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INTEGRATED WASTE PACKAGE EXPERIMENTS PROJECT PLAN

TEST PLAN FOR SUBTASK 3.2: GROWTH RATES AND STABILITY OF THICK-OXIDE FILMS IN CANDIDATE COPPER AND COPPER-BASED ALLOYS FOR HLW CONTAINERS

(Intermediate Milestone No. 20-3704-043-201)

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OBJECTIVE

The objectives of this subtask are to study the rates of oxide-film growth in the candidate copper and copper-based alloys for HLW containers, and to determine the critical thickness for spallation of oxide to occur as a function of specimen configuration/metal-oxide interface stresses.

SCOPE

The experimental activities will involve the growth of thick oxide-films on specimens of various configurations under a range of temperatures, exposure times, and environments representative of conditions which may occur in a geologic repository. The intent is to determine if thick oxide-films on copper and copper-alloys are subject to spallation (due to debonding at the metal-oxide interface or fracturing in the oxide layer) under such conditions. If spallation occurs, the critical oxide thicknesses at which it occurs will be quantified for the three alloys under investigation. Relationships between the oxide growth/spallation and the specimen configuration, material, test environment, and exposure times will be studied.

DESCRIPTION OF EXPERIMENTAL TESTS

Test Specimen Materials:

The samples will be fabricated from the same heats of materials being used for the other experimental investigations under the IWPE program. All three copper-based alloys will be included in the test matrix, viz. Oxygen-free High Purity Copper Grade CDA-102, Aluminum-Bronze Alloy Grade CDA-613, and Cupro-Nickel Alloy Grade CDA-715.

Specimen Configuration:

Experiments will involve exposing cylindrical samples of various configurations (examples are shown in the attached figures) to gaseous and liquid environments for various lengths of time and evaluating the surface oxide film morphology and characteristics. Depending upon the configuration of the test specimen, i.e., convex or concave surface, the oxides that develop will have compressive or tensile stresses. The magnitude of the stresses is expected to increase with increasing oxide thickness. The majority of the specimens in the test matrix will be stress-relief annealed and mechanically/chemically polished prior to testing. A limited number of test specimens in the as-machined condition will be included to study the influence of cold-work introduced during the specimen fabrication process. Also, a few flat (plate) specimens will be tested in as-received condition.

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Test Matrix:

It is estimated that about 100 samples will be used; a majority of them will be cylindrical in shape as shown in Figure 1. The aspect ratio of the cylindrical samples will be maintained between 5 and 10, depending on the diameter of the sample. Limited samples of special configurations, approximately 15 in number, will be included in the test matrix to provide different levels of tensile or compressive stresses in the oxide film within a single specimen. For example, (a) of Figure 2 shows a specimen configuration which would lead to progressively increasing compressive stresses from the base to the apex of the conical specimen. On the other hand, a hollow specimen, as shown in (b) of Figure 2, is expected to have uniform compressive stresses in the oxide film on the outer surface, with progressively increasing tensile stresses from the base to the apex, of the inside surface of the 'hollow' conical specimen. In Figure 3, (a) and (b) show other specimen configurations that would result in stresses similar in nature to those shown in (a) and (b) of Figure 2, respectively, i.e., compressive or tensile, but the changes in magnitude along the length of the specimen will be abrupt (step changes rather than gradual).

Test Environment and Exposure Times:

Tests will be conducted in air, water vapor, and liquid environments at temperatures in the range of approximately 95°C to 350°C, in a furnace or an autoclave, as appropriate. Oxidation tests in controlled humidity air will be conducted at 350°C, 250°C, and 150°C. The water vapor tests will be conducted at 150°C in an autoclave. The aqueous environment tests will be conducted initially at 95°C, which may be increased if the rate of oxide growth is too slow. Oxide film growth times will range from 1 to 15,000 hours, with visual observations and weight measurements at approximate intervals of 1, 10, 50, 100, 500, 750, 1000, 2000, 5000, 7500, 10,000, and 15,000 hours. Specimens will be exposed to steady (in the first phase of the subtask) as well as changing environments (in the second phase of the subtask), e.g., specimens with pre-film grown in air will be exposed to water vapor environment followed by aerated-aqueous environment. This sequence of exposures is considered an appropriate scenario for the unsaturated geological repository. In the initial series of tests to be conducted under this test plan, only deionized water will be used for the vapor and aqueous phases. In a later series, aqueous environment, representative of the geological repository or the surroundings (such as from a J-13 well) may be used. The aqueous phase environment, in later series tests, is expected to include bicarbonate, chloride, and sulfate ions. The exact ionic species and their composition will be provided in the test matrix that will be submitted to the NRC prior to initiation of such experiments. Should exposure of the test samples in deionized water exhibit very slow oxide growth rates, the test matrix will be modified to include the use of a more aggressive aqueous environment.

Post-Test Evaluation:

The specimens will be examined visually and at low-magnification using optical and scanning electron microscopy (SEM) for characterizing the surface oxide morphology and any unusual differences between the oxides on different test materials, e.g., nodular growth, patchy discoloration, etc. Particular attention will be paid to the oxide-film morphology on alloy CDA-613, because of the finely dispersed iron-rich second phase particles present in the wrought material. In addition, all specimens will be weighed during each observation period to estimate the surface oxide thickness. Selected samples will be cross-sectioned and metallurgically examined to verify the thicknesses and the uniformity of oxide over the sample surface, and to characterize (on microscopic scale) the degradation front in advance of the metal-oxide interface, e.g., extended grain boundary oxidation, etc. Correlations, if any, observed between the stresses at the metal-oxide interface at various exposure times and the thickness, extent of spallation, and morphology and characteristics of the oxide (e.g., micro- or macro-fissuring and fracturing) will be recorded. Estimates of the stresses in the oxide layer will be obtained from the specimen configuration and the thickness of the oxide. If extensive spallation is observed, the specimens may show reduction in weight (instead of weight gains) with increasing exposures. Under these circumstances, oxide thicknesses will be experimentally measured via destructive examinations of the test samples. Selected samples at different exposure intervals will be used to determine the stoichiometry of the compounds in the surface oxides using x-ray diffraction techniques. In addition, selected samples will be examined, using Auger spectroscopy, for depth profiling of alloying elements, mainly nickel in alloy CDA-715 and aluminum and iron in alloy CDA-613.

The specimens exposed to gaseous and aqueous (vapor and liquid) environments will be examined at each examination interval listed above. Specimens exposed to air will be weighed at each interval listed earlier, while weighing of specimens exposed to water vapor and aqueous environment will commence after at least 50 days exposure. Metallographic examination of selected samples, for verification of oxide thicknesses, structural characterization, and identification stoichiometry of the oxide, will commence after at least 100 days exposure. Depth profiling, principally for nickel, aluminum, and iron, using a sputtering technique will be undertaken when sufficient oxide thickness has developed. The time intervals for the three exposure environments may be quite different to reach comparable oxide thickness. There may also be significant difference in the oxide growth rates of the three materials in the matrix. Therefore, the exposure time of the specimens for depth profiling will be decided later.

Analyses of the Test Data:

The test data will be analyzed to determine oxide growth rate as a function of the specimen configuration, material, test temperature, environment, exposure time, and the influence of the sequence in which multilayered pre-film is developed on the test specimen prior to extended exposure in a single-phase/steady state environment (to be undertaken in the second phase of this subtask). The critical oxide thickness(es) at which spallation initiates will also be reported for the three materials.

If the oxide growth and spallation phenomenon is cyclic in nature, it would be necessary to obtain understanding of the shape(s), and frequency and periodicity of the oxide-growth/spallation cycle(s) in order to evaluate the likely service-life of the container. Attached Figure 4 shows schematically how information related to the cyclic oxide-growth/spallation phenomenon could be used is estimating the container-life. If the time t_3 is greater than the minimum acceptable service-life, the container material/design would be acceptable in spite of the periodic spallation of its protective oxide. The long-term goals are to obtain quantitative oxide growth and spallation data on the candidate copper-based alloys for the HLW containers, which could be used in developing predictive models for evaluating the selection of the material and design for the HLW container. However, the development of predictive models would require generation of substantially more data than what is currently planned under this subtask. Therefore, such an exercise is considered outside the scope of this subtask, but may be undertaken as an extension of the subtask at a later date.

PERIOD OF PERFORMANCE:

Upon approval of this test plan, specimen preparation and testing will be initiated. It is expected that preliminary results of the investigation will be compiled and communicated to the NRC as an intermediate milestone deliverable [Intermediate Milestone #3203] by November 26, 1991, and that a second letter report on the subtask will be completed and submitted to the NRC by December 21, 1992, as another intermediate milestone deliverable [Intermediate Milestone #3205]. The schedule for the deliverables is documented in the IWPE Project Plan, Rev. 3. The progress on this subtask will also be reported in the CNWRA Monthly Report to the NRC and the CNWRA Quarterly and Annual Research Reports. The results of significant findings will be presented at technical conferences, published in scientific journals, and submitted to the NRC for release in the form of NUREG reports, as appropriate.

COST AND SCHEDULE:

This Test Plan can be executed consistent with the cost and schedule information provided in the current IWPE Project Plan. No contractual modifications are judged to be necessary.

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NRC Project Officer

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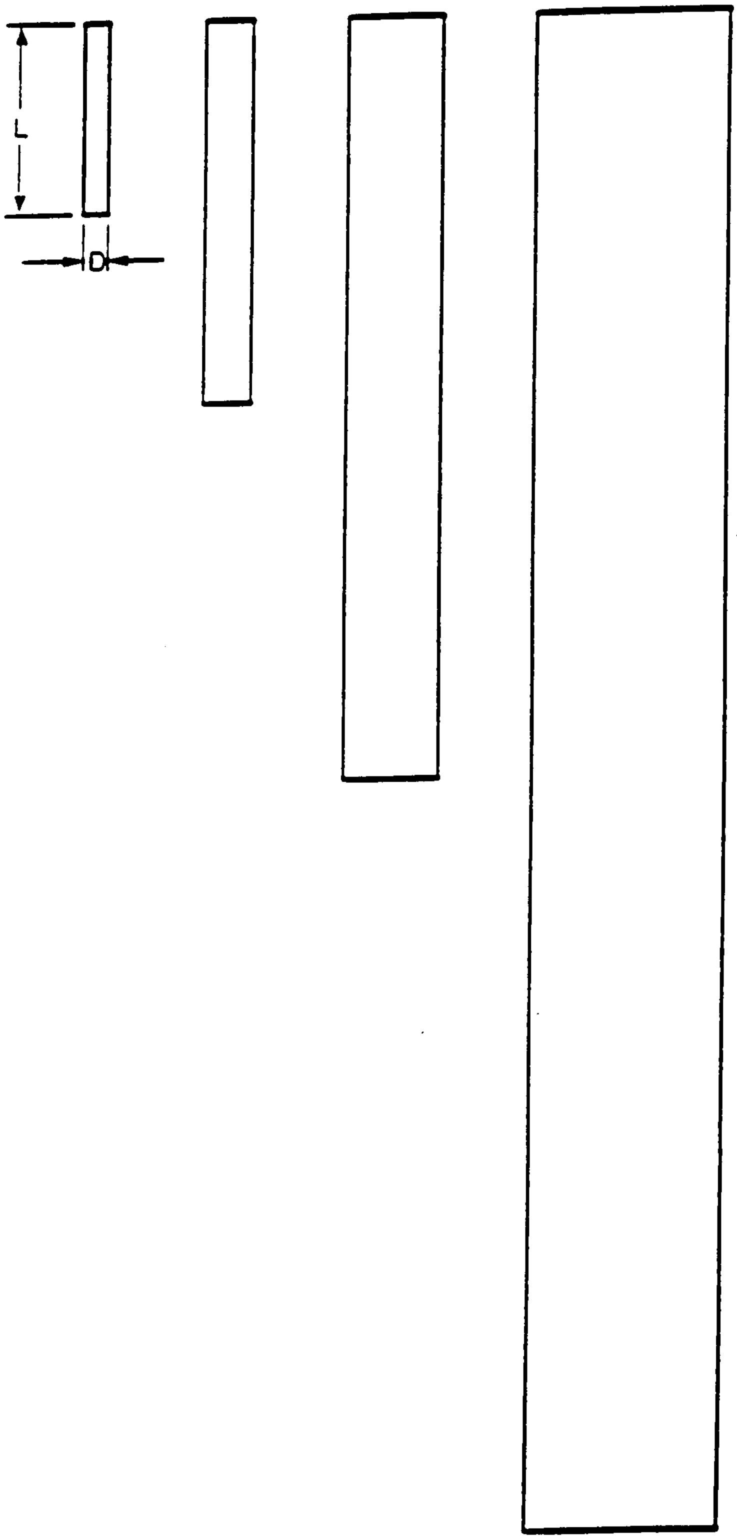

Figure 1. Test Specimen Configuration [Cylindrical Specimens]

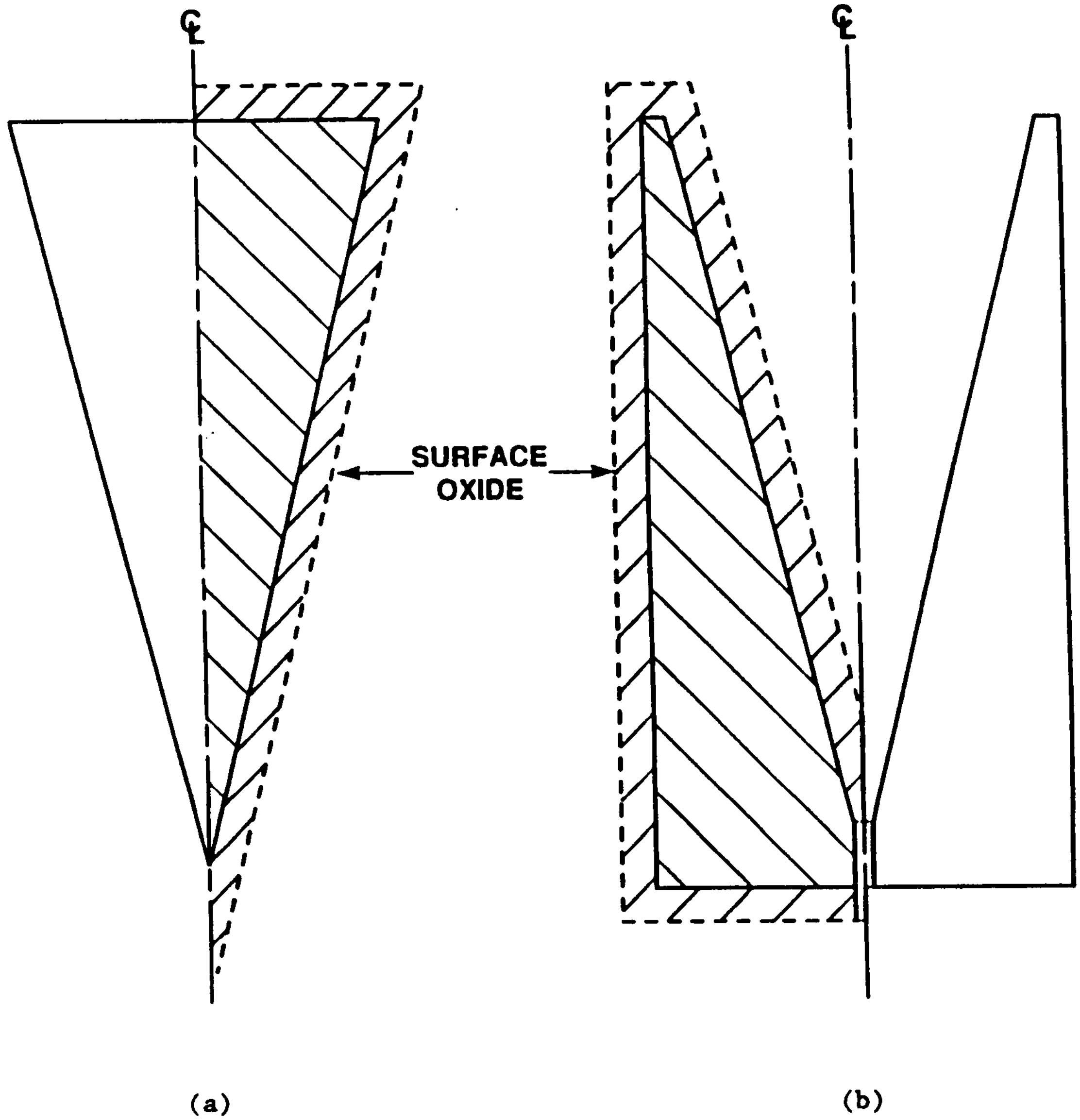

Figure 2. Test Specimen Configuration [Conical Specimens]
(a) Solid Specimen, (b) Hollow Specimen

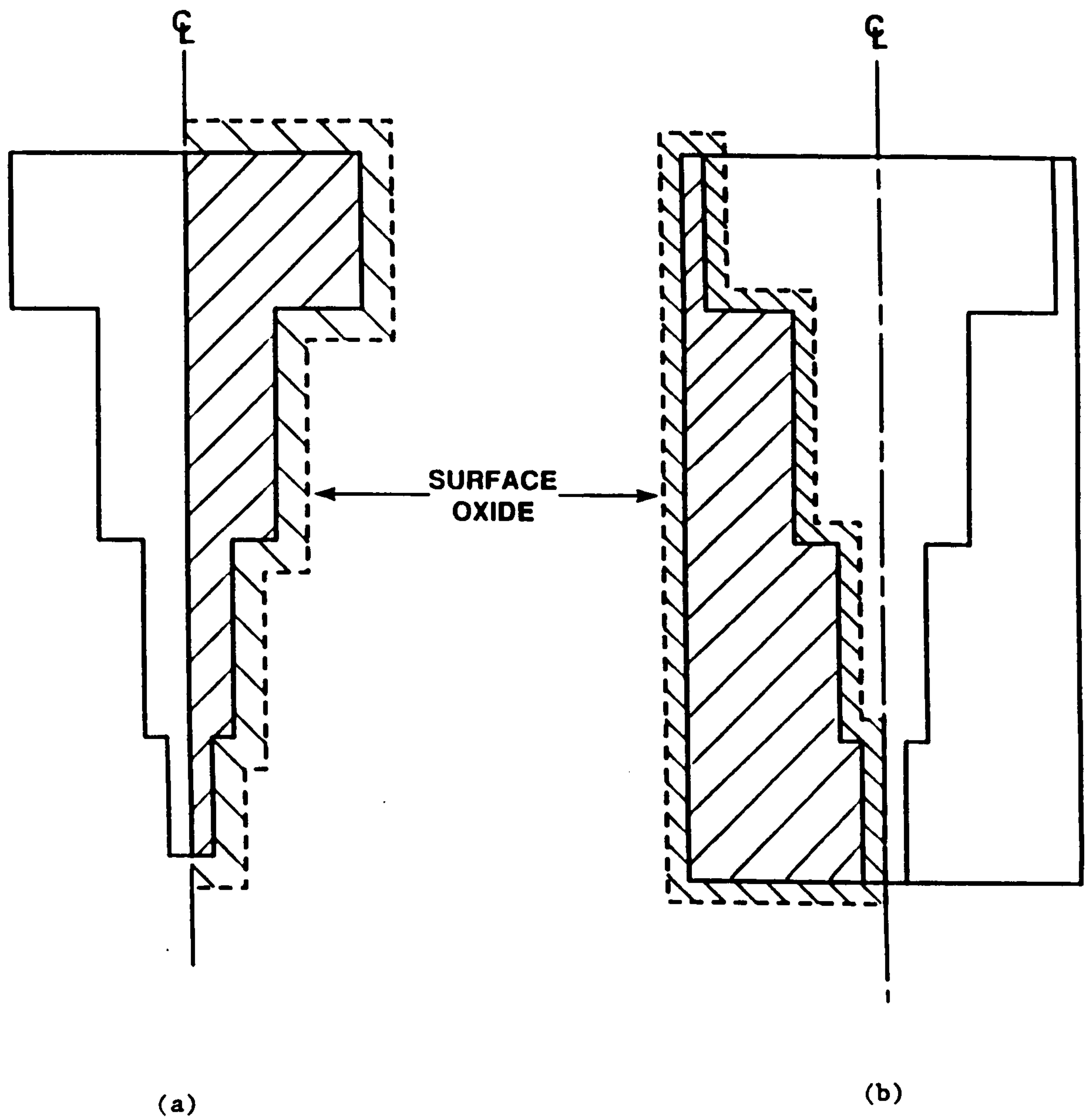

Figure 3. Test Specimen Configuration [Stepped Specimens]
(a) Solid Specimen, (b) Hollow Specimen

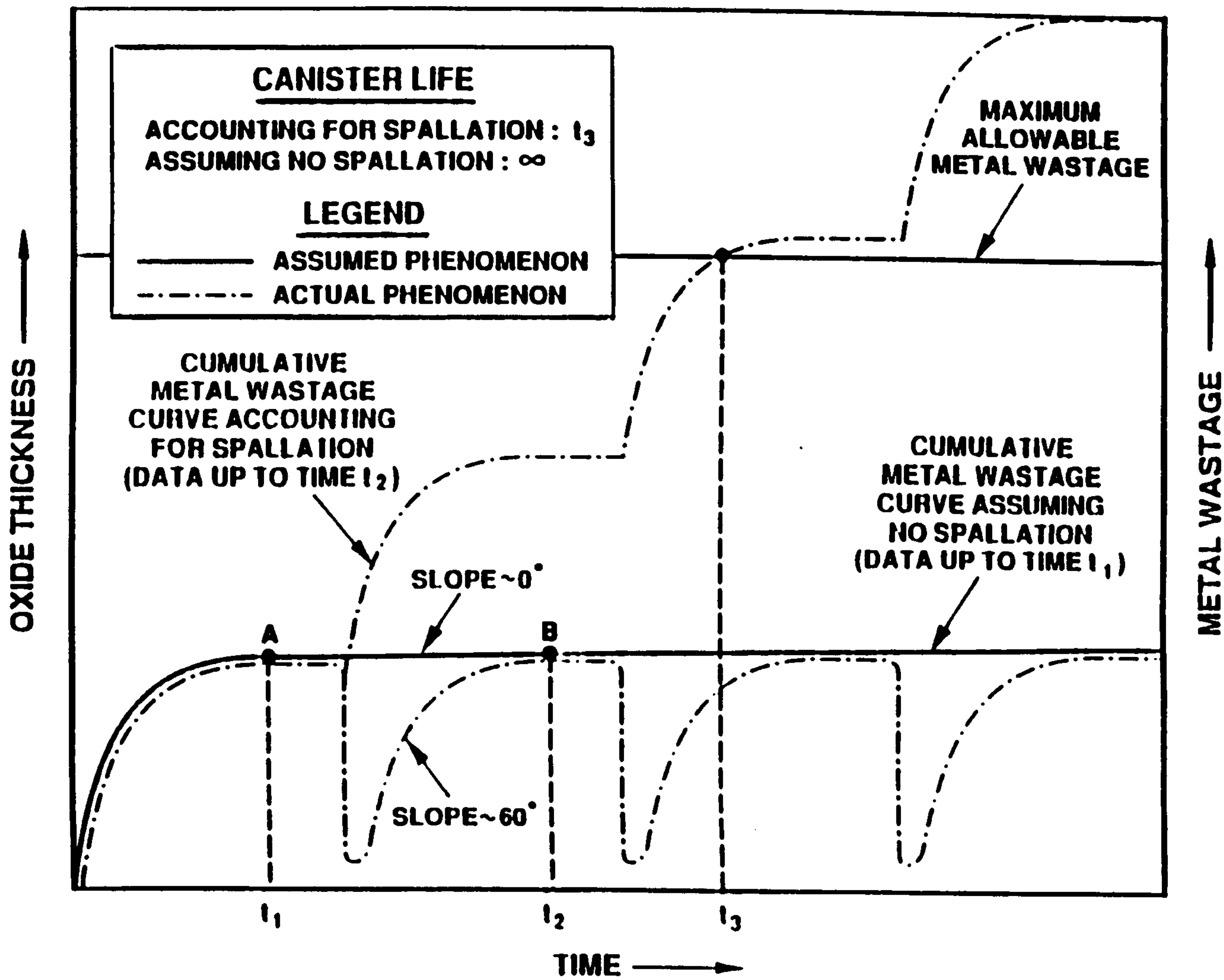

Figure 4. Schematic of Thick Oxide Growth, Spallation, and Regeneration