

CONF-821053--3

Statement on

CONF-821053--3

SOLUTION PREPARATION

DE83 014285

by

Martin G. Seitz
Argonne National Laboratory
Argonne, Illinois 60439

for the

Workshop on Standardization of Methods

United States-Federal Republic of Germany
Cooperative Agreement

Reviewed in this statement are methods of preparing solutions to be used in laboratory experiments to examine technical issues related to the safe disposal of nuclear waste from power generation. Each approach currently used to prepare solutions has advantages and any one approach may be preferred over the others in particular situations, depending upon the goals of the experimental program. These advantages are highlighted herein for three approaches to solution preparation that are currently used most in studies of nuclear waste disposal. Discussion of the disadvantages of each approach is presented to help a user select a preparation method for his particular studies.

Also presented in this statement are general observations regarding solution preparation. These observations are used as examples of the types of concerns that need to be addressed regarding solution preparation. As shown by these examples, prior to experimentation or chemical analyses, laboratory techniques based on scientific knowledge of solutions can be applied to solutions, often resulting in great improvement in the usefulness of results.

MASTER

APP

Approaches to Solution Preparation

The approach selected to prepare solution for use in an experimental program should depend on the goal of the experimental study. Many laboratory procedures are used in the formulation of these approaches. Examples of these procedures are 1) distillation of water under vacuum to remove dissolved gases, 2) filtration to remove or to concentrate suspended matter in water, 3) dialysis to remove or to concentrate organic constituents in water, 4) centrifugation, 5) addition of chemicals to control pH or oxidation potential, 6) introduction of electrode potentials to control oxidation potential, and 7) modification of isotopic composition to monitor physical or chemical behavior. These diverse procedures give an experimenter flexibility that is fundamental to the successful study of questions related to nuclear waste disposal. The diversity should be nurtured; recommendation of preferred procedures will, therefore, be avoided in this discussion. Three approaches to solution preparation most often used in laboratory studies of nuclear waste disposal are listed in Table 1 and subsequently discussed further.

Table 1. Three Approaches to Solution Preparation Used in Laboratory Studies of Nuclear Waste Disposal.

Approach
1. Prepare Natural Groundwater for Experimentation
2. Mix Chemicals to Give Desired Solution
3. Mix Chemicals to Form Solution, then React this Solution with Rock

Groundwater

The first approach to solution preparation discussed here is to sample groundwater directly from the geologic site at which the experimental work is directed. This may be simple for surface waters or for waters in aquifers that are accessed by good-quality bore holes and where equipment such as packers and down hole pumps are available to obtain the desired sample. Without these facilities, considerable expense could be incurred to obtain the groundwater. This approach may not always produce a representative sample since contaminants such as drilling fluids may be mixed with groundwater obtained from bore holes.

Preparation of the groundwater for experiments may be geared to preserving the chemical and physical properties of the sampled water. This preparation, for example, could require the groundwater to be isolated from air and to be maintained at the temperature of the natural environment.

Alternatively, the preparation of the groundwater may include specific laboratory procedures such as the filtering of suspended matter or the regulation of dissolved gases. These procedures could be performed to address, experimentally, the relationship of components of the water (dissolved solids, suspended matter, dissolved gases) to radionuclide behavior.

A major disadvantage with the use of groundwater is that the solution composition cannot readily be treated as an experimental variable. Only experimental data for a particular groundwater composition is obtained. In practice, a range of compositions often has to be considered to assess the safety of nuclear waste disposal of one site. For example, groundwater

may change in composition by reacting with repository components. This altered groundwater will not exist as naturally-occurring groundwater.

Mix Chemicals to Obtain Desired Solution Composition

The second approach to solution preparation is to mix chemicals to produce the desired solution. An advantage is that solution compositions are controlled in the laboratory. Also, with accurate specifications, the solutions may be reproduced by different laboratories. An additional advantage is that phenomena can be studied for a range of solution compositions that could be expected for a repository site.

Chemicals used to prepare solutions representative of most groundwaters are listed in Table 2.

A disadvantage to this approach is that the solution would only approximate, in the detailed analyses, actual groundwater composition. For example, trace constituents added as contaminants of the major chemicals may not be present in the proportions that they would be in groundwater.

As another example, organic constituents of groundwater can only be approximated by chemical additions to solutions. Fulvic and humic acids, the major organic components of groundwaters, can be added to solutions at concentrations observed in groundwater. However, the properties of the acids depend on their origin, and upon the purification and concentration methods they experienced during preparation. A complete replication of all organic acids that occur in a groundwater would not be feasible.

Filterable material is often a natural and important constituent of groundwaters. Filterable material in detectable quantities can also be

Table 2. Reagents Used as Constituents of Solutions. The reagents supply the major inorganic constituents found in most groundwaters.

HCl	H ₄ SiO ₄	Na ₂ SiO ₃ ·9H ₂ O
NaCl	Na ₂ CO ₃	CaSO ₄ ·2H ₂ O
KCl	NaHCO ₃	MgSO ₄ ·7H ₂ O
CaCl ₂	NaF	Na ₂ B ₄ O ₇ ·10H ₂ O
MgCl ₂	Na ₂ SO ₄	NaOH
SrCl ₂	K ₂ SO ₄	

introduced into laboratory-prepared solutions as the insoluble component of chemical reagents, the likelihood that the insoluble components in reagents are equivalent in any experimental program to the naturally suspended material is remote, at best.

An attractive methodology for experimenting with chemically mixed solutions is first to make measurements of nuclide behavior using solutions having a range of chemical compositions, and then to make similar measurements using groundwaters. Comparison of the data obtained from both chemically mixed solutions and groundwaters are then used to indicate how accurately the measurements obtained with chemically mixed solutions can be expected to reflect the behavior of groundwaters. This methodology combines the first and second approaches to solution preparation discussed here. The methodology exemplifies the attractiveness of making measurements by a variety of experimental approaches.

Mix Chemicals to Form Solution, React this Solution with Rock

The third approach discussed here is to mix chemicals to form a solution, then to react the solution with rock. The approach is intended to remove the incompatibility of the prepared solutions with the rock-- for example, exchange of major cations between rock and solution can take place before the radionuclides react with the solution and rock.

In this approach, however, the water obtained may be considerably modified from that existing at the site of interest. This can occur because reaction of water with fresh rock surfaces differs from reaction with the naturally occurring highly altered surfaces of old rock fissures. Alternatively, if one were interested in water reacted with the fresh surfaces of a repository that are introduced by excavating and crushing rock for backfill, the water modified by contact with fresh surfaces would be of great advantage experimentally.

General Observations Regarding Solution Preparation

The handling and storage of solutions form an integral part of the preparation of solutions for experimental programs. The specific objectives of an experimental program determine the handling and storage procedures that are warranted.

Basic groundwater solutions are unstable in air and react with carbon dioxide in the air, with subsequent lowering of the solution pH. Even solutions stored in closed containers undergo this reaction, as evidenced by data in Table 3. Also, basic solutions will react with glass vessels to produce changes in solution composition. The oxidation states of solute species of both acidic or basic solutions can be modified by exposure to air, exposure to metals, or exposure to other materials that can participate in redox reactions.

Table 3. Carbonate Content of a Chemically Mixed Solution*

Days After Preparation	pH	Carbonate [CO ₃ ²⁻] + [HCO ₃ ⁻], mmol/L	Pickup of Atmospheric CO ₂ , mmol/L
0	10.21	1.51	0
75	9.81	1.78	0.27

*Solution stored under nitrogen gas in a capped 40-liter polyethylene bottle after the solution was sparged with nitrogen. Measurement of carbonate was by titration.

Filterable material forms an important component of many solutions. Therefore, treatment of solutions by filtration (or centrifugation) is significant to solution preparation and can influence the results of an experimental program. Many solutions that have contacted rock have particles in suspension up to several micrometers in size. These particles can serve to adsorb nuclides from solution, they can buffer solutions by dissolving with changes in pH, or they can affect the chemistry of dissolved species in other ways.

Illustrated in Figure 1 is the distribution of particles according to size in a hypothetical solution. Such information could be obtained, for example, by analyses of an insoluble component (Fe or Al) associated with the solutions that had passed through filters of various pore sizes.

The figure illustrates that the particles exist in two groups distinguishable by particle size. The large particle size group could be removed by using filters with pore sizes from 0.002 to ~0.1 μm without affecting the particles in the smaller size group. Filtration at a pore size that is within this window between particle size groups would be

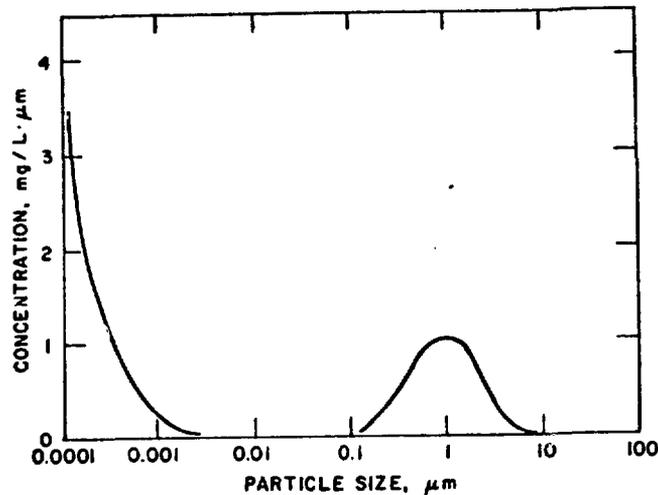


Fig. 1. Particle-Size Distribution in Groundwater. The distribution shows particles in two size groups, with an absence of particles between 0.002 and 0.1 μm .

convenient for standardization since it would effectively separate the two groups of particles and be insensitive to the specific filtration procedure used.

Questions and Answers

Kim: What ionic strengths would you recommend for the filtered groundwater?

Seitz: The ionic strength of the solution that is prepared would depend on the purpose of the experiments for which the solution is intended. Concentrated brine solutions may be quite appropriate in studies relating to salt deposits. Alternatively, if the experimental study is to be concerned with groundwater that is extensively diluted with rain water, then water of low ionic strength would be most appropriate.

I don't think we want to specify one composition of groundwater--say, the "average" groundwater--that would be used in studies.

In contrast, many compositions, some specific to each circumstance studied experimentally, should be contemplated.

Kim: Do you consider heavy ions, that influence the formation of colloids even at microconcentrations, in your thinking?

Seitz: Heavy metals may form colloids even at very low concentrations. If we are to consider the possibility of radionuclide migration by colloids then we must consider the role of heavy metals. But we would not want to burden everyone with the task of working with heavy metals by specifying that every experimenter must always include heavy metals even when their work is not concerned with colloids. The task of knowing what is important for a particular line of study is a scientific issue and cannot be cut short by specifying standard procedures.

Kim: How do you specify standards? Do you have any recommendations?

Seitz: Standard procedures can be very valuable in studies relating to nuclear waste disposal, but the procedures would serve a particular need and that need must be defined before the procedures can be identified. For example, a very simple batch test may be specified and the successful performance of the test would indicate the proficiency of an experimental group to perform the filtrations and radiochemical counting specified for the test. If procedures are developed to assure that experimental groups have good control of the gases that contact their solutions, then the procedures might specify that a solution be maintained at

high pH for periods of weeks or months in the atmosphere-controlled environment. So by these examples, I attempt to show how substantially a standard procedure would depend on the purpose for which it is intended. To try to anticipate all purposes for a standard procedure and then to accommodate the purposes by that one procedure would be very cumbersome and, I think, doomed to frustrate all parties involved.

Meier: If you discuss the migration of small particles in nature, how do you bring in a particle-size limit into this discussion?

Seitz: I cannot generalize from our observations of particulate in groundwater to the migration characteristics that we would expect for this particulate. The example was to show how standardized procedures relating to filtering could take advantage of natural features such as a large region on a particle-size scale that is devoid of particles. This region would be the logical place to make the distinction between particles that are suspended (the larger particles) and particles that are part of the solution (the smaller particles).

The distribution of particles I've shown is very comparable to that in groundwater from basalt with which I am familiar. The feature may result from particles of a certain size being unstable, apparently; the particles either dissolve to form small particles or they agglomerate to form larger particles.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.