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Session III - Leaching Science

Organic Leaching Science - Dr. William Rixey

William Rixey, Associate Professor, Department of Civil and Environmental, Engineering, University of Houston, Houston, TX, presented a discussion of the state of organic leaching science, developed for the American Petroleum Institute (API). A copy of his presentation materials (in pdf format) is available through the following link: rixey.pdf.

Dr. Rixey described the key issues that need to be addressed in the field of leaching, including the role of batch tests for describing leaching for organic compounds and incorporating factors such as presence of residual non-aqueous phase liquids (NAPL), kinetics, and various loss processes.

He described the issues raised by the EPA Science Advisory Board (SAB) with respect to the current leaching tests, including:

1. Liquid/solid ratio
2. Kinetics
3. pH
4. Colloid/emulsion formation/oily phase
5. Particle size reduction
6. Volatile losses
7. Interactions with other wastes

and noted that his presentation addressed the liquid/solid ratio, kinetics, and the presence of an oily phase. (For more information on the EPA SAB report on leaching see the presentation by Murarka. [murarka1.pdf])

Dr. Rixey compared the use of batch leaching and fixed-bed leaching on oily wastes. He noted that batch tests can be used to obtain appropriate leaching parameters such as C_{Lo}, the leachate concentration at a leachate/waste ratio extrapolated to zero, and K_w, the partition coefficient. One approach requires either a batch leaching test and an analysis of the waste ("totals" analysis) or multiple batch leaching tests. An alternative is to estimate K_w and C_{Lo} from the oil content of the waste or results for total petroleum hydrocarbons (TPH) and the application of Raoult's Law. Dr. Rixey described these options in detail, and described the derivation of a theoretical description of fixed-bed leaching under equilibrium conditions.

Dr. Rixey concluded that a simple batch test can be used to describe more realistic leaching if one takes into consideration that batch tests work when equilibrium leaching conditions apply, and in the absence of other loss processes, e.g., volatilization and degradation.

The second portion of Dr. Rixey's presentation addressed the effect of non-aqueous phase liquids (NAPL) on partitioning. He noted that in equilibrium partitioning among air, water, and soil, the effect of NAPL is accounted for in the measured values of K_w, resulting is increased equilibrium partitioning. Dr. Rixey presented data for the observed and theoretical K_w values for benzene, toluene, ethyl benzene, *m*-xylene, *p*-xylene, and naphthalene in tank bottom sludge, hydro-refining catalyst, and soil. He concluded that residual NAPL in oily wastes significantly increases K_w compared with K_d for sorption only. Based on a comparison of theoretical partition coefficients and those measured in 48-hour batch experiments, Raoult's law is a useful measure of equilibrium behavior and can be used to indicate the presence or colloids/emulsions, and sequestration (kinetics).

Dr. Rixey's conclusions regarding residual NAPL are that it can have a significant impact on the relationship between the concentration in the leachate (C_L) and the total concentration in the waste (C_T). He found that Raoult's Law can be used to assess whether equilibrium conditions exist in batch tests, and it is useful especially for oily wastes which tend to have high K_w and that Raoult's Law can also be useful for estimating leaching in the absence of leach tests.

In order to determine when rate limitations exist, Dr. Rixey recommended comparing actual leaching results with predicted leaching, using batch tests at a fixed L/S ratio, as an initial assessment. The alternative is to use more definitive rate of release (ROR) tests. He found that kinetics can be accounted for using rate of release (ROR) tests, such as modified batch, fixed-bed and other rate of release approaches and that rate constants can then be compared with those for other loss processes using an appropriate modeling framework.

Dr. Rixey pointed to aqueous modified batch methods and aqueous fixed-bed methods as examples of current ROR methods. He noted that several alterative ROR methods are being developed, including:

8. Supercritical Fluid Extraction (SFE)
9. Accelerated Solvent Extraction (ASE)
10. Thermal Desorption Mass Spectrometry (TDMS)

Dr. Rixey presented an example of slow release that involved the fixed-bed desorption of benzene from an aged silty loam soil. He presented data for k_2, the slow rate constant, and F, the available fraction of NAPL in the soil, that were derived from a laboratory-spiked silty loam soil, using both a one-site equilibrium model and a two-site rate-limited model conducted over a 60-day period. He indicated that slow release is important relative to leaching and also relative to biodegradation or volatilization under two sets of conditions that can be described in terms of k_2 and F.

Based on his work, Dr. Rixey concluded that:

11. Simple batch tests are useful for describing leaching for organic compounds from oily wastes, especially if equilibrium conditions occur.

12. Separate test methods should be used to determine kinetics when needed.
13. Estimation methods/separate tests should be used to account for other loss processes, e.g., volatilization and degradation.
14. Appropriate tests should reflect a tiered approach to waste assessment.

Among the other issues that must be considered are:

15. NAPL migration, volatilization, degradation.
16. Lab-to-field translation.
17. Field-scale heterogeneities:
    - soil type
    - contaminant distribution
    - paths for various transport processes, e.g., leaching, volatilization, etc.

- Sampling considerations.
- Modeling considerations.
- Other specific test-related issues.

During the question and answer period, David Friedman (EPA) asked how one could use the available information with the current regulations. Dr. Rixey replied that researchers need to work together to develop better descriptions of leaching and need some flexibility.