

Environmental Management Science Program

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Modeling of Diffusion of Plutonium in Other Metals and of Gaseous Species in Plutonium-Based Systems

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Research Objective

The problem being addressed is to establish standards for storage conditions for containers (e.g. stainless steel containers) meant to hold nuclear waste for long periods of time, e.g. fifty years, such as to ensure the integrity of the containers without being excessively conservative, i.e., being unnecessarily costly.

Allowable storage temperature is an important parameter for the standards. Diffusion processes are central to certain processes that initiate corrosion of the containers or that lead to the release of gases increasing pressure that can rupture the container. The scientific goals of this project are: (1) to predict diffusion constants on an ab initio basis, i.e. diffusion distances in specified time at specified temperature, for atomic species from plutonium-based waste materials into storage container materials such as stainless steel or vice versa, (2) to predict the time development at specified temperature of complex diffusion processes in plutonium-based oxide type waste materials in the presence of water vapor such that gases may be released within a container. This predictive ability will help to provide information relevant to setting standards for waste container vessels and storage conditions.

Research Progress and Implications

This project was initiated on September 15, 1997, so that this summary reports progress after about 2/3 of the first year of a three-year project. The diffusion processes of interest will be modeled using kinetic Monte Carlo techniques. The use of this technique in an abinitio-based calculation involves generating atomistic potentials providing the interactions between the atomic species of interest in the solid-state geometry being treated. For systems containing plutonium, we anticipate that the key technical difficulty will be to generate atomistic potentials of sufficient physical accuracy to capture the nature of the interactions involving plutonium in the diffusion processes.

Our initial effort is on the first of the two scientific goals listed above, predicting interfacial diffusion between two metallic systems, one of which is plutonium-based waste, the other of which is a container material such as stainless steel. The necessary modeling involves three steps: (1) ab initio generation of a total energy data base from which atomistic potentials can be extracted, (2) extracting those atomistic potentials in a form tractable for use in the dynamic simulation and sufficiently sophisticated to contain the necessary physics, (3) using these atomistic potentials in a kinetic Monte Carlo calculation to obtain the desired diffusion information.

Initially, we have verified our ability to carry out this procedure on 3d-electron transition metal systems. We have generated our data base by use of our full-potential linear-combination of muffin-tin-orbitals (LMTO) local density approximation (LDA) total energy capabilities; extracted atomistic potentials by use of our previously developed capabilities, already used in such applications as surface relaxation and thermal expansion calculations; and used these potentials in a kinetic Monte Carlo simulation. We have obtained results in excellent agreement with experiment and with other calculations in the literature.

For systems containing plutonium, we anticipate that the enabling steps in the three-step procedure described above are the first and second ones, generating the ab initio data base and extracting the atomistic potentials. We anticipate this because of the well-known limitations of the LDA, in adequately capturing the total energy-density relationship in plutonium. To the best of our knowledge, among all materials to which LDA has been applied, plutonium is the only one for which LDA

apparently fails to yield the correct volume within at worst 10% for a structure which is present in the experimentally observed thermal behavior. Typically LDA gives a slightly overbonded prediction of volume, which varies between a volume too low by one or two percent or less at best and eight or nine percent at worst. For plutonium, while a state-of-the-art LDA calculation predicts a volume for the low-temperature monoclinic alpha phase within the usual error bounds, such a calculation for the higher-temperature cubic close packed (fcc) delta phase gives an overbonded volume that is about 30% too low. The legacy wastes of interest are for delta structure materials, so we will have to address this issue. Results, not yet published, from ad hoc refinements of LDA such as LDA+U or LDA-SIC (self interaction corrected) provide a volume for fcc Pu within the usual acceptable error bounds with respect to experiment. These calculations use a different effective potential to treat one-electron dynamics than conventional LDA. This is designed to provide a better treatment of local environment effects for the f-electrons near a Pu nucleus. We do have established LDA+U and LDA-SIC capabilities, and we anticipate having to use such a calculation to generate our data base. We also anticipate the need to use a three-term potential, containing a directional (covalent) term as well as density (embedding) and pair terms. If necessary, we have a detailed working plan for using two-electron dynamics to calculate total energies. We will use such a calculation only if the refinements of LDA fail when our predictions are compared to validation experiments to be carried out at Los Alamos National Laboratory.

As part of our systematic approach to this problem of generating adequate atomistic potentials involving plutonium, we are engaged at present in first calculating the diffusion properties of Pu in a Ni matrix. This is probably the simplest meaningful situation that can be compared to a controlled validation experiment to be conducted at Los Alamos. The calculations are being done for an fcc structure. This initial calculation involves only the density (one-body) and pair terms in the atomistic potential. To obtain the necessary Ni-Pu interactions as well as the purely Pu and Ni effects, we have calculated LDA total energy changes with uniform expansion and fixed volume distortion for a model NiPu intermetallic as well as for pure Pu and Ni. The equilibrium fcc Pu volume is 17% less than experiment, and the muffin-tin spheres occupy about 65% of the total volume. For the model NiPu intermetallic, the muffin-tin radii were consistently chosen such that the spherically averaged potentials at the muffin-tin radii were approximately equal. The absolute values of the total energy were slightly dependent on the choice of muffin-tin radii, although the equilibrium properties such as volume appear to be stable. We have extracted the atomistic potentials using the technique we have previously used for transition metals. The atomistic potentials for this initial Pu in Ni model situation are now being used to calculate the migration energies and attempt frequencies, and their reliability is being analyzed.

Planned Activities

We will compare to the results for the initial Pu-Ni system to validation experiments at Los Alamos if available. In any case we will systematically proceed to improve the data base and the form used for the atomistic potentials. We will then go on to simulations involving fcc iron containing additives corresponding to stainless steel of interest. We will simulate the diffusion in both directions at the interface between the plutonium-based waste and the metallic container material. We anticipate obtaining meaningful results for the Pu-Ni model system early in the second year and meaningful results for stainless steel interfacing Pu-based waste by the end of the second year. We will then go on to model the oxide-type waste systems.

Other Access To Information

We have established a web page (<http://compmat.phys.wvu.edu/Pu-EMSP.html>) where we will post our progress. We anticipate submitting our first journal publications by the end of the first year or early in the second year.