
Long-Term Kinetic Effects and Colloid Formations in Dissolution of LWR Spent Fuels

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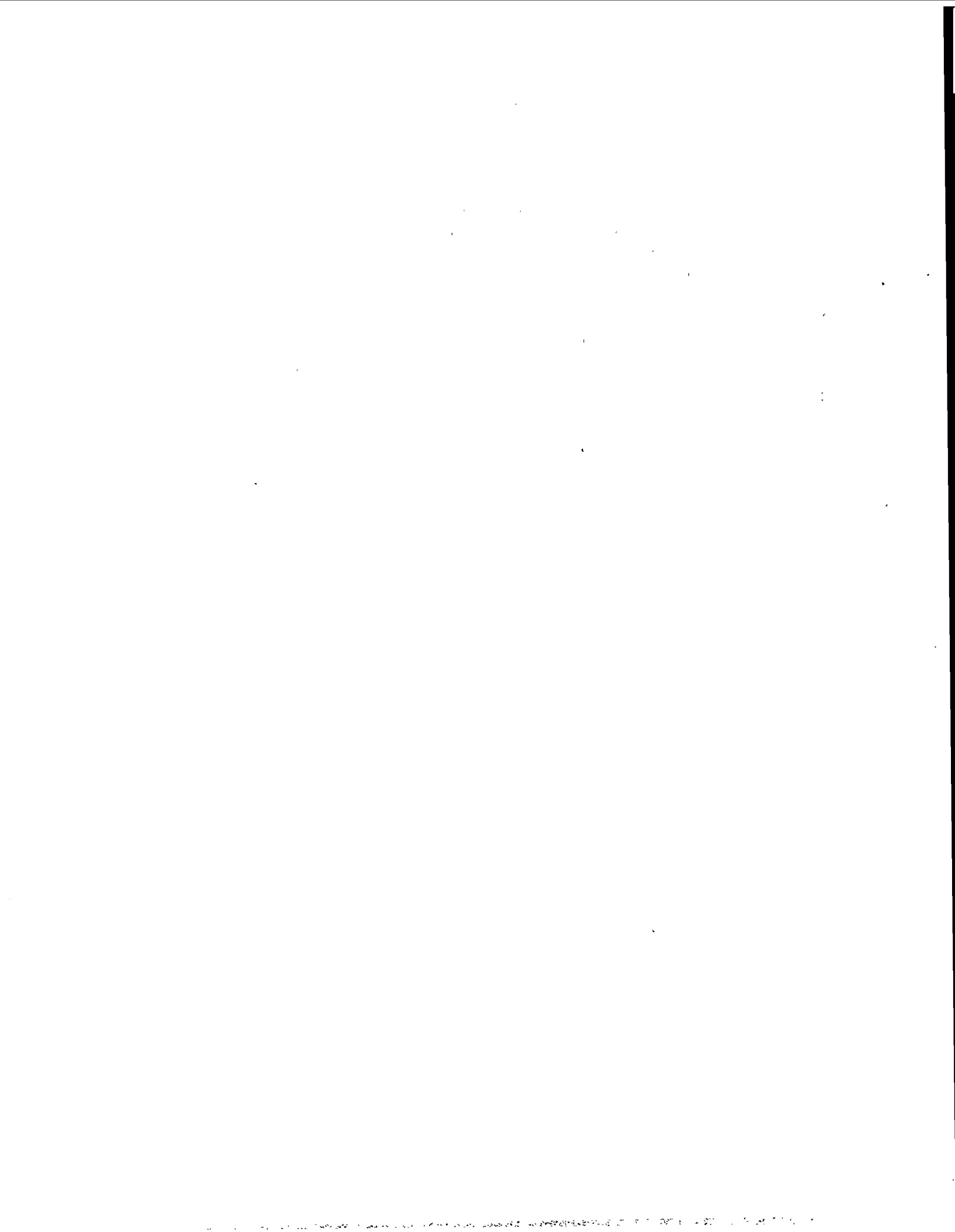
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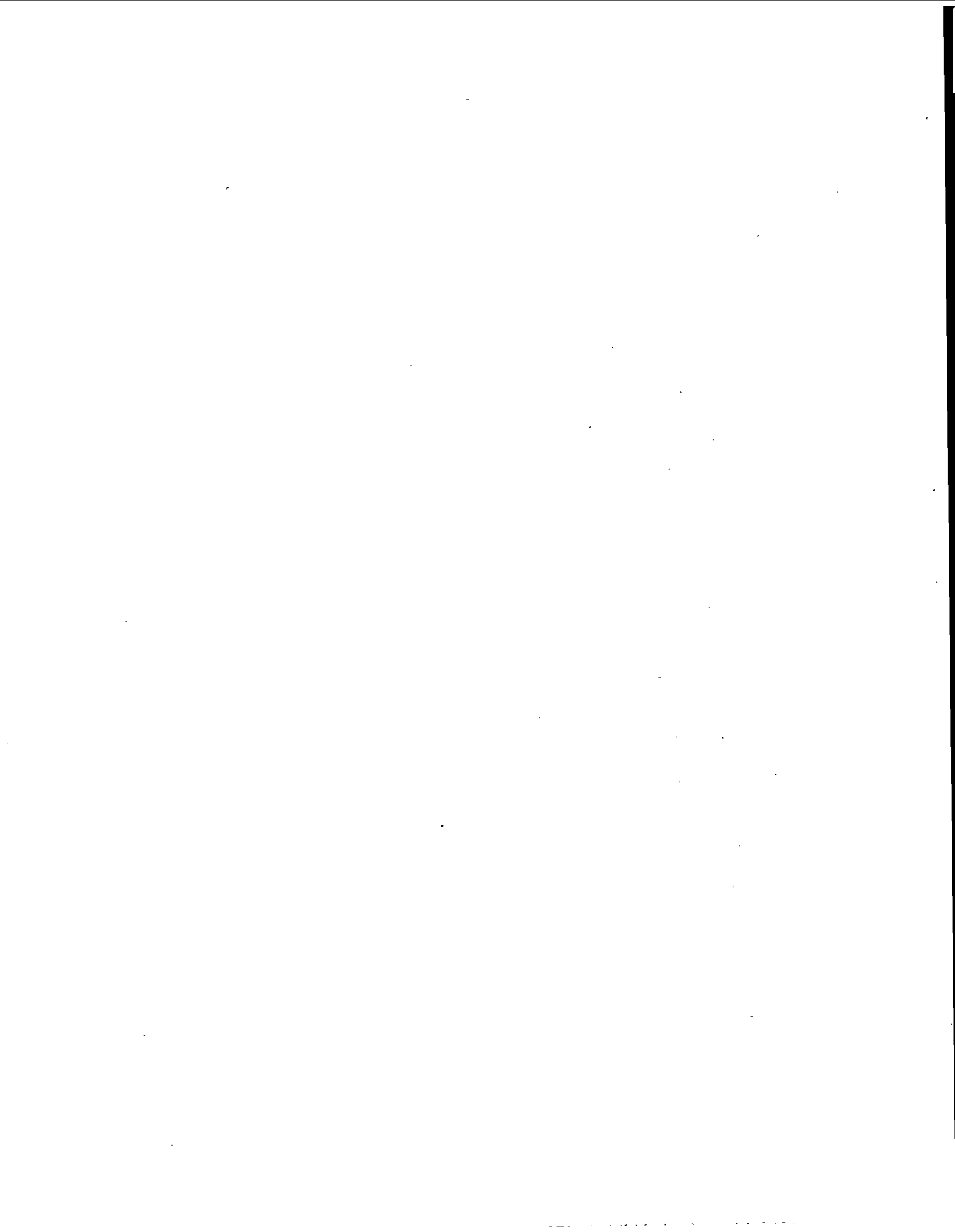
ABSTRACT

This report evaluates continuous dissolution and colloid formation during spent-fuel performance under repository conditions in high-level waste disposal. Various observations suggest that reprecipitated layers formed on spent-fuel surfaces may not be protective. This situation may lead to continuous dissolution of highly soluble radionuclides such as C-14, Cl-36, Tc-99, I-129, and Cs-135. However, the diffusion limits of various species involved may retard dissolution significantly. For low-solubility actinides such as Pu-(239+240) or Am-(241+243), various processes regarding colloid formation have been analyzed. The processes analyzed are condensation, dispersion, and sorption. Colloid formation may lead to significant releases of low-solubility actinides. However, because there are only limited data available on matrix dissolution, colloid formation, and solubility limits, many uncertainties still exist. These uncertainties must be addressed before the significance of radionuclide releases can be determined.



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ABBREVIATIONS

ACD	advanced conceptual design
AECL	Atomic Energy of Canada, Ltd.
ANL	Argonne National Laboratory
DI	deionized
DOE	Department of Energy
EBS	engineered barrier system
EPA	Environmental Protection Agency
HLW	high-level waste
KTI	key technical issue
LWR	light-water reactor
MGDS	mined geological disposal system
PNL	Pacific Northwest Laboratory
SEM	scanning electron microscopy
SF	spent fuel
TSPA	total system performance assessment
WIPP	Waste Isolation Pilot Plant
YM	Yucca Mountain

1 INTRODUCTION

The implementation of the Nuclear Regulatory Commission's Key Technical Issue (KTI) plan for the Container Life and Source Term evaluates and conducts sensitivity analyses on the performance of the U. S. Department of Energy's (DOE's) engineered barrier system (EBS) for the mined geological disposal system (MGDS) planned at the Yucca Mountain (YM) repository site. A technical assessment requirement of this KTI is to evaluate radionuclide releases during spent fuel (SF) dissolution. The SF is a primary EBS component.

This report evaluates assumptions, numerical estimates of radionuclide releases, mathematical formulas, and many potential physical processes involved in radionuclide releases during SF dissolution. The assessment made here will support the development of methodology for evaluating licensing applications for high-level waste (HLW) disposal. In the total system performance assessments (TSPAs) for emplaced HLW, verified values (or formulas) of radionuclide releases will be used in calculations; and assumptions and potential physical processes will be used in determining various cases (scenarios) in the calculations. Additionally, this analysis is the staff's detailed technical rationale for its performance assessment models.

Radionuclide releases from SF dissolution, under HLW aqueous oxidizing repository conditions, have been assessed using two different postulates (Ahn, 1994; Eslinger et al., 1993; Barnard et al., 1992; Wilson and Gray, 1990). Fission products such as Cs-135, I-129, or Tc-99 and activated radionuclides such as C-14 and Cl-36 have high solubility limits. Previous analyses approximated elements with high solubility limits as released at dissolution rates of the (SF) matrix (i.e., dissolution control). Matrix-dissolution rates have been, in turn, approximated as reprecipitation rates of dissolved matrix ions on SF surfaces or other available substrates (i.e., alteration control). Actinides such as Pu-(239+240) and Am-(241+243) have low solubility limits. In assessing these releases, previous analyses have used an equilibrium approximation (i.e., solubility control).

Recently, progress has been made in understanding dissolution control. Nevertheless, it is still unclear whether the matrix will continue to dissolve or practically cease to dissolve during long-term SF performance (Grambow et al., 1990; Grambow, 1989). Here, the continuous dissolution of SF matrices is called "long-term kinetic effects." Very recently, it has been also recognized that colloid (or complex) formation cannot be ignored in solubility control (Barnard et al., 1992; Gray, 1992; Stout, 1992; Kim, 1986). Colloids can be dominant over dissolved ions in radionuclide releases.

For dissolution-controlled radionuclides, high solubility limits may not be reached by leachate replenishments. Therefore, the release of these radionuclides is likely to depend on the matrix dissolution rate. Attempts have been made (Forsyth and Wermer, 1992, 1985; Grambow et al., 1990; Johnson et al., 1988) to relate the release of these radionuclides to matrix dissolution. For instance, the Sr-90 release was assumed to represent the matrix dissolution. However, the use of Sr-90 release rates for SF dissolution rates was not validated. Whereas some data on Sr-90 release showed constant release rates (Wilson,

1990a,b), other data showed decreased release rates (Forsyth and Wermer, 1992, 1985; Forsyth, 1991; Grambow et al., 1990; Forsyth et al., 1986). These two trends partly suggest that SF dissolves continuously or that dissolution rates decrease over time.

Traditionally, solubility-controlled radionuclides were assumed to equilibrate at their solubility limits in leachates. This comes from either assuming no matrix dissolution or from assuming total conversion of the supersaturated radionuclides into reprecipitates. The equilibrium assumption also implies that reprecipitates can be defined uniquely and are stable chemically and physically over an extended period. However, long-term effects may lead to continuous formation of mobile colloids (or complexes). This colloid formation is likely to be driven by deviations from the traditional assumptions used for equilibrium approaches. This report reinvestigates matrix dissolution and examines colloid formation. It presents some observations that may lead to the continuous dissolution of dissolution-controlled radionuclides, or to continuous formation of colloids (or complexes). Regarding these observations, analyses are made of (a) the kinetics of matrix dissolution and reprecipitation; and (b) colloid formation. In colloid formation, this evaluation pertains to the macroscopic processes extending the traditional processes of chemical bondings. Three different macroscopic processes are evaluated: (a) condensation, (b) dispersion, and (c) sorption (formation of pseudo-colloids). The condensation process involves the condensation of individual ions and molecules and is normally accompanied by leachate supersaturation. The dispersion process involves the disintegration of block solid materials. Pseudo-colloids form by sorption of dissolved ions on or into groundwater colloids. These processes, if they occur, result in uncertainties in using traditional solubility limits. In Section 7, the significance of radionuclide releases will be discussed for both matrix dissolution and colloid formation.

2 OBSERVATIONS ON LONG-TERM KINETIC CONDITIONS IN SF DISSOLUTION UNDER OXIDIZING CONDITIONS

This section summarizes long-term kinetic conditions in SF dissolution under oxidizing conditions. It also discusses information pertinent to SF dissolution, from literature on mineral dissolution. Reprecipitates formed on SF surfaces are unlikely to protect against continuous dissolution of the (SF) matrix in oxidative HLW repositories. The proposed YM site is an oxidative repository. The site is unsaturated with groundwater. For this report, near-static immersion or drip conditions are assumed and a completely dry condition is not considered.

The unprotective nature of reprecipitates is likely to arise from (a) displacement damage of alpha particles (or recoil) or radiolysis effects; (b) stress generated during reprecipitation, oxidation, or gas (such as helium) generation; and (c) microbial activities. Moreover, reprecipitates may have, inherently, micro-pores, crystallographic channels, and water molecules. Large intracrystalline spaces within reprecipitates are necessary for the mass transport required to dissolve the matrix and to reprecipitate dissolved species. Environmental variations can also lead to the instability of reprecipitates. Wet-dry cycles may be present under drip conditions of groundwater. The wet-dry cycles may vary the groundwater chemistry, and lead to dry-out, redissolution, or spall-off of the reprecipitates.

Similarly, any disturbance caused by external stress waves such as intermittent seismic events will destroy the integrity of reprecipitates. Occluded areas may also vary the groundwater chemistry.

In addition to these general hypotheses, there is more direct evidence for the unprotective nature of reprecipitates, in literature pertinent to SF dissolution. In analogue studies, Percy and his coworkers (1993) identified massive transformation of uraninite into uranosilicates, in the Pena Blanca uranium deposits. The environment of the Pena Blanca uranium deposits is very similar to that of the YM site. The temperature of the deposits is postulated to have been < 50 to 200 C (Percy et al., 1993). The analogue studies in this temperature range suggest that SF may be transformed into schoepite or uranosilicates in the YM site (Ewing, 1993). Electrochemical studies in various solutions at room temperature have shown the irreversible dissolution of UO_2 (Shoesmith and Sunder, 1992, 1991); reprecipitates formed may be unprotective in carbonate solutions at room temperature (Shoesmith et al., 1984). SF tests in J-13 well water at near room temperatures did not show stable reprecipitated phases on the SF surfaces (Wilson, 1990a,b; Wang, 1981). Also, in drip tests with J-13 well water at 90 C, the reprecipitated layer was offset from the dissolving UO_2 surface (Wronkiewicz et al., 1992). Other possible indications of unstable reprecipitates may include the cyclic behavior of leachate concentration. Semi-static tests showed the cyclic behavior in J-13 well water for over two years at room temperature and 85 C (Wilson, 1991). Leachate supersaturation, formation of protective layer, and loss of protection could have been repeated, to cause the cyclic behavior of leachate concentration. It is deduced, from these observations, that reprecipitation may continue in aqueous oxidizing environments during SF long-term performance in a repository.

Leachate conditions during continuous reprecipitation are important in colloid formation and summarized here. It is generally known that reprecipitation rates are faster than or nearly the same as dissolution rates. This postulate is justified, under the same degree of undersaturation or supersaturation, for a specific mineral phase in near equilibrium (Zhang and Nancollas, 1990; Ohara and Reid, 1973). As the extent of undersaturation or supersaturation increases, dissolution rates or reprecipitation rates may change. The change can be drastic or moderate, depending on the involvement of (a) diffusion-limited aqueous mass transfer and (b) surface nucleation (Lasaga, 1990). The processes of dissolution and reprecipitation are discussed in review papers and related referenced literature: (Steefel and Van Cappellen, 1990; Zhang and Nancollas, 1990; Lasaga, 1990; Blum and Lasaga, 1987).

In SF dissolution, dissolving phases are different from reprecipitating phases. Therefore, the above general rule does not apply to comparing relative magnitudes of dissolution rates and reprecipitation rates in SF dissolution. The dissolution rates can be faster than the reprecipitation rates. The relative magnitudes of these two rates are governed by the nature of dissolving or reprecipitating phases, as, for example, by electric charge, atomic bond, crystallographic orientation, or affinity with leachates. Additionally, relative magnitudes of these two rates also depend on surface areas of the dissolving phase and the reprecipitating phase. As long as the mass transfer from dissolving phases is greater than that to the reprecipitates, the leachate will be supersaturated (above solubility limits) with respect to reprecipitates. The leachate can be also supersaturated by groundwater flow. Upon

groundwater replenishment, some elements, such as silicon, common in reprecipitates and in groundwater, become supersaturated with respect to reprecipitated phases (Nguyen et al., 1991; Wilson, 1990b). Under near-static conditions, concentration gradients are not expected in leachates. Normally, liquid diffusion is not rate-limiting for low-solubility ions (Mendel, 1984). Therefore, it can be assumed that leachate concentrations are constant spatially. This supersaturation will result in reprecipitation and colloid formation through condensation processes. Supersaturation will increase until the total surface area of reprecipitates and colloids leads these two rates of mass transfer to equal one another. At this point, the leachate will be in a steady state. In the steady state, leachates will maintain supersaturation; the growth of reprecipitates will continue. The practical significance of supersaturation will be determined by various parameters such as surface area, rate constants, and flow rates.

The steady state described above pertains to the transformation of a phase. The paragenesis of secondary phases may continue. For each transformation, a new steady state will form. Analogue studies (Percy et al., 1993) claim that the paragenesis of uraninites in the Pena Blanca uranium deposits is the same as that of UO_2 in drip tests at 90 C (Ewing, 1993). The formation of uranosilicates took only about 200 weeks in the UO_2 drip tests. Therefore, the paragenesis appears to take place in a short period at temperatures of above 90 C. The presence of intermediate phases in uranium deposits implies that paragenesis may be still going on. Also, there is a possibility that paragenesis of secondary phases to unknown phases can continue. Whenever paragenesis continues, leachates can be newly supersaturated with respect to the newly transformed phase.

All the aforementioned observations suggest conditions that may lead to a continuous dissolution of dissolution-controlled radionuclides or to the continuous formation of colloids (or complexes). The following sections analyze and discuss these concerns. The next section will first analyze the behavior of dissolution and reprecipitation, using existing data on flow-through, semi-static, and electrochemical tests. The analysis is only possible for immersion conditions because quantitative experimental data for drip conditions are not available. Drip conditions inferred from analysis of immersion tests will be discussed.

3 MATRIX DISSOLUTION AND REPRECIPITATION

If the release of a type of radionuclide represents the matrix dissolution rate, it can be used as a measure of releases of all dissolution-controlled radionuclides. Literature data in this regard are inconclusive, because of inconsistency among the databases. Some data on the release of Sr-90, Tc-99, and Cs-137 show linear behavior with time, as for example, those data from light-water reactor (LWR) SF in J-13 well water at 25 or 85 C (Wilson, 1990a,b; Wilson and Bruton, 1989) or those data from CANDU SF in granitic groundwater or distilled water at 25 C (Johnson et al., 1982). On the other hand, other data on the release of Sr-90 or Cs-137 from the same experiments don't show linear behavior. This inconsistency regarding releases of Cs-137 and Sr-90 will be considered here:

(a) In Swedish data of high-burnup LWR SF in oxic granitic groundwater at 20 to 25 C (Forsyth and Wermer, 1986), the curve fit of \log (the release rate of Sr-90) to \log (the time)

does not show a slope of $(-1/n, n \geq 2)$. Typically, such slopes are expected in diffusion control. In the same Swedish data and in data regarding LWR SF in J-13 well water at 25 and 85 C, there is a good curve fit of the cumulative release of Sr-90 to the square root of time. There can be such a good curve fit also to linear time law (Wilson, 1990a,b; Grambow et al., 1990);

(b) Referring to the same experiments in (a), in some cases, the cumulative release of Sr-90 is nearly constant over test time (Forsyth and Wermer, 1992; Wilson, 1990b; Wilson and Bruton, 1989); in other cases, the slope of log (the release rate) versus log (time) is nearly minus 1 (Forsyth and Wermer, 1992).

Several causes for nonlinear release rates (i.e., decrease of release rates over time) can be considered from a mechanistic viewpoint:

(i) Sr-90 saturation cannot be ruled out even under the replenishing condition of leachates. There were indications that highly soluble Sr-90 and Cs-137 were incorporated in the reprecipitates from LWR SF tests in J-13 well water at 25 and 85 C (Argonne National Laboratory, 1996; Wilson, 1990a,b);

(ii) The contribution of grain boundaries and rims may be important (Forsyth and Wermer, 1992; Gray et al., 1992b; Wermer and Forsyth, 1988) as transient effects, especially for high-burnup fuels;

(iii) Another transient effect can be the gradual masking of the pristine surface (or grain boundary) (Heppner et al., 1992; Shoesmith et al., 1984). However, some flow-through tests of LWR SF in carbonate solutions at 25 C do not exhibit transient phenomena (Gray, 1992; Steward, 1992);

(iv) Diffusion of oxidants or radionuclides may be the rate-limiting step (Grambow et al., 1990); and

(v) Radiolysis may be the rate-determining step (Grambow et al., 1990).

These possibilities from (i) to (v) make it difficult to determine true rates of matrix dissolution, based on the release rate of Sr-90 or Cs-137. Alternatively, releases of Tc-99 or uranium may be used to represent the matrix dissolution. However, Tc-99 data have uncertainties associated with dissolution of fine intermetallic particles, for example, particles along grain boundaries (Gray and Thomas, 1994). Uranium release may also represent matrix dissolution because uranium is the major constituent of SF matrices. The measurement of uranium releases involves not only dissolved ions, but also reprecipitated phases. The uranium data reported up to now involve large errors arising from undissolved fuel grains commingled in the analysis of reprecipitates (Wilson, 1990b). Therefore, it is very likely that the present analysis of uranium later (Section 3.1) is only a confirmatory practice of the analysis of fission product data.

The aforementioned possibilities in (i) to (v) are further considered. In U.S. tests of LWR SF in J-13 well water, the grain boundary effects could be separated. Wilson used several cycles in semistatic tests. The first cycle is tests of as-received samples. From the second cycle, the samples of the previous cycle were reused after removing reprecipitates. Earlier cycles eliminated grain boundary radionuclides by their fast releases (Wilson, 1990a,b). Therefore, later cycles did not include fast releases of grain boundary radionuclides. Gray and his coworkers used individual grains in flow-through tests to exclude the effects of grain boundaries (Gray et al., 1992a,b).

The effects of gamma radiolysis on UO_2 dissolution have been studied jointly by Swedish and Canadian scientists (Sunder et al., 1990, 1989). They have found that gamma radiolysis related to electrochemical processes in series is not rate controlling in UO_2 dissolution (Sunder et al., 1989). However, the radiolysis can increase overall reaction significantly as the amount of oxidants increases. Although independent Swedish work presented the important contribution of alpha radiolysis (Christensen and Bjergbakke, 1985), both groups believe that alpha radiolysis can be represented by gamma radiolysis. This is because radicals formed are mainly responsible for the dissolution and similar radicals form in the two processes (Christensen and Bjergbakke, 1985). The hypotheses on all these radiolysis effects may need to be demonstrated in the U.S. HLW project.

Therefore, kinetic observations of linear dissolution are obtained for; leachate saturation (i); surface-area dependent dissolution (iii); diffusion-limited dissolution (iv); or radiolysis-controlled dissolution (v). Linear dissolution and saturation (i) can be combined as an (interface) reaction-controlled dissolution. Also, surface-area dependent dissolution (iii) and radiolysis-controlled dissolution (v) can be combined in diffusion-limited dissolution (iv) for phenomenological nonlinear kinetics. In the dissolution process, reaction-controlled dissolution, in turn, involves (a) electrochemical (irreversible) dissolution and (b) affinity (or solubility)-controlled dissolution. Therefore, there are three processes for dissolution (i.e., electrochemical control, affinity control, and other nonlinear controls) and two processes for reprecipitation (affinity control and other nonlinear controls). If the dissolution process is coupled to the reprecipitation process, the overall kinetics would be either reaction-controlled or nonlinear-controlled. Reaction control is of primary concern, because it is likely to lead to continuous matrix dissolution.

3.1 Reaction-Controlled Kinetics

For reaction control, a steady state between matrix dissolution and reprecipitation is expected. Consequently, linear time law will govern dissolution behavior. Simple quantitative formulas will be presented for this process of an element (primarily uranium) dissolving from SF and forming reprecipitates (Wilson, 1990a,b; Wang, 1981).

The dissolution rate of first-order kinetics (see Casas et al., 1993; Shoesmith and Sunder, 1991; Posey-Dowty et al., 1987; Stumm and Morgan, 1981) may be approximated by

$$R_{dis} = \frac{S}{V} k_e f(E) \quad (1)$$

or

$$= \frac{S}{V} k_- (C_s - C_t) \quad (2)$$

and balanced by

$$= \frac{A}{V} k_+ (C_t - C_o) + \frac{F}{V} C_t + N_{par} C_t \quad (3)$$

In these equations, "S" is the surface area of the dissolving phase; "V" is the leachate volume; " k_e " is the rate constant for electrochemical dissolution; "f(E)" is the dependence of dissolution rates on electrochemical potential "E"; " k_- " is the rate constant for SF dissolution; " C_s " is the effective solubility limit of the dissolving phase, including activated complexes (either on the surface or in leachates); " C_t " is the elemental concentration under consideration; "A" is the surface area of the reprecipitated phase (including colloids); " k_+ " is the rate constant for growth of the reprecipitated phase; "t" is time; " C_o " is the solubility limit of the reprecipitated phase; "F" is the flow rate of groundwater; and " N_{par} " is the formation or growth rate of colloids per unit leachate concentration, if any. Under long-term conditions, "V" may be dropped out as the dissolution becomes independent of "V."

For many elements, the activity product to the power of stoichiometric value should be used instead of the concentration. The groundwater inflow should be included too. Also, the reaction orders may be different from the first order adopted in the above equations. Therefore, Equations 1 to 3 are used for a simple illustration. For the simple illustration, the congruent dissolution is assumed to assess releases of elements other than uranium.

Equation 1 represents electrochemical dissolution and Equation 2 is for affinity-controlled dissolution. In Equation 3, the first term represents the reprecipitation rate; the second term represents the convection rate of materials with the flowing groundwater; and the third term represents the formation or growth rate of colloids. In Equations 1 and 2, both electrochemical dissolution and affinity-controlled dissolution were considered. It has been demonstrated that UO_2 dissolution is controlled by electrochemical overpotential (Shoosmith and Sunder, 1992, 1991). However, it still may be necessary to consider Equation 2 under near-static conditions such as supersaturation.

In the steady state of the nearly constant value of "E" (or " C_t "), Equations 1 and 2, and the first term of Equation 3 suggest that the rate of reprecipitation or dissolution is constant. The constant rate leads to the linear time law for matrix dissolution under slow flow conditions. (For Sr-90, based on congruent dissolution, the steady state may not occur. Before reaching

the steady state, " R_{dis} " is (dC_t/dt) in Equation 2. Then, $(dC_t/dt) \sim e^{(-\text{constant} \times t)}$ {or $\ln(dC_t/dt) \propto -e^{(\ln t)}$ }. This relation may not be distinguishable from $\ln(1/t)$, in a short time interval, as " t " becomes very long. This lack of distinction is one possible reason the apparent slope is minus 1 in the plot of $\ln(\text{dissolution rate})$ versus $\ln(\text{time})$ in Swedish data of LWR SF in oxic granitic groundwater at 20 to 25 C (Forsyth and Wermer, 1992).

Equations 1 and 2 are set to be equal to Equation 3 and a few algebraic arrangements give " C_t " as

$$C_t = C_o \left[1 + \frac{\frac{S}{V} k_e f(E) \frac{1}{C_o} - \left(\frac{F}{V} + N_{par} \right)}{\frac{A}{V} k_+ + \frac{F}{V} + N_{par}} \right] \quad (4)$$

or

$$C_t = C_o \left[1 + \frac{k_- \frac{S}{V} \left(\frac{C_s - C_o}{C_o} \right) - \left(\frac{F}{V} + N_{par} \right)}{\frac{A}{V} k_+ + \frac{S}{V} k_- + \frac{F}{V} + N_{par}} \right] \quad (5)$$

Assuming that " N_{par} ," " A ," and " S " are insensitive to the variation of the " C_t " value in Equations 4 and 5, " C_t " can be supersaturated with respect to C_o , theoretically. The supersaturation is shown by the righthand term in the bracket of Equation 4 or 5. When activity products are substituted for concentrations or flow rates of groundwater, similar expressions can be obtained. As values of (S/V) are increased or values of (F/V) , (A/V) , or N_{par} are decreased, leachate becomes more supersaturated. (For elements of J-13 well water such as silica, higher (F/V) increases the supersaturation.) Also, (a) a large difference between " C_s " and " C_o ," or (b) a bigger ratio of the normalized value of " k_e to k_+ " (or the normalized value of " k_- to k_+ ") leads to a higher supersaturation. In other words, SF will be undersaturated, whereas the reprecipitates are supersaturated with respect to the steady-state concentration, " C_t ." The leachates will maintain a balance between the dissolving mass and the reprecipitating mass. In this interpretation, it has been assumed that " A ," " S ," and " N_{par} " are insensitive to " C_t ." The reality is far more complicated. Nevertheless, realistic complications will not alter the general functional behavior presented above. These equations are numerically evaluated using existing experimental data obtained mainly from tests of LWR SF in J-13 well water. Electrochemical test results from chloride solutions by Atomic Energy of Canada, Ltd (AECL) (Shoesmith and Sunder, 1992, 1991) are also considered, for a relative comparison.

Table 1 presents calculated results for terms in Equations 1 through 5, using data from semi-static tests for reprecipitation, convection and colloid formation (Wilson, 1991, 1990a,b; Wilson and Bruton, 1989) and flow-through tests (Gray, 1992; Gray et al., 1992a; Steward, 1992). Uranium in reprecipitates was calibrated by undissolved Tc-99 to eliminate

undissolved fuel grains (Wilson, 1990b). Radionuclide releases in flow-through tests are based on the congruent dissolution. The dissolution rates for LWR SF, " R_{dis} ", were from the flow-through tests (Gray et al., 1992a). These values are somewhat lower than many data obtained in pure carbonate solutions (Gray, 1992; Gray et al., 1992a; Steward, 1992; Grambow, 1989), presumably because of the contribution of other cations such as Si and Ca (Gray, 1992; Wilson, 1990b). At higher temperatures, only data at 75 C in carbonate solutions are available (Gray et al., 1992a). (For a direct comparison, the data in J-13 well water at 85 C is required.) AECL dissolution rates were from electrochemical tests of UO_2 at 25 C (Shoosmith and Sunder, 1992, 1991). A range of the electrochemical potential was chosen in the tests. Values of " $(A/V) k_+ (C_t - C_o)$ " and " $(F/V) C_t$ " are from the analysis of reprecipitates and leachates, respectively, in semi-static tests (Wilson, 1990a,b). Values of " $N_{par} C_t$ " are from the data of particulates formed during leachate replenishment. For uranium, it is not certain that particulates form from reprecipitates in J-13 well water (see details in Section 4.2).

Counting uncertainties involved in semi-static test results, the following general conclusions are drawn from Table 1:

(a) In the steady state, the material balance stated in Equations 1, 2, and 3 is made within an order of magnitude. This apparent mass balance suggests that the matrix can dissolve nearly linearly with time. It also agrees with results of uraninite alteration kinetics (Percy et al., 1993) of approximately 10^{-7} fraction per day in the Pena Blanca uranium deposit. The uraninite alteration kinetics itself has uncertainties arising from the uncertain deposit history in temperature, wetting characteristics, or size of uraninite deposits. Analogue studies at Alligator Rivers address also the potential concern of continuous matrix dissolution (Fabryka-Martin and Curtis, 1992).

There is an indication that immersion tests resulted in slightly more releases than flow-through tests. The difference may come from different radiolysis effects between flow-through tests and semi-static tests. In flow-through tests, radiolysis is unlikely to affect the dissolution rates because no difference is noticed in dissolution rates between UO_2 and SF (Gray, 1992); and

(b) Colloid formations cannot be ignored at lower temperatures. The amount of plutonium colloids was comparable with or dominant over dissolved ions. Americium and curium colloids behave similarly. At higher temperatures, or in longer-term performance, colloid formation or stability of colloidal suspension was less significant.

The evaluation of Equations 4 and 5 is more qualitative. The significant colloid formation means that actinides could be supersaturated significantly. It is difficult to evaluate details of the second term in the brackets of Equations 4 and 5. Nevertheless, experimental data for colloid formation (see Section 4) suggest that actinide concentrations can be higher than their solubility limits in many orders of magnitude. This is consistent with large discrepancies in radionuclide concentrations from colloids and dissolved ions (see Figure 1 in Section 4.1). This is also understandable from Equations 4 and 5. The supersaturation in near-static leachates is determined not only by $[(k_- \text{ or } k_e)/k_+]$ but also by other factors such as (C_s/C_o)

Table 1 Rates of Dissolution, and Precipitation and Convection in J-13 Well Water
(Equations 1 to 3)

Radionuclide	Dissolution Rate (Flow-through Tests) [(S/V) k _d f(E) or S/V k _d (C _i - C _j)]		Dissolution Rate (Electro-chemical Tests) [(S/V) k _d f(E)]	Rate of Precipitation (Semi-static Tests) [(A/V) k _p (C _i - C _o)]		Rate of Convection [(F/V) C _j]		Colloid Formation Rate (N _{par} C _j)
	25 C	85 C		25 C	25 C	85 C	25 C	
U	(0.3 ~ 1.2) x10 ⁻⁶ g/day, or (1.7 ~ 6.0) x10 ⁻⁶ fraction (f) /day (A1) ^a	(A2) ^b	(10 ⁻⁸ ~ 10 ⁻⁹) g/day (A3,A4) ^c	~0.5x10 ⁻⁶ g/day (A5) ^d	~8x10 ⁻⁶ g/day (A5) ^d	~1x10 ⁻⁶ g/day (A5)	~0.8 x10 ⁻⁶ g/day (A5)	
Pu- (239 +240)	(0.3 ~ 1.2) x10 ⁻⁸ g/day (A1) ^e			~4x10 ⁻⁸ g/day (A5) ^f	~7x10 ⁻⁸ g/day (A5) ^f	~2 x10 ⁻⁹ g/day (A5) ^f	~7 x10 ⁻¹¹ g/day (A5) ^f	(A6) ^g
Sr-90	(2 ~ 4)x10 ⁻⁶ f/day for 20 ~ 120 days (A1)			~5x10 ⁻⁸ f/day (A5) ^h	~1x10 ⁻⁶ g/day (A5) ^h	~4x10 ⁻⁷ f/day, ~7x10 ⁻⁷ f/day, ~2x10 ⁻⁶ f/day (A5) ^h	~1x1 0 ⁻⁶ f/day (A5) ^h	

- ^a : Dissolution rates are normalized over the surface area of 205 cm² to compare with those from immersion tests. Dissolution rates for 20 to 250 days are used. Most dissolution rates reported in the literature are higher, as summarized in reference Grambow, 1989 (Swedish synthetic groundwater data by Bruno et al. ranged from 10⁻⁸ to 10⁻⁴ g/cm²-day). Recent data by Bruno et al. are of lower values (Bruno et al., 1992; Ollia, 1992). Canadian data are 10⁻⁷ f/day of uranium and (10⁻⁶ ~ 10⁻⁷)/day of Sr-90 in air-saturated granite groundwater at 25 C (Johnson et al., 1982).
- ^b : Direct measurements were not made at 85 C in J-13 well water containing approximately 2 x 10⁻³ M bicarbonate ions and other constituents. Indirect data were obtained in pure carbonate/bicarbonate solutions. Approximately 3.4 and 21.3 times the dissolution rates increased by raising temperature from 23 to 75 C in 2 x 10⁻² and 2 x 10⁻⁴ M carbonate/bicarbonate solutions, respectively. Minor pH corrections are not made.
- ^c : Dissolution rates are from UO₂ tests in chloride solutions. Values varied significantly, depending on corrosion potentials under various oxidizing conditions, including the radiation effects.
- ^d : Cycle 2 tests for 180 days are corrected, based on Tc-99 releases, to exclude any undissolved fuel grains from the stripping process of the altered layer on SF surfaces. Cycle 2 tests were retests of first-cycled samples that had been placed in new leachant, after removing the altered layer.
- ^e : Congruent dissolution is assumed.
- ^f : Plutonium concentrations were from 0.4 μm filtrates, including colloids.
- ^g : At (O/M) = 2.33, 75 percent were colloids. At (O/M) = 2.00, 37 percent were colloids.
- ^h : If normalized over the sample weight used in flow-through tests, it will go much higher. Data of Cycle 3 in Series 2 appear to be lower by a factor of about 0.2 than the value in this table.

References: (A1) - Gray, 1992; (A2) - Gray et al., 1992a; (A3) - Shoesmith and Sunder, 1991; (A4) - Shoesmith and Sunder, 1992; (A5) - Wilson, 1990b; and (A6) - Wilson, 1991.

or (S/A). With J-13 well water, elements such as silica or calcium, leachates are also supersaturated upon leachate replenishment, if solubility data (Nguyen et al., 1991) are referred.

Next, the realistic behavior of important variables in Equations 1 to 5 is considered. "S" is the initial geometric surface area. It will be changed as the protective layer masks the geometric surface area (Heppner et al., 1992; Wilson and Gray, 1990); the reprecipitated layer becomes offset from the bare SF surface (Wronkiewicz et al., 1992); preferential dissolution takes place along grain boundaries (Wilson, 1991); oxidation induces micro-cracks (Einziger et al., 1992); or the remaining volume of bare SF shrinks upon the dissolution. On the other hand, values of "A" increase, at least, to the geometric surface area. "A" can be further modified by the development or masking of the surface roughness, or by colloid behavior (formation, escape, or sedimentation). Real complications may arise regarding the effectiveness of "S" and "A" for dissolution and reprecipitation. Depending on the crystallographic nature or electric charge properties, the effectiveness of "S" and "A" may vary.

"N_{par}" is also important in determining leachate concentration, regardless of its origin (see Sections 4 and 5). When colloids are formed more than dissolved ions, the total surface area of colloids can become comparable with the surface area of the reprecipitated layer. As a result of the balance of (a) formation and accumulation; (b) flocculation, growth, disintegration, or sedimentation; and (c) escape by groundwater flow, the relative importance of "N_{par}" over reprecipitation or convection will be determined. For instance, one type of likely kinetics is (a) the rapid increase in "N_{par}" leading to a large "A" arriving at a steady-state value "C_t"; (b) decrease of "A" with flow of "N_{par}"; and (c) leachate resupersaturation. The (a), (b), and (c) steps can be repetitive. The sensitivity of "F" and of "S" was also evaluated. In the extrapolation of the laboratory data in Table 1 to repository conditions of "F" and "S," the expected increase of (C_t/C_o) values can be more than an order of magnitude.

In determining the amount of radionuclides released from SF, it is important to determine the size of fuel particles. If grain boundaries are dissolved preferentially, and, subsequently, each grain is exposed to leachate, the radionuclide release will be far more than that from outside surfaces of fuel particles. Currently, there is no consensus about the exposure of individual grain to leachates. However, recent DOE experimental results (Lawrence Livermore National Laboratory, 1995) indicate that individual grains may be exposed to leachates when pre-oxidized UO_{2.4} dissolves in J-13 well water. If SF oxidizes to a higher (O/U ≥ 2.4) oxidation state (e.g., U₃O₈ in matrices), it is possible that powdering will expose large surface areas.

Another area that needs to be considered further is the alteration of groundwater chemistry. If SF is subjected to drip conditions, the groundwater chemistry may be altered (Finn et al., 1994a; Walton, 1993). It is not clear whether alteration of groundwater chemistry increases or decreases matrix dissolution rates significantly. For instance, test results in brine solution do not show a clear trend (Wang, 1981). The significance of effects of pH or ionic concentrations is not certain, either (Bates et al., 1995; Steward and Weed, 1994; Gray et al., 1992a). Additionally, the roles of backfill, concrete, container metals, or other man-made materials such as diesel fuel, in this regard, are largely unknown. In any of these cases, the framework of Equations 1 to 5 will be bases to evaluate the SF dissolution process. For instance, the correlation made by Steward and Weed (1994), by Gray et al.

(1992a), by Bates et al. (1995), or by Gray and Wilson (1995) can be used as a basis to determine the matrix dissolution rates in various altered groundwaters for linear dissolution behavior with time.

3.2 Nonlinear Dissolution Kinetics

Up to this point, there has been discussion about reaction-controlled kinetics for SF dissolution, primarily linear time law for LWR SF in J-13 well water. The next is nonlinear time law, which cannot be neglected for the following reasons:

- (a) There are uncertainties about the amount of reprecipitates (Table 1). Reprecipitates may have been commingled with fuel grains (Forsyth and Wermer, 1992; Wilson, 1990b).
- (b) Diffusion-limited dissolution (or surface area change) may still lead to continuous reprecipitation.
- (c) Radiolysis can be attenuated as time elapses.

It should be noted that the diffusion limit considered here involves dissolution and subsequent reprecipitation, leading to the release of soluble radionuclides. On the other hand, there will be other diffusion limits when direct alteration takes place (Finch and Ewing, 1993) without involving dissolution and reprecipitation. In either case, radionuclide releases are likely to be slowed.

Under nonlinear dissolution conditions (including diffusion limit, surface area change, or radiation attenuation), dissolution rates will decrease gradually. In this case, the dissolution rate can be written phenomenologically as

$$R_{dis,d} = k \frac{S}{V} (t+a)^{-\frac{1}{n}} \quad (n \geq 2) \quad (6)$$

where "S," "V" and "t" represent surface area of the dissolving phase, leachate volume, and time, respectively; "k," "a," and "n" are constants; and n is an integer. In many kinetic problems, n=2 is expected. However, various geometries involved, such as varying surface area or radiation effects, may result in "n" values other than 2. The aforementioned nonlinear data in Section 3 can be explained by Equation 6. More rigorous treatments of diffusion-limited alteration have been made by Lichtner (1994) recently, using the code GEM (General Electrochemical Migration).

For solubility-controlled radionuclides in nonlinear kinetics, leachates will be at solubility limits, be supersaturated, or form colloids. This is similar to the case of linear time law and will proceed until the overall SF dissolution is retarded significantly by the nonlinear time law so that leachates will be undersaturated. For dissolution-controlled radionuclides, radionuclide releases will decrease gradually in nonlinear kinetics.

In this section, data on long-term SF dissolution and equations that govern the dissolution have been presented. The dissolution governed by linear time law is of utmost concern for dissolution-controlled radionuclides. Traditionally, solubility-controlled radionuclides have not been a regulatory issue because of their low solubility limits and high sorption capacity. However, if they are released in colloids, they can pose a potential problem, because radionuclides associated with colloids can be of large amounts and colloids can be transported in long distances. In the next two sections, colloid formation will be analyzed as another regulatory issue.

The traditional processes of colloid formation (especially in actinide colloids) have been investigated under near-equilibrium conditions. Most studies in this regard pertain to chemical bondings among ions. The study of the chemical aspect can be found in references of Kim (1993, 1986) and Nitsche (1991b). Extending the chemical bonding process in equilibrium or disequilibrium states, the colloid formation may be described in macroscopic ways by three different processes (Yariv and Cross, 1979): (a) condensation, (b) dispersion, and (c) sorption (pseudo-colloid formation). The traditional bonding process can be regarded as the condensation process. The important point is whether or not colloids form and grow continuously. This will be determined by whether leachates are supersaturated or in equilibrium states. In this report, these three macroscopic processes are investigated.

It is difficult to judge the relative importance of the three processes. In this work, knowledge pertinent to all three processes is summarized. The conditions under which each process takes place have not been well understood. Immersion tests will be discussed as the condensation condition, drip tests as the dispersion condition, and both types of tests as the sorption condition. However, it is suspected that two or more processes may take place simultaneously. The most information is on the condensation process. Therefore, the following sections investigate the condensation process more extensively than the other processes. The condensation process can also contribute to pseudo-colloid formation. Pseudo-colloids can form by precipitation (rather than sorption) of radionuclides or by sorption of precipitated radiocolloids, on groundwater colloids.

4 CONDENSATION PROCESS FOR COLLOID FORMATION AND UNCERTAINTIES ABOUT SOLUBILITY LIMITS

4.1 Immersion Test Results

Wilson (1991, 1990a,b) claimed that plutonium, americium, curium, and silica colloids form during LWR SF dissolution under the immersion condition of J-13 well water. Figure 1 shows his results illustrating releases of Pu-(239+240), Am-241, and Cm-244 at 25 and 85 C. The 25 C tests were conducted in a loosely sealed open system and the 85 C tests were conducted in a tightly sealed closed system. Leachates were filtered using two different sizes of pores: 0.4 μm and 1.8 μm . The difference of radioactivities between as-received leachates and filtrates was attributed to colloids. Uranium colloids were also identified in independent experiments of (a) UO_2 dissolution in J-13 well water at room temperature (Veleckis and Ho, 1991) and (b) UO_2 and SF dissolution in brine and deionized (DI) water (Wilson, 1985; Gray

and McVay, 1984; Wang, 1981) at 25 C. The difference in uranium concentrations between as-received leachates and filtrates was attributed to colloids. In the filtration of leachates for radionuclides or uranium, either filter papers alone or filter papers attached to the centrifuge were used. Silica colloids were observed directly by Scanning Electron Microscopy (SEM) after immersion tests in J-13 well water at 25 and 85 C (Wilson, 1990a,b, 1987).

The Swedish work by Forsyth and Wermer (1992) could not confirm plutonium, americium, and uranium colloids from LWR SF tests in synthetic groundwater at 20 to 25 C. There was an indication of the presence of curium colloids. Nevertheless, Forsyth and Wermer have not completely ruled out the formation of plutonium, americium, and uranium colloids. This was because (a) detached fuel grains and precipitated colloids were not differentiated and (b) actinide elements were left on the filter paper. Canadian scientists also considered the possibility that colloids form in immersion tests of CANDU fuels in various leachants at 25 C (Johnson et al., 1982). Although the Canadians suspected that these colloids came from the dispersion process (see Section 5.1), the details were not investigated.

In solubility experiments without SF, many researchers have observed colloid formation. In supersaturated J-13 well water (or other solutions) with plutonium (or americium), radionuclides, themselves, form radiocolloids (Nitsche, 1991a; Ramsay, 1988; Newton et al., 1986; Kim, 1986; Buckau et al., 1986; Olofsson et al., 1983; Benes et al., 1979; Cleveland, 1979). They are of polymeric hydroxide phases and can be very small (<1 nm) and may not grow.

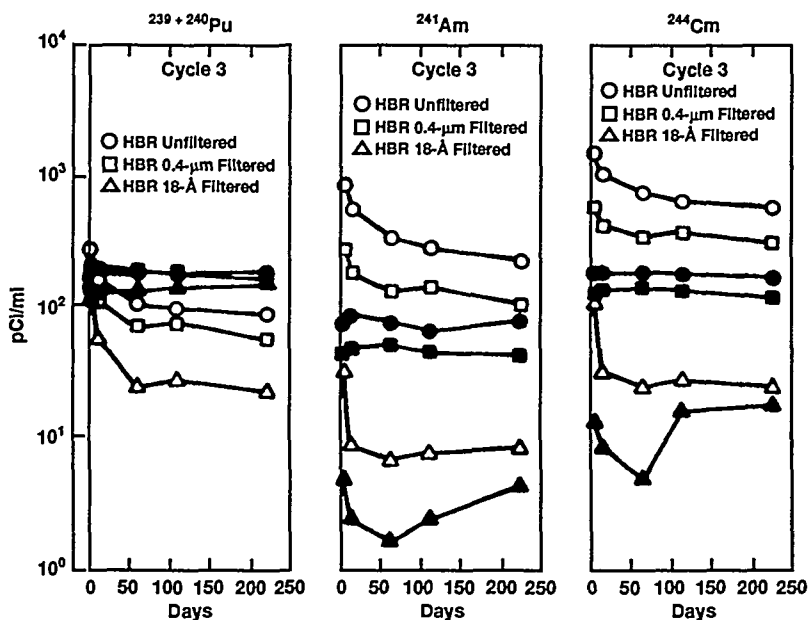
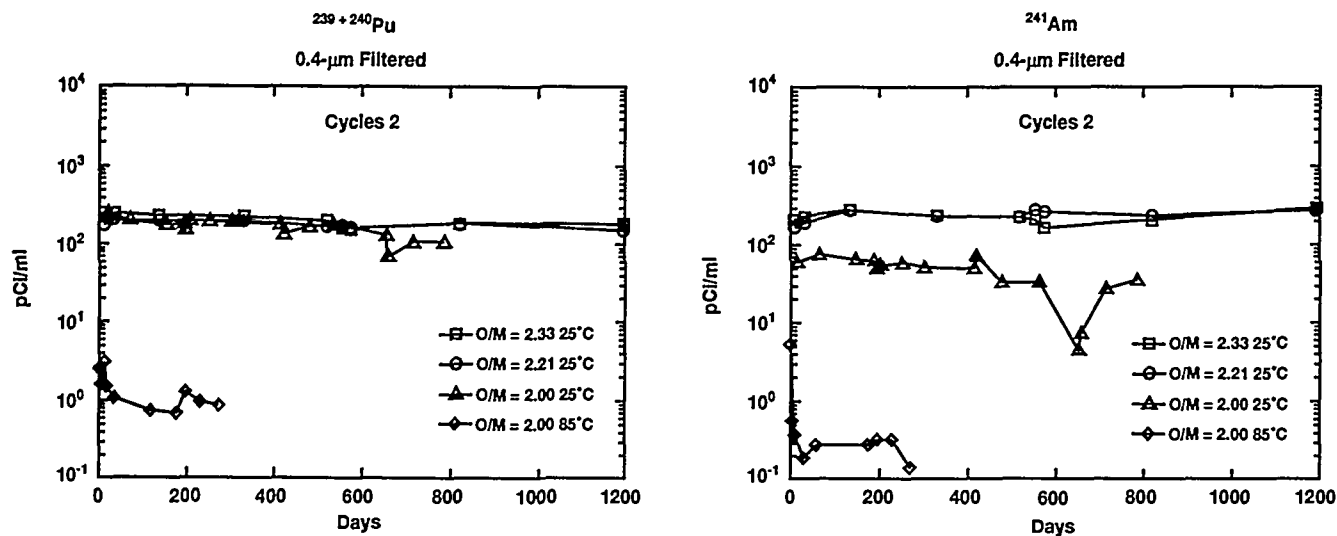
4.2 Condensation Process

It is believed that the condensation process is primarily responsible for colloid formation under immersion conditions. This section discusses the condensation process and potential artifacts involved in colloid experiments conducted to date.

The first concern is whether a leachate analysis with a filter paper attached to a centrifuge is a valid experimental technique. The filter paper, alone, could have absorbed even dissolved ions. To clarify this possibility, Wilson (1991, 1990a,b) allowed the filter paper to absorb dissolved radionuclides, until the filter paper was saturated with the dissolved radionuclides (data in Figure 1 were obtained by this method). After the filter paper was saturated, the difference in the radionuclide activities, between filtered and unfiltered leachates, was attributed to colloids. Some actinide colloids are so small that they could have passed through filters. SEM studies identified silica colloids from SF tests in J-13 well water at 25 to 85 C (Wilson, 1990a,b, 1987). Wang conducted dissolution tests of UO₂ single-crystal blocks and filtered leachates (Wang, 1981). He observed the difference in uranium concentration after filtration for DI water and Waste Isolation Pilot Plant (WIPP) brines, but not for carbonate leachants, at 75 and 150 C. No difference of uranium concentration in carbonate solution may imply that uranium sorption in the filter paper is little for all three leachants. (However, it may also suggest little uranium sorption in carbonate solutions. Therefore, this inference must be confirmed by further experimentation.)

Figure 1 Effects of Filtration of Measured Activity in Solution Samples from Bare LWR SF Tests in J-13 Well Water

(a) 25 C Open System (Wilson, 1991, 1990a)

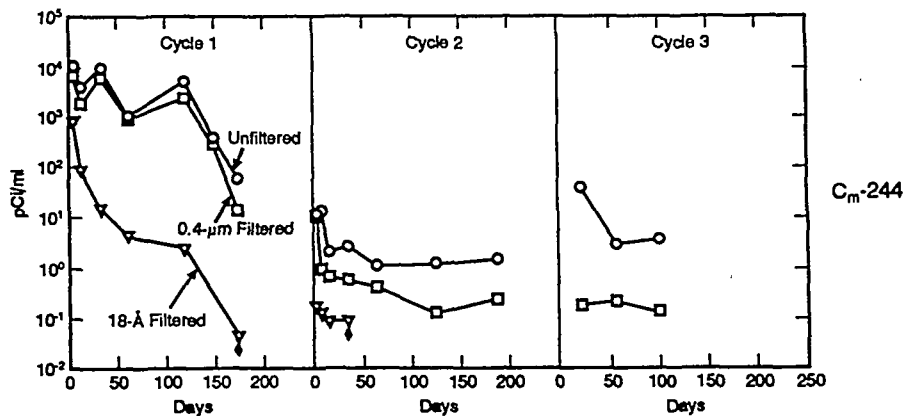
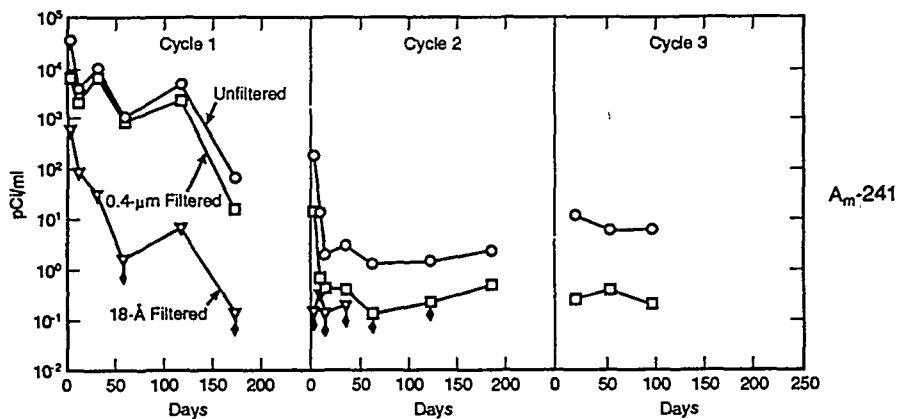
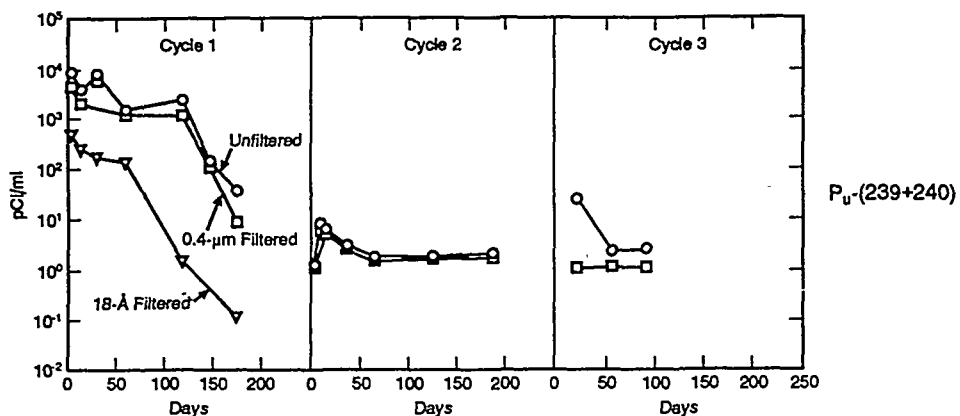


Open Symbols: H.B.Robinson Fuel, and Solid Symbols: Turkey Point Fuel

[Conversion: 1 pCi Pu-(239+240) = 1.1×10^{-5} μg ; 1 pCi Am-241 = 3.6×10^{-7} μg Am; and 1 pCi Cm-244 = 1.2×10^{-8} μg Cm].

Actinide, Log($\mu\text{g/ml}$)	Filter Size	O/M = 2.33	O/M = 2.00
Pu-(239+240)	0.4 μm	- 2.7	- 2.7
	2 nm	- 3.3	- 2.9
Am-241	0.4 μm	- 4.1	- 4.7
	2 nm	- 5.4	- 6.1

(b) 85 C Closed System (Wilson, 1990b)



The second concern is whether colloids in immersion tests are detached SF or UO₂ grains. This question is also answered by the same tests of UO₂ single-crystal blocks (Wang, 1981). The single-crystal multimillimeter block does not consist of small detachable grains. Moreover, colloids described above in SF tests are smaller than the SF grain size of about 10 μm (Einziger et al., 1992). Even if the dissolution of these grains is allowed (Leider et al., 1991), the grain will be bigger than the colloidal particle. There might be arguments that subgrain splitting may cause the formation of these small-sized colloids. Alpha particles and recoil damages may cause the subgrain splitting (Matzke, 1992) after or before grain detachments. However, microstructural analyses did not show such indications (Wilson, 1991). The filtration of uranium was pronounced in DI water, compared with that in J-13 well water (Wang, 1981). If grains were detached, the filtration in J-13 well water should have been pronounced also (Wilson, 1991, 1985). Also, the size distributions of plutonium colloids and of americium (or curium) colloids were different (Wilson, 1991, 1990a,b). If grains were detached, the size distributions of these colloids should have been similar. All these observations do not suggest subgrain detachment.

The third concern is whether colloids formed are from the spallation (or erosion) of the reprecipitated layer. This is an important question that needs to be answered more definitively in the future. In the UO₂ single-crystal tests in WIPP brine and DI water (Wang, 1981), the apparent particles had formed, before the reprecipitated layer formed. This is consistent with the observation that colloids form early in SF tests in J-13 well water (Wilson, 1991, 1990a,b; Veleckis and Ho, 1991). The morphology of a settled calcium-uranium-silicate particle from the SF tests in J-13 well water implies that the settled particle is unlikely to come from spallation (Wilson, 1990b). Wilson's tests (Wilson, 1990b) in Figure 1 show decreased amounts of colloids in later cycles. One possibility is that the decreased supersaturation in the presence of residual reprecipitates in later cycles decreases amounts of colloids formed. If spallation is involved, radionuclide releases in later cycles are unlikely to decrease. All these observations do not suggest the spallation mechanism.

The fourth concern is whether radioactive colloids form by the absorption of actinide ions on or into groundwater colloids (i.e., pseudo-colloid formation). The calculations in Section 5.2 show that reversible ionic sorption is unlikely to yield the radioactivities observed in immersion tests. The contribution of sorption, although existent, may not be significant. The calculations used sorption coefficients measured with mineral particles larger than colloidal particles. The two underlined assumptions for this calculation are that (a) the sorption takes place reversibly and (b) the sorption coefficients are independent of surface areas. The reality may deviate from this ideal situation. Therefore, there are several possibilities that groundwater colloids play an important role in radionuclide releases. For instance, (a) actinide ions precipitate (as a condensation process) on groundwater colloids, (b) actinide ions form radiocolloids (as a condensation process) and the formed radiocolloids are adsorbed on groundwater colloids, (c) sorption coefficients are unusually large. For colloidal size, the large surface area will lead to effectively large sorption coefficient compared with those derived using mineral particles (Vilks and Degueudre, 1991). However, if the minerals had been highly porous as in smectite (or clay in general), the surface area effects would not have existed; and (d) unusually large amounts of nonradioactive colloids form and the formed colloids absorb radionuclides. This has not been observed. These observations (a) to (d)

suggest that pseudo-colloid formation can be treated as the condensation process or as the sorption process when the surface area effects are important.

The data compiled above suggest that the condensation process derived from leachate supersaturation is potentially an important process for colloid formation. More definitive evidence for the condensation process was obtained in the systems without involving SF. For instance, in HLW glass leaching, Transmission Electron Microscopy studies showed that condensation takes place in static immersion tests for the formation of radioactive clay colloids (Buck et al., 1993). Also, actinide condensation for true radiocolloids is well recognized in solubility tests or related work in supersaturated leachates (Nitsche, 1991a; Ramsey, 1988; Kim, 1986; Newton et al., 1986; Olofsson et al., 1983; Rai and Ryan, 1982; Benes et al., 1979; Cleveland, 1979).

Unlike the formation of uranium colloids in DI water and brine at 75 and 150°C (Gray and McVay, 1984; Wang, 1981), the formation of uranium colloids in J-13 well water is less clear. Wilson observed uranium colloids only in a few cases among many experimental runs made. The observed colloids were primarily attributed to iron ions released from the test vessels (Wilson, 1990b). SF tests with brine at 25 C also showed more colloids with iron ions (Gray and McVay, 1984). The effects of iron ions are not regarded as artifacts because container or canister materials of HLW packages are expected to release iron ions. Veleckis and Ho (1991) observed uranium colloids more definitely from the UO₂ tests without iron in J-13 well water at 25 C. However, UO₂ used in this test was polycrystalline powder composed of very fine grains much less than 1 μm in size. Therefore, it has not been clarified yet whether the colloids were detached grains or precipitated particles. Nevertheless, it cannot be ruled out completely that uranium colloids form through the condensation process in J-13 well water without iron. The observed radioactivities associated with colloids could be composites of uranium and these radionuclides. Colloids of uranium with minor elements of plutonium (americium or curium) could form.

4.3 Nucleation Process

It is well established that dissolved actinides hydrolyze (Kim, 1986). Through the subsequent dehydration of hydrolyzed ions, ions condense for colloid formation (Maiti et al., 1989; Stumm and Morgan, 1981; Wendt, 1973). A similar type of condensation is the complexation with ligands such as carbonates or organic molecules. Large clusters of ions or ligand complexes can be regarded as colloids, or the clusters can be insoluble as colloids. Other studies postulate that the individual molecule becomes neutral as the hydrolyzed ion oxidizes/reduces. The subsequent condensation of neutral molecules results in colloids (Ramsay, 1988; Newton et al., 1986).

These condensation processes can be either ionic or molecular. They may be described by (a) stability constants in near-equilibrium states, (b) reaction kinetics in terms of electronic reactivities, or (c) reaction kinetics in terms of thermodynamic energetics. Case (a) applies to near-equilibrium states without spontaneous reactions. It is believed that Case (b) applies to the earlier stage of condensation such as dimer formation. On the other hand, Case (c)

extends to spontaneous reactions derived from leachate supersaturations and to insoluble bigger particles.

When dissolved condensed ions are in equilibrium (or at least in meta-stable supersaturation) with dissolved individual ions, the stability constants " β " traditionally determine the amount of dissolved condensed ions (Stumm and Morgan, 1981). For simple condensation as in dimer formation, the electronic reaction kinetics are fast (Stumm and Morgan, 1981). For spontaneous reactions derived from supersaturation, the kinetics become slower as the number of ions increases to form a larger particle. This slowed kinetics for a larger sized particle can be considered due to the energy barriers from overall thermodynamic energetics. As ions are added consecutively, the particles will become insoluble for spontaneous reactions. The condensation of approximately six ions or approximately 25 ions has been reported to make the particle insoluble (Yucca Mountain Site Characterization Colloid Workshop, 1993; Yariv and Cross, 1979).

In thermodynamic treatment, two different approaches can be considered, in turn. For the usual crystal formation, the classical theory of nucleation and growth can be adopted. However, the situation is complicated because (a) radiation involves amorphization (Cleveland, 1979) and (b) the condensation process often involves polymers even without radiation (Yariv and Cross, 1979). In the formation of amorphous polymers, the concept of miscibility gaps (i.e., spinodal decomposition) may be more applicable (Cowie, 1973). Unlike nucleation, spinodal decomposition does not require energy barriers to overcome, to form the new phase. However, spinodal decomposition takes place only with abundant polymer-forming constituents in leachates. This does not seem to be the case in the SF dissolution. Additionally, the process of actinide polymerization has not been understood well. Some postulate that micro-crystal formation precedes polymerization (Cleveland, 1979). Others postulate that partially crystallized phases form initially (Rai and Ryan, 1982; Yariv and Cross, 1979). If crystals form, they are likely to form through the nucleation process. Furthermore, the traditional view of the spinodal decomposition is that it can be interpreted in terms of nucleation and growth processes (Doremus, 1973). Therefore, it is believed that formation of amorphous polymers in SF dissolution can be regarded as the nucleation process too. The nucleation process is an established concept explaining the formation of generic colloids, without SF dissolution (Yariv and Cross, 1979).

Nucleation kinetics involving many ions is of direct interest. As pointed out by other researchers (Yariv and Cross, 1979), both dissolved polynuclei and insoluble colloids can be regarded as nuclei. Therefore, a nucleation model can be applied to all three cases of condensation (i.e., dehydrational condensation, complex formation, or condensation of molecules or ions). Theories involved in allotropic (Christian, 1975) or allomorphic (Sautoff, 1976) nucleation can be applied to the condensation processes. The measured kinetics of colloid formation may become further complicated by the growth of the formed nuclei. The growth kinetics involve ionic growth, flocculation, or disintegration. None of these phenomena has been examined closely yet. It is assumed that the number of particles is equal to the number of nuclei. Modifications in the nuclei number incorporating settled particles do not appear to be necessary. The numerical evaluation of nucleation models is reasonable, without such modifications, as will be shown below.

4.4 Nucleation Kinetics

Although heterogeneous nucleation on a substrate (such as groundwater colloids) is more favorable, energetically, uncertainty regarding the geometries involved makes the calculation less straightforward. However, heterogeneous nucleation can be interpreted based on homogeneous nucleation in a relatively simple way. For instance, the energy barrier for heterogeneous nucleation is obtained by simply scaling the energy barrier for homogeneous nucleation with geometric factors. Therefore, the following evaluates homogeneous nucleation of a phase (or an element).

The nucleation rates of these colloids (Ahn et al., 1993, 1981; Kerrick et al., 1991; Yariv and Cross, 1979; Christian, 1975) can be expressed as:

$$R_{nuc} = n k \frac{T}{h} e^{-\Delta G_d / RT} e^{-\Delta G_c / kT} \quad (7)$$

where "n" is the number of rate-limiting ions in leachates, "k" is the Boltzman constant, "T" is the temperature, "h" is the Planck constant, " ΔG_d " is the activation energy for the ionic diffusion in leachates, "R" is the gas constant, and " ΔG_c " is the activation energy for the formation of the critical size of a nucleus. " ΔG_c " is given as $(16 \pi \gamma^3 M^2) / (3 \rho^2 \Delta G_v^2)$, where: " γ " is the surface energy per unit area of the colloid. Surface energy is of effective values, taking into account ionization with zeta potential; "M" is the molecular weight of the chosen second phase; " ρ " is the density of the second phase; and " ΔG_v " is the driving force for nucleation. " ΔG_v " is approximated by $[- R T \ln(C_s/C_o)]$ for a rate-limiting species (Stumm and Morgan, 1981; Sauthoff, 1976). " C_s " is the concentration of the species and " C_o " is the solubility limit of the species. Alternatively, $\{- R T \ln[Q \text{ (activity product to the power of the stoichiometric value)}/K \text{ (equilibrium value of Q)}]\}$ can be used as " ΔG_v ." Both expressions are approximations. In the former, " C_o " for multicomponents or multiphases is not well defined as SF dissolves. The latter does not apply to the nucleation of individual elements or of many phases. Because only one or two species control nucleation kinetics, the use of the former is more practical. Proton releases during hydrolysis do not appear to change the leachate pH, and, subsequently, the solubility limit, significantly (Wilson, 1990b; Grambow, 1989). Therefore, the approximation used in " ΔG_v " will not be affected significantly by the pH change. In Equation 7, we have dropped the number of atoms in the critical cluster (Kirkpatrick, 1981). Adding this term has been debated for a long period. Regardless of this debate, conclusions drawn in this section will not be affected.

Equation 7 is evaluated with experimentally measured values in colloid formation, to determine whether this model is valid for explaining the process involved in observed colloids. Using known nucleation rates and reasonable values of other parameters, values of the most uncertain parameter, " γ ," are extracted in Equation 7. It is evaluated whether the extracted values are reasonable or not based on current knowledge of surface energy. If those values are reasonable, the nucleation model is accepted. Uranium, plutonium, and silica are considered in this analysis. Data are chosen for uranium colloids in DI water at 25 C (Wilson, 1985) and plutonium colloids in J-13 well water at 25 C (Wilson, 1991). It is

estimated that colloid formation rate is the product of (number of particles per unit leachate volume) x (replenished leachate volume)/(replenishment time). This estimate is based on approximately constant leachate concentrations of these elements, despite nearly 100-percent replenishments of leachates. An example of the constant leachate concentration is shown in Figure 1(a). For silica colloids in J-13 well water at 85 C (Wilson, 1990b), it is assumed that the initial silica ions present in leachates, excluding surface reprecipitates, form colloids.

The following values are used in evaluating Equation 7 and the extracted " γ " values. Using these values, the critical number of ions for nucleation was also calculated. For uranium colloids, approximately one $\mu\text{g/ml}$ of uranium was maintained in leachates. It took approximately 180 days to replenish 80 ml of leachates. The particle size is at least about 10^{-4} cm. Approximately 10^3 are (C_s/C_o) values from leachate filtration. (ρ/M) values are for schoepite. Approximately 10^{-2} to 10^{-4} are " $e^{-Gd/RT}$ " values (Christian, 1975). The extracted " γ " values in Equation 1 are approximately 100 erg/cm^2 . For plutonium, approximately 200 pCi/ml of plutonium were maintained in leachates. For different SF, it took approximately 780 days to replenish approximately 300 ml of leachates or approximately 1,200 days to replenish approximately 120 ml of leachates. The particle size is approximately 10^{-6} cm. Approximately 7.5×10^3 are (C_s/C_o) values for PuO_2 (Wilson, 1991; Wilson and Bruton, 1989). Approximately 10^{-2} to 10^{-4} are " $e^{-Gd/RT}$ " values (Christian, 1975). The extracted " γ " values are approximately 180 to 190 erg/cm^2 . Approximately 10 $\mu\text{g/ml}$ of silica particles of 10^{-4} cm were obtained for approximately 20 days. Approximately 10^4 are (C_s/C_o) values (Nguyen et al., 1991; Wilson, 1990b). (ρ/M) values are for silica. Approximately 10^{-2} to 10^{-4} are " $e^{-Gd/RT}$ " values (Christian, 1975). The extracted " γ " values are approximately 240 erg/cm^2 .

The critical number of ions, " n_c ," can be calculated using the relation of

$$n_c = (32 \pi \gamma^3 M^3)/(3 \Delta g_v^3 \rho^2 N^2) \text{ (Christian, 1975),}$$

where N is the Avogadro number and " Δg_v " is " ΔG_v " divided by " N ." Values of " n_c " in the above three cases are about 18 to 19, 15 to 17, and 13 to 14, respectively. The " γ " values or the critical numbers will be reduced further if (a) the ungrown particles (nuclei) are used in the calculation, (b) many particulates are settled down; and (c) the chosen durations above are too long (colloids may nucleate in shorter periods compared with replenishment intervals). Therefore, actual reaction rates can be shorter than the nucleation rates calculated above. However, if the observed colloids comprise SF grains or are in larger sizes, the " γ " values can increase because the number of nuclei decreases.

The formation of uranium colloids or silica colloids was driven by the large amount of uranium or silica ions. On the other hand, the formation of plutonium colloids was driven by the small amount of plutonium ions. Therefore, colloids of smaller sizes are likely to form and are subsequently sorbed on groundwater colloids. Alternatively, plutonium ions precipitate directly on groundwater colloids. For instance, if the colloid size is approximately 10^{-8} cm, the " γ " values are from 160 to 170 erg/cm^2 and the " n_c " values are from 11 to 13. If precipitation takes place, effective values of these quantities will decrease.

The above " n_c " values are usual values in many nucleation problems (Adamson, 1990). The extracted " γ " values above are smaller than the typical values, approximately 26 to 1,600 erg/cm², for mineral-aqueous interfaces (Steeffel and Van Cappellen, 1990) and approximately 1,000 erg/cm² for a common dehydrated crystalline phase. Small " γ " values are acceptable if

- (a) The reprecipitated phase is hydrated, amorphous, or polymeric (Cherepanov, 1979; Deanin, 1972; Shand, 1958);
- (b) Small particles are ionized and dissolved foreign ions are adsorbed.

The contribution of ionization (zeta potential (van der Lee et al., 1993; Park, 1990)) alone may not change " γ " values. However, the adsorption of foreign ions may change the value in an order of magnitude. Less than 250 erg/cm² of " γ " values are expected for a stable particle suspension (Stol and de Bruyn, 1980).

- (c) Anisotropic phases form.

For instance, two-dimensional polymeric nucleation may not involve large energy barriers (Tirrell et al., 1991).

- (d) Heterogeneous nucleation takes place on surfaces of groundwater colloids.

If heterogeneous nucleation rates are converted to the corresponding homogeneous nucleation, the effective " γ " values will decrease significantly as in an order of magnitude. Finally, it is noted that variation of other uncertain parameters such as " C_0 " are unlikely to result in unacceptable values of " γ " or " n_c ."

It should be noted that americium and curium colloids may form more readily (Figure 1) (Wilson, 1990b; Kim, 1986). The present analysis is equally appropriate for analyzing americium and curium colloids. Unfortunately, the lack of thermodynamic data on these colloids makes it difficult to include them here. In the above analysis, radiation effects have not been considered in the formation of plutonium colloids. Nevertheless, the analyzed results of silica and uranium colloids suggest that the radiation effects appear to be unimportant.

For low or near-zero " γ " values, polynuclei or colloids will form spontaneously. This will continue, until the consumption of dissolved ions to form or grow these particles is so fast that leachates are no longer supersaturated. There would be a balance among nucleation, growth, flocculation, sedimentation, disintegration, and escape by groundwater flow. On the other hand, when the " γ " values are large, the " n_c " values increase. Under these circumstances, most observed particles will be in a meta-stable state because of the large energy barrier to overcome for spontaneous nucleation. The reality might be between these two extreme cases of small or large values of " γ ", depending on (a) environmental conditions such as temperature, (b) characteristics of the paragenesis of reprecipitated phases, (c) the radiation-induced amorphization of reprecipitates (Rai and Ryan, 1982), or (d) other unknown factors involved in unstable reprecipitates. Meta-stable states or very small

polynuclei (< 1 nm) are often observed (Kim, 1986; Stumm and Morgan, 1981). Most polynuclei observed in a near-equilibrium state have resulted from the condensation of two to three ions (Nitsche, 1991a; Kim, 1986; Gordon and Sullivan, 1986). A maximum of seven ions was postulated by Kim (1986).

From these representative cases, it is noted that nucleation rates may be fast, upon leachate replenishment. This leads to nearly constant leachate concentrations. The reason for the fast nucleation is implied in the above formula of nucleation kinetics. The nucleation rates increase very fast as the supersaturation increases above a critical leachate concentration. After the fast formation of colloids, leachates will be either in a supersaturated state (but not sufficient to form colloids further) or in a near-equilibrium state. One of these states will be maintained until there are significant leachate replenishments. The leachate replenishment will decrease the total surface area of colloids. This will lead to the resupersaturation of dissolving elements from SF. Groundwater elements such as silica will be resupersaturated by the leachate replenishment itself. The resupersaturation will perpetuate colloid formation. Alternatively, if nucleation rates are slow, there will be a gradual accumulation of colloids, by the continuous formation of colloids. If the accumulation is slow, it may not be observed in laboratory tests (although it is possible under repository conditions). The real situation is more complicated. For instance, colloids may disintegrate because of radiation effects. Settled particles increase or decrease the surface area of reprecipitates.

Temperature effects are considered by quoting Wilson's data on plutonium at 85 C (Figure 1(b)) (Wilson, 1991, 1990a,b). At 85 C, Wilson believed that the size of colloids was bigger so that colloids could be regarded as precipitates (Wilson, 1991). Cycle 2 of his tests showed such a trend. Because the leachate concentration at 85 C was much lower than that at 25 C (Wilson, 1991, 1990a,b), this trend is consistent with the von Weimarn relation (Adamson, 1967). The von Weimarn relation postulates that smaller supersaturation results in fewer, but bigger, colloids. This is also consistent with the expected fast growth (or flocculation) of colloids at higher temperatures. The sedimentation of the bigger colloids explains that the colloid formation was less pronounced at 85 C (Wilson, 1991, 1990b).

Based on the above representative analysis, the nature of colloid formation can be considered as (a) homogeneous nucleation (of uranium, plutonium, americium, curium, or silica); (b) heterogeneous nucleation and growth of radionuclides on groundwater colloids; (c) incorporation of plutonium, americium, or curium colloids into U-bearing or silica colloids; or (d) homogeneous (or heterogeneous) nucleation of new phases containing uranium, plutonium, americium, curium, silica, and other rare-earth elements. It is also noted that the above evaluation is applicable to determining nucleation rates as leachates migrate to a lower temperature field. The nucleation rates are very sensitive to temperature variations. However, leachate concentrations also become diluted in the lower-temperature field. Therefore, the net effects may not be significant.

Finally, it should be noted that true solubility limits are very difficult to determine because meta-stable polynuclei are present or leachates are supersaturated. Besides this theoretical ambiguity in solubility limits, it is also difficult to determine true solubility limits, experimentally. Even the insoluble colloids (regardless of their origins) are not easily

separable because of their small sizes. Kim (1986) has recognized these difficulties in experiments for many years. The implications of these ambiguities and uncertainties may be important in SF performance assessment because (a) most colloids observed were larger in quantity than the dissolved ions, (b) colloids can accumulate in near-static conditions, and (c) the degree of supersaturation can be significant if colloid formation is hindered kinetically.

This section summarizes experimental observations related to the condensation process. Among several submechanisms involved in the condensation process, it is believed that the nucleation mechanism explains the measured data on colloid formation. Thus, consequences of the nucleation process and uncertainties associated with solubility limits were discussed. In the next section, other mechanisms for colloid formation are presented.

5 DISPERSION PROCESS FOR COLLOID FORMATION AND PSEUDO-COLLOID FORMATION

5.1 Dispersion Process

Whereas ionic (or molecular) condensation is one method of colloid formation, colloids can also form through the disintegration of bulk solid materials (i.e., the dispersion process) (Yariv and Cross, 1979). The dispersion process arises primarily from physical or chemical weathering. Among the various weathering processes (Yariv and Cross, 1979), two types of disintegration have been considered in SF dissolution. The first arises from the disintegration of unstable reprecipitates. The second arises from the intergranular preferential dissolution of SF matrices.

5.1.1 Dispersion of Unstable Reprecipitates

The integrity of reprecipitates can be lost by (a) alpha particle and recoil damage (Kim, 1986) and radiolysis (Wang, 1981); (b) internal stress associated with phase transformations and external stress; (c) microbial activities (Jones-Meehan et al., 1991); and (d) environmental variations. In these processes, stress is the main cause for the dispersion process. Internal stress is particularly emphasized because it is considered a sustained effect. After internal stress is discussed, other reprecipitate-integrity compromisers will be discussed. Such compromisers include radiolysis, microbial activities, and environmental variations. Drip tests are chosen as the dispersion condition to lead to unstable reprecipitates.

In SF drip tests with J-13 well water at 90 C for a few months, Argonne National Laboratory (ANL) scientists (Finn et al., 1994a,b; Bates et al., 1995) obtained approximate maximum releases of 4×10^{-2} $\mu\text{g/ml}$ Am-241, 9×10^{-3} $\mu\text{g/ml}$ Am-243, 5×10^{-6} $\mu\text{g/ml}$ Cm-244, and 1×10^{-2} $\mu\text{g/ml}$ Pu-239 from alpha spectroscopy (details are in Table 2). Significant amounts of these releases were believed to be associated with colloids. The following are potential reasons why the dispersion process is responsible for the formation of these colloids: (a) some colloidal phases in SF were the same as the reprecipitated phases in the drip tests (i.e., uranyl silicates or uranyl hydrates) and (b) a similar inference was made, regarding colloid

Table 2 Actinide Released ($\mu\text{g/ml}$) From Drip Tests of LWR SF With J-13 Well Water at 90 C in Argonne National Laboratory*

	Reference		
Actinide	Finn et al., 1994a	Finn et al., 1994a	Bates et al., 1995
Am-241	4×10^{-2} (3×10^{-1})	4×10^{-2}	4×10^{-6}
Am-243	9×10^{-3} (5×10^{-1})	9×10^{-3}	
Cm-244	5×10^{-3}	5×10^{-3}	8×10^{-7}
Pu-238		2×10^{-3} ⁽¹⁾	
Pu-239	1×10^{-3}	1×10^{-2}	2×10^{-4}
Time	at 127 days	at 275 days	at 581 days

* Maximum values of radionuclide releases from alpha spectroscopy are quoted. Parentheses are from gamma spectroscopy.

⁽¹⁾ The value is greater than the actual value due to Am-241 masking.

formation, during drip tests of HLW glasses (Bates et al., 1992). However, this hypothesis of the dispersion process for ANL data has not been confirmed yet. The condensation process could be responsible for the colloid formation. Additionally, fuel grains could have been dislodged (grain detachments, see Section 5.1.2) (Bates et al., 1995).

It is believed that stress-induced spallation is primarily responsible for the disintegration of reprecipitates. It is not known exactly how the formation of secondary phases is related to the spallation. If the formation itself is rate-limiting, the formula presented in Section 4.4 is one treatment. However, the reality is far more complicated because the fracture process is involved. One way to quantify disintegration is to convert strain energy to the energy to create new surface areas. Strain energy results from volume changes during alteration. Using the elastic strain energy stored per unit volume as

$$\epsilon = \frac{E}{2(1-2\nu)} \left(\frac{\Delta V}{3V} \right)^2 \quad (8)$$

where "E" is Young's modulus, " ν " is Poisson's ratio, and $(\Delta V/V)$ is volume expansion.

Data on reprecipitates appropriate to evaluate Equation 8 are limited. Therefore, the proposed model of Equation 8 was tested in another system. The adopted system is the oxidation of UO_2 to U_3O_8 . The oxidation of UO_2 to U_3O_8 involves approximately 35.8-percent volume expansions (Thomas et al., 1989). With approximately 4-percent conversion of the strain energy to the energy associated with new surfaces (this value, obtained for HLW glass by D. Martin (1985), can be smaller by grain boundaries or phase transformation

in SF), with approximately 145,000 MPa of "E" values (Schackelford, 1992), with approximately 0.3 of "ν" values (Schackelford, 1992), and with approximately 1,000 erg/cm² of surface energy, the fractured particle size is approximately 3x10⁻⁶ cm. This is in the size of U₃O₈ formed within U₄O₉ matrices, taking into account grain boundary effects (Thomas et al., 1989; Stacey and Goode, 1978). Therefore, the proposed model of Equation 8 seems to be reasonable. From this sample evaluation, the author also learns that the powdering of U₃O₈ is another potential dispersion process for colloid formation. As in this sample calculation, the volume expansions associated with the uranosilicate (or schoepite) formation are likely to be large (CRC Press, 1975) enough to cause fractures. Therefore, observed colloids in the drip tests are possibly attributed to the spallation process of uranosilicates. Equation 8 calculates the number of colloids per unit SF volume. Thus, the total number of colloids formed can be estimated by the dissolved (or oxidized) volume of SF at various times. However, the use of Equation 8 in uranosilicates (or schoepite) may lead to an overestimation. Unlike direct solid-state transformation in U₃O₈, the formation of uranosilicates involves dissolution and subsequent reprecipitation.

Another alternate mechanism to stress-induced spallation is erosion as addressed in immersion tests of CANDU SF in sulphate and carbonate water at 25 C (Johnson et al., 1982). Considering that erosion is one mode of wear, the dispersion process may involve various modes of wear. The following equation may provide guidelines for more quantitative tests. Phenomenologically, the wear (volume per time) may be given as $w = f(A, F, L, 1/K_{IC}, 1/H)$ (ASM International, 1992; Bhushan and Gupta, 1991; Rigney and Glaeser, 1978), such as

$$w \propto \frac{A F^k L^l}{K_{IC}^m H^n} \quad (9)$$

where "f" is an appropriate function; "A" is the wet surface area of SF; "F" is the flow rate; "L" is the load applied and can be replaced by the liquid impact pressure; "K_{IC}" is the fracture toughness of reprecipitates; and "H" is the hardness of reprecipitates. The latter two values may depend on temperature or on fuel type, and (k, l, m, and n) are appropriate constants.

Besides the internal stress, radiolysis, microbial activities, and environmental variations should also be noticed. There has been no detailed explanation of radiolysis effects yet. One possibility is that reprecipitates become unstable with new Eh or pH conditions. Although it is known that microbes cause corrosion products or coating materials in metals to deteriorate (Jones-Meehan et al., 1991), their potential role in colloid formation is not known. Under radiation fields near the boiling point of groundwater, microbes may become sessile. They can be active in the later stage of waste package performance, as temperatures and radiation levels decrease. Environmental variations can also induce mechanical damages in reprecipitates. For instance, the wet-dry cycles may vary the groundwater chemistry and subsequently lead to dry-out, redissolution, or spall-off of the reprecipitates. Equation 8 is certainly one treatment of some of these processes. Similarly, any disturbance caused by external stress waves, such as seismic events, may break reprecipitates.

5.1.2 Intergranular Dissolution

It was also observed that colloids form through intergranular preferential dissolution. The intergranular preferential dissolution led to the subsequent detachment of each grain. The grain detachments were observed most distinctly during UO_2 dissolution in drip tests with J-13 well water at 90 C (Wronkiewicz et al., 1992). (Detachments of some grains were also observed in immersion testings of CANDU SF in sulphate and carbonate water at 25 C (Johnson et al., 1982) and in immersion testings of LWR SF in J-13 well water at 25 C (Wilson, 1991).) UO_2 drip tests conducted for up to 469 weeks (Bates et al., 1995; Wronkiewicz et al., 1992) showed pulse-like release of uranium in maximum 90 to 20,240 $\mu\text{g/ml}$ (see details in Table 3). This release is mainly attributed to grain detachments.

Table 3 Maximum Uranium Released ($\mu\text{g/ml}$) From Drip Tests of UO_2 With J-13 Well Water at 90 C for up to 469 weeks (Bates et al., 1995; Wronkiewicz et al., 1992)

Test Number	1	2	3	4	5	6	7	8
$\mu\text{g/ml}$	2,920	1,810	90	3,870	300	1,830	1,710	20,240

However, the process of grain detachments ceases as the reprecipitates cover the UO_2 surface. Also, uranyl silicate colloids were observed after eight years. Therefore, uranium release could be associated with colloids formed through spallation or nucleation also, especially in later stages.

Quantitative equations describing the grain detachment process are not available because the physical process itself is not well understood. One simple and conservative method for quantification is to use the SF dissolution rates from flow-through tests (Table 1) and to calculate the dissolution rates of grain boundaries. However, because reprecipitates mask the grain detachments, a detailed validation of this model is not presently available. Additionally, the detailed process of grain detachments after grain boundary dissolutions is not yet fully understood.

It is believed that the dispersion process (Sections 5.1.1 and 5.1.2) potentially will release more radionuclides than the condensation process. Colloids may form continuously by the dispersion process without solubility constraint.

5.2 Pseudo-Colloid Formation

Besides the colloid formation through the condensation process or through the dispersion process, pseudo-colloids may also form. J-13 well water is generally known to have 0.01 to 1 $\mu\text{g/ml}$ groundwater colloids (Yucca Mountain Site Characterization Colloid Workshop, 1993). Their sizes are similar to the three size groups (less than nm, in between nm and μm , and greater than μm). Groundwater colloids are composed mainly of silicate- or iron-based

minerals (Yucca Mountain Site Characterization Colloid Workshop, 1993). Organic colloids cannot be ignored either. However, the amount of organic colloids reported so far is 0.01 to 0.1 ppm which is less than inorganic colloids (Yucca Mountain Site Characterization Colloid Workshop, 1993). Radionuclides released from SF are sorbed onto or into these groundwater colloids. The sorption will form pseudo-colloids carrying radionuclides. The amount of sorbed radionuclides is approximated by the operational definition:

$$W_a = M_g K_d C_a \quad (10)$$

where " M_g " is the mass of groundwater colloids and " C_a " is the radioactivity in leachates. By the operational definition of sorption coefficient " K_d ," this relation can be applied to surface sorption or to bulk sorption.

This equation is evaluated for plutonium colloids under the immersion conditions quoted in Section 4.4. This evaluation will clarify whether plutonium colloids formed through sorption or formed through other processes such as nucleation. For the range of " K_d " values from batch sorption experiments, 100 to 5,000 ml/g (U.S. Department of Energy, 1988), the radioactivities from radionuclide sorptions in Equation 10 are lower than the observed values. For organic colloids, " K_d " values range from 10 to 10^4 ml/g at room temperature (from Am-241 data obtained in the salt environments of the Gorleben repository site of Germany (Kim et al., 1989). " K_d " values for Am-241 are normally bigger than those for Pu-(239+240). From this equation, it is noted that " K_d " should be the inverse of " M_g ," to obtain the observed " W_a " values in the range of " C_a " values: " K_d " values should be approximately 10^6 ml/g for $C_a = 1 \mu\text{g/ml}$, to obtain the same order of magnitude in radioactivities for filtrated leachates and colloids (Wilson, 1990a). This is a conservative estimate. For instance, Figure 1 shows that " W_a " values can be much larger than " C_a " values. This will require larger " K_d " values. Values of " K_d ," approximately 10^6 ml/g, are very large, from the usual batch sorption experiments. Large K_d values suggest that the pseudo-colloids formed by reversible ionic sorption may not be sufficient to explain the plutonium colloids observed. If silica colloids of approximately $10 \mu\text{g/ml}$ are considered, the pseudo-colloid formation is also unlikely to be the magnitude of radioactivities observed. The required " K_d " value of 10^5 ml/g is still a large value for silica (Ames and Rai, 1978).

Other evidence supports this hypothesis in part. For instance, if colloids formed by the reversible sorption process, each cycle in Wilson's test (Figure 1) (Wilson, 1990b) should have shown the same behavior. Likewise, data at higher temperatures should be similar to those at 25 C. This was not the observed case. Also, some data on uranium quoted in Section 4.2 were obtained in DI water that presumably does not contain groundwater colloids. In addition, the sorption is a competitive process of various kinds of ions. Effective " K_d " values may decrease in SF dissolution.

Nevertheless, it is possible that pseudo-colloids contribute significantly to observed radioactivities, as discussed in Section 4.2. The first case is when " K_d " values from batch sorption experiments increase for colloids of large surface areas (Vilks and Degueudre, 1991). It is not known whether this hypothesis is valid or not for some minerals. For instance, highly sorptive minerals such as clay are composed of pores smaller than colloid

sizes. This will lead to " K_d " values insensitive to surface areas, regardless of mineral sizes. The second case is that radionuclides precipitate on the surfaces of groundwater colloids. The third case is that radiocolloids are precipitated and subsequently sorbed on surfaces of groundwater colloids. The second and the third processes involve nucleation processes and can be treated in Section 4.3. These observations suggest that pseudo-colloid formation can be treated as a condensation process, unless the surface area effects are important.

Pseudo-colloids, discussed here, are important vehicles for the far-field transport of radionuclides. The colloids formed near SF may redissolve during their migration in the far field. The concentrations of dissolved radionuclides are expected to be dilute in the far field. Under these circumstances, pseudo-colloids will become dominant over other types of colloids. Other types of colloids are unlikely to form in dilute solutions away from waste packages. Electric charge characteristics of colloids are likely to be responsible for radionuclide transport. Colloids may be charged differently from dissolved ions (Nitsche, 1991b); colloids may not be easily sorbed on tufaceous matrices. However, there are uncertainties in determining the amount of groundwater colloids. The sampling process normally involves significant artifacts. There are additional complications. As groundwater migrates, groundwater colloids may form by the condensation process or by the dispersion process, or they may redissolve.

This section summarizes the dispersion process and the sorption process for colloid formation. The important processes are spallation of reprecipitates, erosion of reprecipitates, intergranular dissolution of SF matrices, precipitation of radionuclides on groundwater colloids, radiocolloid precipitation and subsequent adsorption on groundwater colloids, and radionuclide sorption on groundwater colloids with large " K_d " values derived from large surface areas.

6 STABILITY OF COLLOIDAL SUSPENSION

Sections 4 and 5 describe various potential processes of colloid formation. Currently, the technical community of HLW is convinced that colloids form during SF dissolution. The next important questions are (a) whether the condition for colloid formation persists and (b) whether the suspension of the formed colloids is stable. In the condensation process, an important ambiguity is that these colloids may disappear as time elapses. Many aforementioned databases show transitory behavior. This is more pronounced for data near the boiling point of groundwater. For instance, Figure 1 shows that some plutonium colloids disappear in later cycles. Colloids can disappear by either (a) increased mass transfer to reprecipitates or (b) the instability of colloidal suspension. Case (a) leads leachates to near-solubility limits. Residual reprecipitates in later cycles increase the mass transfer, or unoxidized SF (compared with surface-oxidized as-received SF) in later cycles decreases dissolution rates. This will lead to insignificant supersaturation for colloid formation, unless the colloid formation does not need to overcome energy barriers. Case (b) is an inference from the ANL experience in HLW glass leaching. In the ANL tests, it was believed that higher ionic strength and pH collapse the double layers on colloid surfaces. This double-layer

collapse was believed to result in flocculation, aggregation, and sedimentation of colloids (Bates et al., 1993).

However, room temperature data, and some 85 to 90 C data of plutonium, americium, and curium (part of data in Figure 1) do not show transitory behavior. Table 4 also suggests the potential stability of colloidal suspension. In this table, stability is assessed through relations among the SF surface area (S), the leachate volume (V), and the flow rate (F), under immersion conditions. These three parameters are likely to be primarily responsible for determining the ionic strength and pH of leachates. Data on HLW glass are also included, to obtain inferences for SF. The stability of colloidal suspension has been examined only in HLW glass leaching (Ebert and Bates, 1992), not in SF dissolution. Flocculation or growth occurred at approximately 200 cm⁻¹ (20,000 m⁻¹) of (S/V) values and approximately 0 of (F/V) values in HLW glass leaching (Ebert and Bates, 1992). On the other hand, most repository or other laboratory test conditions for SF and HLW glass have higher values of F/V and lower values of S/V. This is a likely condition for lower ionic strength. If pH is responsible for the stability of colloidal suspension, similar conclusions may be drawn. Flocculation or growth occurred at pH values of 11 to 12 and S/V values of 200 cm⁻¹ in the immersion tests of HLW glass (Ebert and Bates, 1992). On the other hand, pH values were 10 to 11 at (S/V) values of 20 cm⁻¹ in the more realistic immersion tests of HLW glass; and pH values were 7 to 8 in the SF immersion tests (Wilson, 1990a,b). These inferences suggest that colloidal suspension may be stable under repository conditions. It is noted that if stable colloids accumulate, radionuclide releases can be more significant under long-term repository conditions.

Table 4 Relations Among Surface Area of Waste Form (S), Leachate Volume (V), and Flow Rate (F) Under Immersion Conditions [An estimate was made using data in Ebert and Bates, 1992; Wilson, 1991; U.S. Department of Energy, 1988]

Parameter	SF		HLW Glass	
	Laboratory	Repository	Laboratory	Repository
S/V (cm ⁻¹)	~ 0.2	~ 1	20 ~ 200	~ 0.4
F/V (year ⁻¹)	0.3 ~ 0.6	10 ⁻⁴ ~ 10 ⁻²	0	10 ⁻³ ~ 10 ⁻¹

* Surface area did not take into account cracks. In Advanced Conceptual Design (ACD) (TRW Environmental Safety Systems, Inc., 1994), "V" and "S" values may be increased by less than a factor of 10.

The stability of colloidal suspension in the dispersion process has not been examined either. Nevertheless, there are indications that colloidal suspension may be stable under drip conditions. In drip tests, S/V values may be much larger than values in Table 4. However, pH values range from 3 to 8 for SF (Bates et al., 1995) and 5 to 8 for UO₂ (Wronkiewicz et al., 1992). Moreover, the residence time of leachates on or near SF is expected to be short. Groundwater may migrate to the far field as fast as the groundwater drips. Under this

circumstance, colloidal suspension can be stable. Similarly, the suspension of pseudo-colloids is also likely to be stable, considering ionic strength and pH only, as pseudo-colloids migrate in the far field.

The fate of colloids formed during the SF dissolution has not been fully investigated. People do not know what range of colloid sizes is subject to falling out of solution, for various ionic strengths or pHs of leachates; how groundwater replenishment affects the ionic strength or pH of leachates; and how the colloid settling affects the uncertainties of solubility limits. Environmental conditions are also uncertain. Leachates may be concentrated by salt precipitation (Walton, 1993) and man-made materials, or may be diluted by backfill. Clarification of these uncertainties will determine the importance of colloids as radionuclide source term.

Colloid transport is another important issue, along with colloid formation and colloidal suspension stability. Although the colloid transport issue is covered separately (Manaktala et al., 1995), a few comments on this issue will be made here, because no colloid transport means no colloid release, despite colloid formation and stability. Colloid transport is also complicated. In the laboratory column tests, German scientists observed more than 70-percent penetration of colloids through German host rocks (Kim et al., 1996). Because colloid transport mainly depends on surface charge properties, colloids may behave differently at the Yucca Mountain site. Additionally, formed colloids may redissolve to a certain extent and, consequently, be absorbed in host rocks. Nevertheless, current uncertainties about colloid behavior at the Yucca Mountain site do not preclude colloids in TSPA. For instance, formed colloids may still survive in the far field because the dissolution rate of secondary phases is very slow; the fracture flow of groundwater may allow all actinides to be transported, whether colloids redissolve or not. Also, redissolved colloids may form anionic complexes as a secondary source term (Kim, 1986).

7 RADIONUCLIDE RELEASE

Compliance with the overall repository system requirement necessitates consideration of all radionuclides, and involves both engineered barriers and natural barriers. In this section, radionuclide sources only from SF dissolution will be discussed. Emphases will be on radionuclides whose releases from SF dissolution are potentially significant in compliance assessments.

Radionuclides such as C-14, Se-79, Sr-90, Tc-99, I-129, and Cs-135 are highly soluble. They tend to be released to the leachate as the SF reaction is in progress (i.e., dissolution control). It is assumed that the effects of grain boundaries and rims disappear in a relatively short period. Then, rates of reprecipitation and convection by groundwater flow will represent the continuous release rates of these radionuclides. However, under near-static conditions, there is still a possibility that the concentrations of these radionuclides can reach solubility limits (Finn et al., 1994a; Wilson, 1990a,b). Nevertheless, the release rates of these radionuclides are approximated as the growth rates of the reprecipitated layers, as an upper bound. There are many evidences that these radionuclides may be released

continuously. For instance, (a) C-14 release was not retarded by leachate saturation in an open system of J-13 well water at 25 C (Ahn, 1994; Wilson, 1990a); (b) Tc-99, I-129, and Cs-135 were released continuously in J-13 well water at 25 and 85 C (Wilson, 1990a).

Following the postulates made in Section 3, the reprecipitated layer grows either linearly with time or by the time to the power of $1/n$ ($n \geq 2$). Using a constant dissolution rate in Table 1 and approximately 10 g/cm^3 of SF density (Wilson, 1990b), the SF matrix of approximately 0.03 mm at 25 C and approximately 0.2 mm at 85 C will dissolve within 10,000 years. If each grain is exposed and dissolved, the radionuclide release will be facilitated because of the small size of each grain. Considering (a) that the average size of SF particles is in the order of mm (Wilson, 1990b; Guenther et al., 1991) and (b) that the average grain size is in the order of $10 \mu\text{m}$ (Einziger et al., 1992; Forsyth and Wermer, 1992), the total radionuclide inventory can be released. In the real repository, SF may be subjected to drip conditions, man-made materials may be introduced, or backfill may be emplaced. Under these circumstances, groundwater chemistry may be altered (Walton, 1993; Finn et al., 1994a). As discussed in Section 3.1, it is not clear, though, whether these alterations of groundwater chemistry would significantly increase or decrease matrix dissolution rates. Nevertheless, the framework of Equations 1 to 5 will be bases to evaluate the SF dissolution process. For instance, the correlation made by Steward and Weed (1994), Gray et al. (1992a), and Gray and Wilson (1995) can serve to determine matrix dissolution rates in various altered groundwaters, for obtaining linear dissolution behavior with time.

For the law of the time to the $(-1/n)$ th power (Equation 6), the release of these radionuclides will be retarded. Assuming that Equation 6 represents the dissolution rates of SF matrices, a sample calculation was conducted for the long-term dissolution of the SF matrix. Transient data of flow-through tests (Gray, 1992) were taken. The data showed a gradual decrease of the dissolution rates of SF matrices as time elapses. Fitting the transient data to Equation 6 with $n=2$ determined "k" and "a" values. The numerically determined Equation 6 was extrapolated to a geological period. The extrapolated values of the amount of the dissolved SF matrix were far less (by many orders of magnitude) than those from the linear time law, Equation 1 or 2. Similar conclusions can be drawn if the data of gradually decreased releases of Sr-90 from LWR SF in Swedish groundwater at 20 to 25 C are extrapolated (Forsyth and Wermer, 1992). However, if diffusion in aqueous environments is rate limiting, the diffusion-limited kinetics may not be slower always than the linear dissolution kinetics.

Although the release of dissolution-controlled radionuclides can be assessed primarily using Equation 1 or 6, other factors need to be included. For instance, colloids formed through grain detachment (Wronkiewicz et al., 1992) will increase the release of these radionuclides.

Many other radionuclides important to HLW isolation are known to have relatively low solubilities. They include Pu-(239+240), Am-(241+243), U-234, Np-237, and Sn-126. Therefore, a small fraction of the inventory will be released by solubility limits and groundwater flow (i.e., solubility control). However, the small fraction of these radionuclides can contribute to the dose in the accessible environment significantly. The cumulative release of radionuclides from SF will be a product of activity per unit leachate volume, flow rate, number of containers for a container in a bore hole, and the time frame for compliance (e.g.,

10,000 years). Linear adjustments can be made for flow rates and number of containers. The contribution of actinide releases to the dose may be much higher than those of other radionuclide releases.

However, low solubilities also mean an easy formation of reprecipitates or colloids. If colloids are generated continuously and their suspension becomes stable, the radionuclide release from the waste form can be more, assuming that the released radionuclides from the waste form are transported instantaneously to the accessible environment, without retardation. The amount of colloids formed is time dependent. For instance, in Equation 7, " R_{nuc} " can be a nearly constant rate or a complicated time function. Quantitative assessments of colloids require time integrations. As time elapses, colloids may accumulate in the near field. Although unit equations for various processes have been developed here, numerical experiments of dynamic mass balance during geologic periods have not been undertaken. These numerical experiments will provide time-dependent amounts of radionuclides associated with colloids. Therefore, radionuclide releases associated with colloids are presented here in pCi/ml that are a dimension of equilibrium values. If colloids form on leachate replenishments quickly, and leachates maintain constant values of activities, this dimension certainly represents real release values. This approximation is likely to be valid in condensation and sorption processes. These constant values of activities are used to estimate radionuclide releases using flow rates, number of containers, and time (equivalent to what is done with solubility limits).

Radionuclide releases from drip tests are potentially significant. The Am-241 colloids released were approximately 10^5 pCi/ml, from SF drip tests in tuffaceous groundwater at 90 C (from a conversion in Table 2, Finn et al., 1994a). If fuel grains are detached, $(7 \text{ to } 1,500) \times 10^4$ pCi/ml of Pu-(239+240) and $(2 \text{ to } 360) \times 10^5$ pCi/ml of Am-241 are expected from drip tests with J-13 well water at 90 C (Wronkiewicz et al., 1992). These values from grain detachments (Table 3) were calculated using the radionuclide fractions in SF (Wilson, 1990a; Oversby, 1986). However, the grain detachments can be decreased as the reprecipitates cover the UO_2 tests. Results of SF tests and UO_2 tests show potentially high radioactivity, compared with those presumably through the nucleation process from immersion tests. From immersion tests, approximately 200 to 300 pCi/ml were reported in J-13 well water at 25 C without cumulative factors (Wilson, 1991, 1990b). At 85 C, less than 1 pCi/ml was reported under the same conditions (Wilson, 1990b). As mentioned in Section 5.2, the contribution of pseudo-colloids formed by sorption can be significant only when surface area effects increase values of sorption coefficient in more than an order of magnitude or when heterogeneous nucleation occurs. Besides radioactivity released, colloid sizes may be also important in the transport of colloids, after their release from SF. Current data have only three colloidal size groups: less than nm, in between nm and μm , and greater than μm .

As an important point in this section, the validity of the above experiments releasing large amounts of radionuclides is discussed. The flow rates used in drip tests were 2 to 80 ml/year, over the surface area of 20 to 500 cm^2 (Finn et al., 1994a; Wronkiewicz et al., 1992). These laboratory flow rates are normalized over the surface area, approximately $5 \times 10^5 \text{ cm}^2$, of an SF waste package without cracks. Then, the equivalent repository flow rates

will be 2 to 2,000 L/year-container. Realistic repository flow rates are about 0.1 to 10.0 L per year and per container in Yucca Mountain (U.S. Department of Energy, 1988). For ACD, these values can be higher.). Therefore, it is possible that drips evaporate instantaneously at very low flow rates. The evaporation is especially likely when the repository is open to air, or when backfill materials are emplaced. It is noted that the surface area under consideration may not be equal to the geometric surface area used in the above analysis. It should be the wet surface area that contributes to matrix dissolution. No details about the wet surface area are available.

Another important issue, the source term of radionuclides, in general, for the Yucca Mountain project will also be addressed. In addition to the above SF contribution, HLW glass also contributes to the source term. Traditionally, HLW glass was ignored in TSPA because the radionuclide inventory of HLW glass is only about 3 percent of the total inventory (an estimate from data of Oak Ridge National Laboratory, 1995). From the above analysis, the neglect of HLW glass vis-à-vis TSPA is likely to lead to inaccuracies in calculating radionuclide releases. For instance, in solubility control, the glass contribution for a specific radionuclide will be proportional to the fraction of HLW glass containers over the total number of containers. The percentage can be increased. Additionally, if colloids are formed more from HLW glass leaching, the HLW glass contribution can be increased further.

The last important point is to summarize how the assessments made in this report may be used for evaluating SF. This report evaluated the principal assumptions involved in SF dissolution and colloid formation, numerical estimates of radionuclide releases, mathematical models, and many potential physical processes. In TSPA, the obtained quantitative values of radionuclide releases may be used in the calculations of source term. Numerical values (e.g., g/day-cm² or pCi/ml) in Section 3 or 7 will be inputs to the system code as source terms; and Equations 1, 2, 6, 7, 8, and 10 are more rigorous and accurate expressions and may be adopted as alternative source terms. All known assumptions and potential physical processes will be used as appropriate in determining various cases (scenarios) in the calculations. For instance, in dissolution-controlled radionuclides, Section 3.1 discusses the kinetics of linear time law, whereas Section 3.2 discusses the kinetics of nonlinear time law. In the colloid formation, various kinetics are also discussed: nucleation process (Section 4.4), dispersion process (Section 5.1), and pseudo-colloid formation (Section 5.2). Additionally, overall knowledge obtained in producing this report and responding to comments is a detailed staff's basis for precicensing reviews. For instance, Sections 2 and 3 are the staff's current view on dissolution-controlled radionuclides; Sections 4 and 5 are that on colloid formation; and Section 6 is that on the stability of colloidal suspension near SF.

8 CONCLUSIONS

The present work has evaluated continuous dissolution and colloid formation in SF performance. The true dissolution rate of the SF matrix is important in determining the release rates of highly soluble or gaseous radionuclides, such as C-14, Cl-36, Tc-99, I-129, and Cs-135. For low-solubility radionuclides, such as Pu-(239+240) and Am-(241+243),

colloid formation is potentially the major vector for their releases. The key question is whether matrix dissolution or colloid formation continues under long-term repository conditions. Uncertainties associated with matrix dissolution and colloid formation are identified to answer these questions, in part.

This report has summarized various observations, regarding the unprotective nature of the reprecipitated layer formed during SF dissolution. Causes for the unprotectiveness include radiation, stress, microbial activities, the inherent nature of secondary phases, paragenesis, and environmental variations. More quantitatively, the true dissolution behavior of the matrix was analyzed, using data on dissolution, reprecipitation, and convection from semi-static, flow-through, and electrochemical tests. The results suggest that continuous dissolution of the matrix cannot be ruled out, unless diffusion or radiation plays an important role. The continuous matrix dissolution (primarily, linear time law) may result in a large amount of radionuclide source in TSPA. On the other hand, the alternative mechanism (primarily, nonlinear time law) is likely to lead to significant radionuclide retention.

Concerning the release of low-solubility radionuclides, the work has assessed colloid formation through condensation, dispersion, and sorption. This is an extended macroscopic view of traditional chemical bonding. Immersion test results suggest the nucleation process as the condensation process for colloid formation; however, because the formation may be transitory, confirmation is necessary, for this hypothesis, during long-term SF dissolution. The analysis of the nucleation process considers an overall thermodynamic energetics, supplementing traditional ionic (or molecular) condensation. Colloids or secondary phases do not nucleate below a critical leachate concentration above the solubility limit, and colloids are not easily filtered. Therefore, traditional solubility limits may represent supersaturated values plus unfiltered colloids, rather than true equilibrium values.

It is believed that the dispersion process potentially results in many more radionuclide releases than those from the condensation process. Simple reversible sorption of radionuclides on groundwater colloids may not contribute significant radionuclide releases. However, significant radionuclide releases as pseudo-colloids are expected (a) if radionuclides nucleate and grow on groundwater colloids, (b) if radionuclides nucleate radiocolloids and are adsorbed on groundwater colloids, or (c) if surface effects are important in sorption. It is also believed that the overall contribution of all these types of colloids to the source term can be significant, especially in compliance assessments with dose-based rules. Nevertheless, many judgments made here come from indirect inferences from experimental observations. Therefore, future work needs to clarify these uncertainties, for proper assessments of SF performances.

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11. ABSTRACT (200 words or less)

This report evaluates continuous dissolution and colloid formation during spent-fuel performance under repository conditions in high-level waste disposal. Various observations suggest that reprecipitated layers formed on spent-fuel surfaces may not be protective. This situation may lead to continuous dissolution of highly soluble radionuclides such as C-14, Cl-36, Tc-99, I-129, and Cs-135. However, the diffusion limits of various species involved may retard dissolution significantly. For low-solubility actinides such as Pu-(239+240) or Am-(241+243), various processes regarding colloid formation have been analyzed. The processes analyzed are condensation, dispersion, and sorption. Colloid formation may lead to significant releases of low-solubility actinides. However, because there are only limited data available on matrix dissolution, colloid formation, and solubility limits, many uncertainties still exist. These uncertainties must be addressed before the significance of radionuclide releases can be determined.

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