varies.

There is some evidence that insoluble as well as soluble forms of Pu may reach the bloodstream, and there is considerable evidence that soluble and insoluble forms of Pu in blood initially are distributed much differently. However, we do not know whether insoluble forms of Pu would reach blood under conditions of typical environmental exposures. Moreover, since little systemic Pu is excreted, and since the relocation of Pu released from organs may be independent of the initial chemical form, it would appear that the initial form of Pu entering blood may not be a particularly important consideration in computing integrated doses over several decades.

The suitibility classification for Pu-239 recommended in ICRP 30 (class Y) appears to describe lung clearance rates of insoluble compounds of that nuclide adequately. However, results of animal studies suggest that Pu-238 dioxide, also listed as a class Y material, is absorbed more readily from the lungs to blood than is Pu-239 and should perhaps be considered a class W compound. In fact, it is suggested by these studies that the ICRP model may lead to an underestimate of the cumulative dose to liver and skeleton by a factor of 5. Similarly, it

would appear that the absorbed fraction from the GI tract of 10^{-5} for insoluble compounds and 10^{-4} for soluble compounds may underestimate the actual absorbed fractions considerably. As discussed elsewhere (see Ref. 76 of Sect. 3), the ICRP 30 metabolic model for Pu apparently does not give an accurate picture of the soluble Pu in the body, particularly with regard to the heterogeneously distributed radiosensitive tissues of the skeleton. We conjecture that this model would be even less accurate when applied to insoluble Pu reaching blood.

Although Am may exist in the valence state III, IV, V, or VI, only the III state is expected to be important under environmental conditions because strong oxidizing agents are required to convert Am(III) to the higher oxidation states. Under acidic environmental conditions, Am(III) would probably exist as Am^{3+}. The exact speciation of Am is not known in the neutral to basic region, but Am will probably exist as some form of neutral species rather than as Am(III), perhaps as very fine colloids.

Americium and curium have a lesser tendency than Pu to form polymers and a greater rate of solubility of any polymers that are formed. As a result, all commonly studied compounds of Am and Cm appear to behave as relatively soluble material in the body. In ICRP 30 all compounds of Am and Cm are assigned to lung clearance class W. Animal experiments indicate that this classification may result in an underestimate of the fraction of inhaled $^{241}AmO_2$ that reaches blood. The GI absorption fraction of 5×10^{-4} recommended in ICRP 30 for Am and Cm seems appropriate for all compounds. In contrast to Pu, organic forms of Am and Cm may be absorbed less readily than inorganic forms.

The valence states of Np of interest in nuclear wastes are IV and V, although Np in aqueous solutions can also exist as Np(III), Np(VI), and Np(VII). The (V) state is stable over a wide range of conditions. In acidic solutions, Np(V) exists as the large, singly charged ion, NpO_2^+, and it probably exists as carbonate complexes in carbonate containing neutral and basic solutions. If Np is present as Np(IV) at some time in its transport to the environment it would probably be adsorbed and particulate transport would be the only mechanism by which it could reach the environment. Thus, it is possible that particulate forms of Np(IV) could be present in the environment.

Data on the metabolism of Np are somewhat confusing. For example, the more soluble Np citrate was found to be retained in the lung to a greater extent than less soluble compounds. It is not clear whether this is a legitimate counterexample to the ICRP lung model or whether lung damage was incurred due to large doses of Np citrate being administered. Similarly, large differences were observed in the GI absorption fraction for different chemical forms, oxidation states, and isotopes of Np. However, large quantities of Np were administered in most experiments, and there is some question as to the extendibility of the results to typical environmental exposures. In one experiment where lower levels of biologically incorporated Np-237 were administered, the absorbed fractions were 10-20 times lower than when Np-237 was administered in the nitrate form.

The only valence state of Sr that can exist in the environment is Sr(II). In general, Sr(II) would be expected to exist as the divalent ion Sr^{2+}. There are two other possibilities, however. If Sr passes through certain types of soils, there is the possibility of formation of negatively charged, low-molecular weight organic complexes. In addition, there is the possibility of transport by colloidal particles of soils.

Although one metabolically insoluble form of Sr has been identified, it is doubtful whether this form ($SrTiO_3$) would be encountered in typical environmental exposures. Strontium usually does not form strong complexes with either organic or inorganic ligands. It is expected that ingested or inhaled Sr would usually be in the form of the divalent ion. The metabolic data for soluble Sr given in ICRP 30 are applicable to the most commonly encountered environmental form, Sr^{+2}.

Although it is not difficult to predict speciation of Pu, Am, Np, and Sr in the environment from existing data bases, it is extremely difficult to verify these predictions. We recommend that increased attention be given to research in the laboratory for the direct determination of speciation of nuclides at environmental (tracer) levels. We think that, for the most part, sufficient attention has been given to generation of data bases and to computer codes which generate speciation diagrams. However, we do recommend experimental determination of formation constants for actinide complexes, especially carbonate complexes,

in the pH region 5-10 of natural waters, and the verification of existing constants. Further, increased attention should be given to the determination of the presence and composition of colloidal particles in groundwaters, to the determination of possible biological reactions such as oxidation or reduction of nuclides and the incorporation of nuclides in large organic molecules, and to the migration of colloids.

In recent years studies of the uptake and metabolism of radionuclides have shifted slightly away from fairly high concentrations of forms encountered in occupational exposures to lower concentrations of forms that may be encountered in environmental exposures. Data for conditions approximating environmental exposures are still rather sparse, so that additional studies in this direction are needed. Of primary importance are studies of the gastrointestinal absorption fraction of various chemical forms of poorly absorbed species. An immediate need is for the development of a mechanistic model of the movement of radionuclides through the gastrointestinal tract that deals in detail with absorption of material to blood. The development of such a model must be preceded by, and based on, a thorough review of the pertinent physiological literature as well as the literature on absorption of radionuclides. This work could lead to better estimates of absorption fractions of some radionuclides in the short term, and it would be valuable in guiding further experimental studies in the long term. Some work has already been devoted to improving existing models of movement of radionuclides through the respiratory tract, and this work should be continued. Also, further mechanistic models should be developed to describe the retention or translocation of radionuclides that have reached blood. Although such models are needed for a variety of reasons, for purposes of studying the metabolism of different chemical forms of a radionuclide they will be useful primarily for sensitivity studies until better information can be gained on the form of radionuclides in blood.

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This report provides an initial evaluation of the dependence on chemical forms of estimates of health effects from radionuclides in high-level waste (HLW). Discussion is limited mainly to a review of studies of plutonium, americium, neptunium, and strontium that may be useful in identifying (a) chemical forms of these radionuclides that are likely to reach humans after migration from a waste repository and (b) differences in metabolism and organ doses that result from intake of various chemical forms of these radionuclides; we also attempt to identify research needs in these two areas. In addition to providing a limited review of the literature, this report identifies some of the problems involved in determining speciation of these radionuclides in the environment and provides a general picture of the potential errors that may be involved in applying models assumed to be independent of chemical form to estimate metabolism and dose from exposure to different chemical species of a radionuclide.

17. KEY WORDS AND DOCUMENT ANALYSIS

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