SANDIA REPORT

SAND2006-3857
Unlimited Release
Printed July 2006

Screening Protocol for Iodine-Specific Getters in YMP-Related Invert Applications

James L. Krumhansl, Jason D. Pless, J. Benjamin Chwirka

Screening Protocol for Iodine-Specific Getters in YMP-Related Invert Applications

James L. Krumhansl*, Jason D. Pless, J. Benjamin Chwirka

*Geochemistry Department
Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185-0754

ABSTRACT

This document defines a standardized screening protocol for use in developing iodine "getters" for placement in the proposed YMP-repository invert. The work was funded by the US Department of Energy (DOE), Office of Civilian Radioactive Waste Management (OCRWM), Office of Science and Technology International (S&T) during 2004-2005. First, the likely environmental conditions in the invert are reviewed as a basis for defining the thermal and geochemical regimes in which a getter must function. These considerations, then, served as the basis for laying out a hierarchy of materials screening tests (Table 1). An experimental design for carrying out these screening tests follows next. Finally, the latter half of the document develops methods for preparing test solutions with chemistries that relate to various aspects of the YMP-repository environment (or, at least to such representations as were available from program documents late in 2004). Throughout the document priority was given to defining procedures that would quickly screen out unpromising candidate materials with a minimum amount of labor. Hence, the proposed protocol relies on batch tests over relatively short times, and on a hierarchy of short pre-test conditioning steps. So as not to repeat the mistakes (and frustrations) encountered in the past (notably in preparing WIPP test brines) particular care was also given to developing standardized test solution recipes that could be prepared easily and reproducibly.

This document is principally intended for use as a decision-making tool in evaluating and planning research activities. It is explicitly NOT a roadmap for qualifying getters for actual placement in the repository. That would require a comprehensive test plan and a substantial consensus building effort. This document is also not intended to provide a complete list of all the tests that individuals may wish to carry out. Various materials will have their own peculiar concerns that will call for additional specialized tests. In many cases additional research will also be needed to verify the exact nature of the chemical process responsible for scavenging the iodine from the test solutions.

ACKNOWLEDGMENTS

CONTENTS

FIGURES

TABLES

APPENDICES

I.   INTRODUCTION

In the 2004-2005 time-frame the US Department of Energy (DOE), Office of Civilian Radioactive Waste Management (OCRUM), Office of Science and Technology and International (S&T) initiated a program to develop getters for possible placement in the invert beneath high level nuclear waste containers at Yucca Mountain. Three radioactive elements were of particular concern, neptunium, technetium and iodine. The first two were dealt with by other parts of this program while this document focuses on establishing a standardized approach for screening potential iodine getters.   From the start, the DOE stipulated that this program be categorized as non-Q (e.g., DOE stipulated the program to be "not quality affecting", meaning it was to be a scoping study only).

The ultimate reason for having a getter is to provide an engineered barrier that prevents (or slows) a radionuclide from leaving the repository. This retardation then lowers the dose at some hypothetical (distant) point of compliance (see MacNeil et al., 1999 for example). Because of its potential impact, the ultimate performance of the getter must clearly be evaluated according to applicable Quality Assurance ("QA") requirements (a process _not_ covered by this document). However, the historical narrative of how such materials were first found and then developed should have no impact on PA calculations so facilitating the discovery process by according the program a non-Q status was a reasonable strategy. Its successes during the first (and only) year of the program are documented elsewhere (Krumhansl, et al., 2005, 2006, Pless et al., 2006; Bontchev et al., 2005; Bontchev, 2005).

The tests described here are intended to provide early "go, no-go" perspectives on potential getters using short-term tests relating to YMP-relevant conditions. The intent here is to indicate whether new materials MIGHT hold promise. This document does NOT define a final decision-making strategy for qualifying getters for placement in the proposed YMP-repository invert. That will only be possible after a substantial amount of additional discussion, and planning and experimentation. Nor is it intended that this be an exclusive list of materials characterization procedures. Individual researchers, clearly, will want to know (much) more about their materials than would become evident from performing the tests described below. Finally, many steps may be needed before suitable materials are actually developed. Hence, an early failure of a material according to this protocol should probably not result in discarding the concept when additional avenues for developing the material are evident.

Broadly speaking, "getters" are materials that retard (and optimally retain) target radionuclides (Tc, I and Np for the overall Getter Program) before groundwater carries them away from the repository. By convention, getter performance is usually presented in the form of a Kd, with reversible sorption being the implicit retardation mechanism. Other mechanisms: precipitation and co-precipitation, for example, may also remove a radionuclide from solution. Further, even when sorption has been demonstrated as the removal mechanism, it is preferable that the getters have the additional "non-thermodynamic" property of releasing their radionuclides much more slowly than they were acquired.   In spite of the complexity inherent in attaching any real meaning to a "batch Kd", the technique still remains a highly efficient screening tool and, as such, is the basic type of test used in this protocol. The intent here is, however, only to assess the

relative scavenging ability of different materials in a systematic manner, and not to define how the material would actually perform in a repository setting.

The published literature contains numerous reports of materials with some apparent ability to scavenge the radionuclides targeted by this program. However, retention mechanisms are generally so poorly described (or understood) that one cannot realistically define performance envelopes for these compounds. Additionally, recent advances in materials science have produced (or suggest the potential for producing) whole new classes of materials whose function as potential getters has yet to be assessed at even the most rudimentary level. This program will exploit both the existing literature and the rapid advances being made in materials science to identify and test a broad range of potential getter materials.

II.   ENVIRONMENTAL CONSIDERATIONS

Any successful getter will have to withstand the rigors of the YMP-repository environment. It can also be presumed that the getter will be mixed in with the rest of the invert components prior to placing the waste in the repository. Consequently, one criterion for a successful getter will be for it to withstand the entire range of temperatures in the thermal cycle of the repository. For the present design the temperature cycle is reasonably well characterized (see, for example, Johnson, 2004). Current plans call for initially ventilating the repository for several decades to remove most of the thermal energy produced by $137Cs$ and $90Sr$. However, in spite of this procedure, temperatures on the waste package surface could be as high as 230° C. Beneath the invert (e.g., at the rhyolite-invert interface) they will be lower, with a maximum around 130° (Fig. 1). Ventilating the drifts will also have the effect of drying out the facility so that the high-temperature period will also be a time of very low humidity (ANL-EBS-HS-000003 Rev.00, Fig. 36, 37).

The highest temperatures will only persist for a decade or two, after which there is a slow exponential decay in temperature. The time needed for the temperature to reach 100° C varies with the presumed water infiltration rate. However, at low infiltration rates (e.g., like those characteristic of the present climate) it might be almost 800 years before liquid water could again enter the repository. Between 1000 and 10,000 years the temperature slowly falls to around 50° C, and one presumes that the humidity will be close to saturation. This range of temperatures, then, defines what a potential getter material must withstand. However, given the (presumed) longevity of the waste package it is likely that most of the actual scavenging of radionuclides will take place later in the repository history and, hence, at temperatures significantly below the boiling point of water.

Whether or not the atmosphere remains **oxidizing** during this time will depend on the relative rates of waste package corrosion and how readily the mountain "breathes"((e.g., changes in air pressure are noted within the mountain in response to outside changes in atmospheric pressure). It is also clear that the most likely place for reducing environments to develop in the repository lies within a waste package (Brady et al., 2005). Conversely, the invert, and associated getters, will reside at the margins of the disposal facility where it will have the greatest access to air from

outside the repository. Consequently, *with regard to testing getter performance, this protocol adopts the YMP program position that conditions will be oxidizing as being appropriate for assessing performance in settings where the getters will actually be called on to perform.*
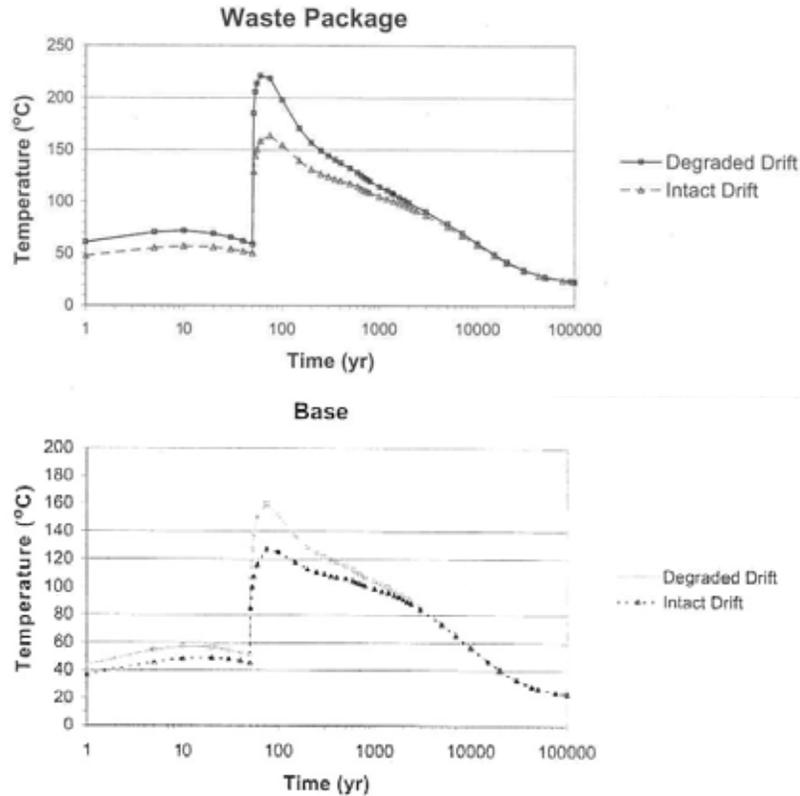
Fig. 1: Time-temperature profiles for the waste package surface (top) and the bottom surface of the drift at a location that would be beneath the invert (bottom). Figures were taken from MDL-NBS-HS-000018 REV 00, Fig. 6.3-2, "Waste Package" and Fig. 6.3-3(c), "Base".

Radiation effects are another environmental factor of potential concern. The projected longevity of the waste packages suggests that the gamma radiation dose received by getters in the invert will be minimal. However, one option suggested also places the getters within waste packages, in which case much higher radiation doses could result. Another concern is that, even with small gamma dose rate, the soluble salts precipitated on the waste package (or drip shield) may accumulate radiation damage for many years. Dissolution of such salts may, then, provide a slug of brine with unusual and otherwise unanticipated chemical properties (Krumhansl, 1986). Alpha dose rates in the invert, of course, will depend on whether significant amounts of actinides are transported into the invert once the waste packages are breached. Because alpha particles produce much greater localized damage than does gamma radiation their potential for altering getter performance is proportionally greater. *For the time being, however, it is probably safe to*

relegate the study of radiation effects to a later round of testing when fewer materials will need to be evaluated and the environmental conditions are better defined.

Fluid chemistry is another environmental factor that may affect getter performance. The types of concerns can be divided into two general categories: (1) whether components from solution may alter the surface chemistry of the getter and, hence, its ability to scavenge radionuclides, or (2) whether the getter phase(s) may become unstable in the presence of certain fluids. In both cases the problem is made more complex by the fact that the relative amounts of solid and fluid can have a significant impact on overall performance. In particular, an experiment will only highlight a potential problem if the solution contains enough of the detrimental component(s) to alter a significant fraction of the getter. With dilute solutions and high solid-to-water ratios this criteria is often not met. However, in a repository, with longer times and possibly significant water fluxes, the solid (getter)-to-water ratio may actually be much smaller. In such a setting the same water that had minimal effect during a laboratory experiment could significantly alter the make-up of a getter. Issues such as this are why, before a getter can actually be qualified for use, a much wider range of tests will have to be performed than are outlined in this document.

Formation waters from the vicinity of the YMP-repository Site, such as "J-13", constitute one potential source of fluid chemistries that might be employed for screening getters. However, although J-13 is the traditional YMP-related test fluid its source is several miles from Yucca Mountain and project scientists have recently also studied fluids that originated nearer to the actual Yucca Mountain site. Project scientists have also defined two general ways in which local groundwater might undergo significant chemical modification in the vicinity of the proposed repository: (1) indigenous site groundwater(s) may be altered by thermal processes, principally evaporative concentration and, (2) waters may interact with the wastes and their containers, thus acquiring both corrosion products and radionuclides.

With regard to waste-package derived fluids this document explicitly considers the importance of sorption onto the rust from the corroding waste package. Although program scientists are well aware of the issue (and its implications), the fact that the codes/databases needed to complete the calculations are not QA-approved (although widely accepted by the geochemical community) has prevented them from evaluating the impact of this process in the formal YMP documents on potential fluid chemistry. Since this is relatively new territory for the program a rather detailed account of our calculations is provided later in the document.

III. TESTING PROTOCOL

Overview

 Clearly, potential getters cannot be "qualified" by simply exposing them to the relevant conditions for times commensurate with the lifetime of the repository (centuries to millennia). The objective of this protocol is to distinguish between promising and unpromising candidates through the use of short-term tests (~24 hours to one week) geared to environmental conditions likely to occur in the repository. The rationale is simple; if a material fails quickly under moderate, though representative, conditions continuing its study is pointless unless – in doing so – one anticipates developing a more robust derivative of the material.

Implicit in any screening protocol is a hierarchy of priorities (Table 1). In this scheme priority is given to tests relating to the best-known environmental factors, and to those with the broadest implications for overall getter performance. The most basic question is whether the "as-received" material has any ability to scavenge the target radionuclide in the most benign fluid that is still representative of the YMP environment ("primary test", Table 1).   For this application low ionic strength fluids similar to indigenous NTS groundwaters (including "legacy fluids" such as J-13) are appropriate. A second question of almost equal importance is whether the material can, for even short times, withstand the thermal rigors of the repository environment? In particular, a phase must both retain its identity, and the capacity for scavenging radionuclides, after being exposed to conditions representative of: (a) the early (relatively short) dry-heat phase of the repository and, (b) the later, longer, period of time when hot water will be present in the repository (taken together: "secondary tests", in Table 1).

It could be argued that the "primary test" (e.g., one using unheated "as-received" materials) is superfluous since any getter placed underground will almost certainly be both "toasted" and "stewed" before ever seeing any radionuclides.   However, particularly in the early "discovery" phases of the program, the "primary" test may be helpful in identifying promising classes of materials that initially lack the requisite thermal stability. Parenthetically, there may also be instances where the synthesis process already involves a thermal treatment (dry or wet), in which case an additional thermal pretreatment would, obviously, be superfluous unless the fluid chemistry has an influence.

A more detailed examination of the YMP program literature also supports the relevance of testing in other fluids. Once the temperature falls below the boiling point the repository may see a pulse of "brines" formed by the rather extreme evaporation of normal groundwaters. The literature also suggests that the early corrosion of the waste packages may provide a different "brine" that is quite acidic with high chromate and nickel concentrations. There is some question about this, however, and these extreme compositions seem partly to reflect the fact that currently the program does not have a QA approved database that allows it to account the sorptive properties of the voluminous amounts of rust that also will also form during corrosion. When this is done (*outside the QA framework*, later in this document) less extreme fluids seem to be indicated.   Given the presumed longevity of the waste containers it is unlikely that significant radionuclide contamination would be present in either type of brines. However, they could react with the getters so the getter seen (much later) by radionuclide-bearing fluids is not the same as what was initially placed in the invert (assuming enough fluid passes through the getter to alter most of the material).

Eventually, however, the waste packages will fail and some (as of yet undetermined) fraction of the waste inventory will leach into whatever fluids are present at the time. It is quite possible that, by then, the overall composition of the fluid will be essentially that of the "normal" indigenous NTS groundwaters (for which getter performance would be already covered by the "primary" test described above). However, an alternate scenario suggests that the corrosion products from the waste packages might still dominate the chemistry of these fluids. Further complexity is introduced because, at this stage, one would also expect that a significant mass of

rust to have formed. Hydrous iron oxides can strongly sorb many of the corrosion products (and radionuclides) but the extent of this interaction is not precisely known.

To summarize getters may be called to scavenge radionuclides from any of three solutions: (a) essentially dilute "indigenous" NTS groundwaters, (b) rather concentrated fluids dominated by waste and waste package corrosion products that have not interacted much with rust (the current program perspective) and (c) fluids dominated by corrosion products and radionuclides which have interacted extensively with rust. Getters may also have to withstand prolonged drying at elevated temperatures, exposure to salty brines derived from evaporation of normal groundwaters, and exposure to chemically aggressive fluids formed during the early stages of waste package corrosion.

Table 1: Prioritization matrix for batch Kd measurements; actual batch testing to be performed at room temperature on variously pretreated materials.

Solid Pre-Treatment→ Batch Test Fluids ↓	As Received	Dry Heated 130° C	Dry Heated 200° C	90° C, DI or or J-13 water	90° C "Brines" and "200-Year Corrosion Fluid"
"dilute" J-13-like (Low Ionic Strength)	**Primary Test**	Stage 4 Test	**Secondary Test**	**Secondary Test**	Stage 3 Test
10X-Waste Leach (With Rust)	Stage 3 Test	*Stage 4 Test*	Stage 3 Test	Stage 3 Test	Stage 3 Test
Waste Leach (No Rust, Late)	*Stage 4 Test*	*Stage 4 Test*	*Stage 4 Test*	*Stage 4 Test*	*Stage 4 Test*

Thermal Pretreatment

Any realistic candidate getter must survive the fairly rigorous thermal environment in the repository. Temperatures as high as 230° C are predicted for the waste package surface and peak temperatures as low as 130° C for the drift wall beneath the invert (Fig. 1). Because the invert lies between these two extremes and, for short term testing a relatively rigorous test criteria is desirable, a test temperature of 200° C (in air) was selected. It is also unlikely that times longer than a week would be required to cause the sorts of immediate degradation that this protocol is intended to detect. Where deterioration is noted, additional testing at 130° C could provide some perspective on how severely the material is affected by heat. Again, a one-week treatment should suffice.

Later sections in this document deal in some detail with testing in different YMP-repository fluids. However, what all these fluids have in common is that they are mostly water and exposure to water (or steam) alone can change a material as a consequence of hydration reactions. There is no correct water to solid ratio for such preconditioning, but over the long term the YMP-repository environment can, clearly, provide much more water than the amount of

getter in the invert.   Thus, a high water to solid ratio was selected for this pretreatment and reaction rates are to be accelerated by using the highest plausible temperature (90° C) that does not require an autoclave.

Toward this end, it is suggested that 1 gram of solid be placed into 50 grams of deionized water (or J-13 surrogate) in a ~100 ml bottle at 90° C (most plastic bottles can take this for a week). This treatment is not intended to evaluate the effects of the dissolved components on the getter, but, rather to observe the impact of hydration reactions. Consequently, any dilute fluid would suffice but, for the sake of being specific, it is suggested that either deionized water or J-13 surrogate be employed here. (The rationale for including the J-13 surrogate is that the fluid could subsequently be analyzed to see what normal groundwater components the getter had scavenged, which could possibly shed some light on getter phase stability in a repository setting where the liquid to solid ratio might be much higher.)   The bottle size and liquid volumes were selected so one could observe whether the getter is prone to oxidation by noting if the bottle sides were pull in during the heating. Smaller bottles can be used where this is not an issue. Parenthetically, the last step in many preparations involves aging materials in their synthesis fluid at about 90° C. In this instance it would clearly be pointless to invest the time needed to assess the thermal stability of a material in hot-water a second time.

Once potentially interesting materials are identified additional insights into the effects of heating/hydration could also be gathered using standard solid characterization techniques: X-ray diffraction, SEM/TEM examination, optical microscopy, surface area (BET, if routinely available), TGA, DTA etc. As noted above, analysis of the leach solutions might also be informative. Such characterization is not part of the formal screening protocol (which, basically, just sets out to establish the viability of getters in various relevant environments). However, such studies might be helpful in explaining the changes in getter performance, in identifying fruitful directions for future materials development efforts, and, potentially, by providing a starting point for (later) discussions regarding longer-term stability issues.

Batch Test Implementation

In spite of its limitations (many of which arise from misapplication or misrepresentation of results, rather than inherent flaws in the technique) the "batch Kd" is still the most efficient way of screening radionuclide getters. The process is, however, most effective when carried out in a standardized manner using solutions that reflect prevailing conditions at the site where the material will be used. This section establishes the standardized testing procedures, with the actual definition of the test solution chemistries being deferred to later sections of the report.

Past experience in performing iodine analyses (inherent precision limits in the analytic techniques, etc.) suggests that one cannot be confident of having a real "hit" on a getter unless at least 10 % in the iodine is removed from the test solution. It was also assumed (arbitrarily) that a "Kd" in excess of 50 is needed if a material is to be worth pursuing from a research standpoint. Parenthetically, *as a metric for actual utility at YMP-repository*, one published YMP-PA model (MacNeil et al., 1999) finds that a perceptible decrease in iodide at a (distant) point of compliance only results if the getter in the invert has a Kd greater than 1000. The utility of this

conclusion is, however, constrained by the fact that the study also assumes readily reversible sorption - which is seldom the case when a material strongly scavenges a particular radionuclide.

About 20 ml of fluid is the minimum amount that can be worked with conveniently from the standpoint of being able to filter samples and then have enough left to easily analyze what remains. Taken together, these constraints allow one to estimate the mass of solid that is needed in a test:

$$Kd = 50 = 20ml [C_{initial} - 0.9 C_{initial}] /[M_{solid-g}*0.9 C_{initial}].$$

$M_{solid-g}$ formally works out to be about 0.044 gram to be added to 20 ml. These are round numbers so standard setup that involves conveniently weighed amounts of material and available bottle sizes would involve about 0.05 g of getter in about 25 ml of fluid. Of course, if good scavengers (Kd>1000) are identified experiments may have to be repeated with (much) more fluid (or less solid) until the residual iodine concentration is compatible with the detection limit of the analytic technique being employed.

Several other procedural matters are also worth mentioning at this point. "Oak Ridge" centrifuge tubes are convenient to use for Kd measurements since they come equipped with a screw-on top and, when the experiment is completed, they can be spun in a centrifuge, which makes it much easier to filter the fluids (0.2 micron filters are recommended) prior to their analysis. However, they do not seem to be able to withstand temperatures much above 60° C, so be careful in drying the materials. Secondly, prior to setting the tubes on a shaking rack for the duration of the treatment it is also a good idea to put them into an ultrasonic cleaner (for about an hour). This will help to further disaggregate the powders and more of the sample will remain suspended as the tubes shake.

It is also worth noting the advantages of expanding the range of Kd tests to include several different solid:liquid ratios. Although a Kd should be a constant, it seldom is; and this procedure can provide some insights into the mechanisms responsible for radionuclide scavenging. An additional advantage from making multiple Kd determinations at different solid-to-fluid ratios arises from the fact that evaluating a Kd also inherently provides an empirical measure of the loading on the solid as it relates to a final, "equilibrium" concentration of the target constituent in solution. Plotting loading against residual concentration then allows one to estimate how much of the getter would actually be needed to scavenge a certain inventory of iodine (or other constituent of concern) at a specified target release concentration (presumably derived from a PA or regulatory source). Since such assessments are essentially empirical they are also independent of the problems that my arise from inappropriately interpreting the meaning of a Kd measurement. However, as always, such applications are still limited to settings where the groundwater chemistry is similar to that employed in the Kd experiments.

Another factor in designing a Kd experiment is defining appropriate target radionuclide (surrogate) concentrations. Ideally, one would like to use radionuclide concentrations that reflect what leaches out of the waste package. However, a quick survey of the literature revealed such a vast spread in values so that such an approach fails to provide any useful guidance. Lacking such guidance, this protocol uses the criteria that: (1) the iodine concentration must be in a range

where it can be easily detected using available instrumentation (Table 2) and, (2) the starting iodine concentration should be *significantly* below the concentrations of the principle solutes in the test solution(s). The latter constraint arises from the desire to have the surface chemistry of the getter reflect the constituents in the test solution and not the iodide supplement that was added to the recipe. Past experience suggests that the iodine levels in Table 2 are reasonable compromises that meet both selection criteria outlined above. Rhenium also appears in Table 2 because ReO_4^- is a surrogate for TcO_4^-, and screening for sorption of this constituent turned out to be a benefit the other Getter Program activities which were being carried out at the time.

Table 2: Reference radionuclide (and surrogates) for batch sorption testing:

Element	Analytic Method	Suggested Concentration	Minimum Workable Concentration
I	ICP-MS*	2 ppm	50 ppb
I	Selective Ion Electrode	2 ppm	50 ppb
I	Chloridometer	1000 ppm	100 ppm
Re (ReO_4^- for TcO_4^-)	ICP-MS	1-2 ppm	25 ppb

* Making samples slightly basic and using a 1:20 V/V rinse of ammonium hydroxide to deionized water containing about 10 ppm Ag (instead of the normal nitric acid rinse) seems to mitigate some of the memory effects that limit the utility of the ICP-MS in performing *iodide* analyses. It is also noteworthy that acidifying samples or standards with nitric acid can result in oxidation of iodide to elemental iodine. On one hand iodine can then be lost (from either standards or unknowns) by evaporation as the samples await analysis. Alternatively, if elemental iodine is formed – but not lost – it can evaporate in the nebulizer and contribute to the signal in the next sample (rather than going down the drain with the rest of the waste) again giving erratic results, although this time biasing results to the higher rather than lower values. In either case, the results are poor reproducibility and calibration problems. Thus, if samples (and multi-element standards) are to be acidified for the analysis of other metals it is important that this happen *after* the iodine analysis is completed. *Iodate* analyses by ICP-MS are less problematic than iodide analyses. It is often helpful to introduce an iodate standard several times during a run to monitor detector response to iodine independently of how well the plumbing is handling the memory effect particular to the presence of iodide.

Finally, it is necessary to decide on how long experiments should equilibrate and at what temperature. Ion exchange processes are usually rapid (on the order of seconds to hours) but other processes responsible for scavenging radionuclides may take substantially longer. For preliminary screenings samples should – at minimum - be allowed to equilibrate overnight at room temperature on a shaker table (but, in practice, setting up experiments to equilibrate over the weekend often proves to be more convenient). Longer, more standardized, tests may then be warranted for materials that respond favorably. To minimize the impact of long holiday weekends (and other interruptions) it seems reasonable to stipulate that the longer tests should equilibrate for a week. This will provide ample time for (most) getter surfaces to hydrate, as well as for the most chemical reactions (between the getters and constituents from the test solutions) to reach completion. Where convenient, carrying out experiments over a range of temperatures

would also certainly be informative, nominally up to about 60°C, which is about the highest temperature where the getters would have to perform. The use of higher temperatures is only relevant in the context of speeding up reaction rates.

IV.   DERIVATION OF TEST FLUID RECIPES

As will become apparent, one cannot define solutions that are uniquely correct for testing getters in YMP-repository invert environments; there are simply too many possibilities and too few constraints.   Having said this, there is still considerable merit to choosing (and documenting) test fluid compositions which: (1) are in "the ballpark" relative to YMP-repository groundwater chemistries and, (2) can be prepared easily, and thus reproducibly, in bulk from standardized recipes. To define appropriate chemistries proved to be a complex undertaking involving the review of numerous YMP documents at various stages of completion. Thus, the recipes are inherently "snapshots" of how the YMP viewed groundwater chemistry issues early in 2004. If the getter program is resumed it might be advisable to revisit this process in light of whatever deliberations have occurred since 2004.

Ease and reproducibility in preparation were the guiding principals in recipe development. Because many of the solutions are, in fact, quite dilute it was found to be advisable to mix more concentrated stock solutions and then further dilute them in the final mix rather than weighing out milligram quantities of various salts directly. This also assures that everything will be dissolved initially so it should be possible to immediately use a mix once it has been prepared - rather than waiting for some component to dissolve. In many cases the concentrated stock solutions are not compatible with each other until diluted. Thus, in preparing any recipe it is highly advisable to add the stock solutions to a vessel that already contains (most of) the deionized water called for in the mix, rather than adding the excess water after mixing the stock solutions. Although every effort was made to develop solution recipes that are stable over time the program was, unfortunately, discontinued before this could be fully tested. Consequently, as a default position, the final step in all preparations would be to filter out any precipitates that form.

The issue of test solution pH value is worthy of particular comment. These recipes were commonly derived by averaging groundwater compositions from a variety of sources. These tabulations also contained pH values that, in principle, could also be averaged. However, with complex recipes it is unrealistic to think that the synthetic fluids will mimic the average pH exactly. In those (few) cases where the pH of the actual mix is outside the range expected for repository waters small amounts of HCl or NaOH may be used to adjust the pH since small amounts of Na^+ and Cl^- are plausible constituents in any fluid that might enter the repository.

"Dilute" formation fluids, definition and selection

Barring the most convoluted and contrived of scenarios it is generally true that getters which fail in "tap water" will not be effective in the more extreme fluids discussed later in this document. Thus, the first priority goes to defining a dilute test solution, with YMP-repository traceable chemistry.   Such a solution needs to have a pH between 7 and 8.5 and contain an assortment of the normal groundwater cations and anions (Na^+, K^+, Mg^{++}, Ca^{++}, $SiO_2(aq)$, HCO_3^-, $SO_4^=$, Cl^-,

NO_3^-, F^-) in amounts similar to (dilute) NTS groundwaters. Parenthetically, even the most dilute Nevada groundwaters still contain enough solutes that deionized water would clearly not be serviceable as a "dilute" fluid for assessing the radionuclide-scavenging properties of a potential getter.

Fortunately, over the years the Yucca Mountain project has developed a number of reference groundwater chemistries that may be used in making appropriate selections. The process started with the definition of the J-13 groundwater recovered from a well in the southwest corner of Jackass Flats near Forty Mile Wash (several miles from what was then the proposed repository block; see, for example, Harrar et al., 1990). Since then, modeling of groundwater-waste package interactions (ANL-EBS-MD-00037) and thermal effects around the repository (MDL-NBS-HS-00018 REV 00) have resulted in the definition of other fluid compositions that are more closely related to the proposed repository site. An overall summary of relevant formation water chemistries assembled from these sources is given in Tables 3 and 6.
What sets J-13 water chemistry (right hand column in Table 3) apart from the other newer compositions is that it is slightly more dilute and relatively poorer in Ca and Mg. There are, however, distinct advantages to continuing with something close to J-13 as a formation test fluid. Such a selection will permit relatively direct comparisons to earlier YMP-sponsored sorption studies and to deviate significantly from "accepted practice" would require a clearly defined argument in support of some other dilute fluid chemistry.

All the potential choices are so dilute the slight differences in ionic strength are not going to matter as far as activity coefficients, aqueous complexing processes, or double layer structures are concerned. Also, neither iodide nor iodate has a chemistry similar to either Ca or Mg. Consequently, there is no reason to think that the slight differences in these constituents are going alter getter performance significantly. In short, although many choices are possible, there seems to be no compelling reason to not adopt a fluid similar to J-13 water as the reference "dilute" formation water.

Formulation of a J-13 surrogate test fluid: When it comes to providing an exact recipe for making synthetic J-13 water, however, the picture is rather clouded. REACT is a reaction path model that is part of the commercially available Geochemist's Workbench package (Bethke, 1998). Note: although the code is widely used by the geochemical community it is not (yet) YMP-QA qualified. Using REACT with the literature J-13 composition indicates that the fluid is unsaturated with regard to both calcite ($CaCO_3$) and fluorite (CaF_2). However, to exactly match the J-13 composition requires adding both minerals to the mix and then waiting (many years, probably) for the powders to dissolve (see, for example, difficulties encountered in Rosenberg et al., 2001). Consequently, this document provides a recipe (Tables 4) that is still close to J-13 (Table 5), but which mostly involves salts that dissolve rapidly. The one exception is calcium sulfate; for which one may wish to prepare a saturated solution the preceding day.

Silica is particularly problematic and leaving it out of the recipe might be considered in some applications. The REACT calculation suggests that quartz should eventually precipitate anyway (but apparently not in geologic time, at least at Yucca Mountain). In actual practice, adding the appropriate amount of sodium silicate does produce a solution that remains clear for several weeks. Thus, the real problem comes from the fact that adding sodium silicate elevates the pH,

from 8.04 to 9.46 - as measured experimentally, or 10.1 -as calculated theoretically based on the carbonate to bicarbonate ratio . Consequently, an acid will then have to be added to bring it back in line (the average pH in Table 3 is 7.7). This will, in turn, also very slightly increase the concentration of some anion. It is apparent that other plausible programmatic groundwater chemistries (Table 3) contain more sulfate and chloride than does J-13 (or its surrogate). Consequently, either HCl or H_2SO_4 may be used to lower the pH, HCl is preferred since the resulting (elevated) Cl^- level will resemble more of the entries in Table 3 than would the resulting sulfate level.

Table 3: Reference Formation Water Compositions Used In YMP Studies

	HD-PERM	ECRB-SYS CS1000/7.3 7.7/UC	ECRB-SYS CS2000/16.5 21.1/UC	SD-9/990.4 991.7/UC	ECRB-SYS CS500/12.0 16.7/UC	ECRB-SYS CS2000/16.3 16.5/UC	J-13
Source	A	A #	A	A	A	B ##	B
pH	8.31	7.6	7.4	7.9	8	7.4	7
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Na	61.5	39	130	84	57	120	45.8
K	8	7.6	10.6	7.9	10.2	6.1	5
Ca	101	94	82	56	120	81	13
Mg	17	18.1	5.3	0.9	19.3	3.3	2
SiO_2	70.5	42	48	50	49	42	28.5
Cl	117	21	26	23	54	24	7.1
SO_4	116	36	39	10	78	31	18.4
HCO_3	200	333	382	313	286	362	152
NO_3	6.5	2.6	4.2	17	6.1	0.41	8.78
F	0.86	3.4	6	2.4	4.8	6	2.18
	molal	molal	molal	molal	molal	molal	molal
Na	2.68E-03	1.70E-03	8.13E-03	3.65E-03	2.48E-03	5.22E-03	1.99E-03
K	2.05E-04	1.94E-04	6.63E-04	2.02E-04	2.61E-04	1.56E-04	1.28E-04
Ca	2.52E-03	2.35E-03	5.13E-03	1.40E-03	2.99E-03	2.02E-03	3.24E-04
Mg	6.99E-04	7.44E-04	3.31E-04	3.70E-05	7.94E-04	1.36E-04	8.23E-05
SiO_2	1.17E-03	6.99E-04	3.00E-03	8.32E-04	8.16E-04	6.99E-04	4.74E-04
Cl	3.30E-03	5.92E-04	1.63E-03	6.49E-04	1.52E-03	6.77E-04	2.00E-04
SO_4	1.21E-03	3.75E-04	2.44E-03	1.04E-04	8.12E-04	3.23E-04	1.92E-04
HCO_3	3.28E-03	5.46E-03	2.39E-02	5.13E-03	4.69E-03	5.93E-03	2.49E-03
NO_3	1.05E-04	4.19E-05	2.63E-04	2.74E-04	9.84E-05	6.61E-06	1.42E-04
F	4.53E-05	1.79E-04	3.75E-04	1.26E-04	2.53E-04	3.16E-04	1.15E-04

A Table III-1 in MDL-NBS-HS-00018 REV 00, p. III-2, December 2003
B Table 2 in ANL-EBS-MD-00037 Rev 03B, p. 21, April 2004
       # "Ca Porewater"   ## "Na Porewater"

Table 4: Salts used for making a J-13 surrogate test solution.

Salt	moles/1000g H_2O	Formula Wt. g per mole	g salt per 1 liter	g salt per 25 liters
NaF	1.15E-04	41.99	4.82E-03	1.20E-01
$CaSO_4$ (anhyd.)*	2.36E-04	136.15	3.21E-02	8.02E-01
$NaHCO_3$	2.36E-03	84.01	1.99E-01	4.96E+00
$Ca(NO_3)_2.4H_2O$	5.74E-05	236.15	1.35E-02	3.39E-01
$CaCl_2$(anhyd)$^\&$	1.79E-05	147.03	2.13E-03	5.33E-02
$KHCO_3$@	1.28E-04	100.12	1.28E-02	3.20E-01
$MgCl_2.6H_2O$	8.23E-05	203.31	1.67E-02	4.18E-01
$Na_2SiO_3.9H_2O$#	4.74E-04	284.2	1.35E-01	3.37E+00

* **Or** 0.885 g of $CaSO_4.1/2H_2O$*, or 1.01 g of $CaSO_4.2H_2O$ per 25 liters.
Use only one form of calcium sulfate in a mix though.
& **Or** 0.0657 g of $CaCl_2.2H_2O$, or 0.0979 g of $CaCl_2.6H_2O$ per 25 liters
Use only one form of calcium chloride in a mix though.
@ Given the great preponderance of NaHCO3 in the recipe it is acceptable to substitute
0.221 g of K_2CO_3, per 25 liters as that preserves the proper level of K and does not materially
alter the carbonate content of the fluid.
Inclusion of silica is optional and may require additional steps to bring the pH in line; see text below.

A second, more difficult, strategy to solve the pH issue associated with adding sodium silicate involves bubbling CO_2 gas through the mix (or dropping a piece of dry ice into the mix; which, I am told can be purchased at local supermarkets) until the pH falls to an appropriate value. From a mass balance standpoint $Na_2SiO_3\cdot9H_2O$ can be treated as a mixture of Na_2O and SiO_2, with a pinch of water on the side. Adding an excess of CO_2 will neutralize the Na_2O as follows:

$$Na_2O + H_2O + 2CO_2 \rightarrow 2Na^+ + 2HCO_3^-.$$

The primary version of the J-13 recipe presented above (Table 4) suggests adding 2.36×10^{-3} moles per 1000 g H_2O of $NaHCO_3$. If sodium silicate and CO_2 are added this already accounts for having added $2x4.74\times10^{-4}$, or 9.48×10^{-4} moles, of $NaHCO_3$ to the mix. Thus, if sodium silicate and dry ice are used, the amount of sodium bicarbonate that would still need to be added

to the mix is decreased to: $2.36 \times 10^{-3} - 9.49 \times 10^{-4} = 1.412 \times 10^{-3}$ moles per 1000 g H_2O (0.119 g per liter, 2.97 g per 25 liters).

Since the weights involved in preparing manageable volumes of the fluid (~ 1 liter) are truly miniscule a more convenient approach (giving essentially the same fluid composition) involves preparing stock solutions that can then be diluted down to a total volume of 1 liter. Dissolve 0.120 g NaF in 25 g of deionized water, add **1 ml per liter** of J-13 being prepared;

   a. Dissolve 3.37 g of $Na_2SiO_3.9H_2O$ in 25 g of deionized water, add **1 ml per liter** of J-13 being prepared;
   b. Dissolve 4.96 g of $NaHCO_3$ and 0.320 g of $KHCO_3$ in 100 g of deionized water, add **4 ml per liter** of J-13 being prepared;
   c. Dissolve 0.339 g of $Ca(NO_3)_2.4H_2O$, plus 0.0533 g of anhydrous $CaCl_2$ (**or** 0.0705 g $CaCl_2.2H_2O$, **or** 0.1052 g $CaCl_2.6H_2O$), plus 0.418 g of $MgCl_2.6H_2O$ in 25 g of deionized water, add **1 ml per liter** of J-13 being prepared;
   d. Prepare a saturated calcium sulfate solution (in advance) and then add **15.6 ml to each liter** of J-13 being prepared (this volume reflects the solubility of "Nat. anhydrite" (e.g., anhydrous calcium sulfate) at 30 degrees tabulated in the CRC handbook, 59th Edition),

A comparison of this recipe with J-13 groundwater is given in Table 5 below.

Table 5: Comparison of recipe and literature values for the J-13 groundwater.

	mg/kg Recipe	mg/kg Ref. J-13
Na	57.0	45.8
K	5.00	5
Ca	13	13
Mg	2.0	2
SiO_2	see note	28.5
Cl	7.1	7.1
SO_4	22.6	18.4
HCO_3	152	152
NO_3	8.78	8.78
F	2.18	2.18
Na*	**78.8**	**45.8**

* If silica is added in the soluble form of $Na_2SiO_3 . 9H_2O$ the Na concentration increases to 78.8 mg/kg, and the acid needed to bring the pH back into line will alter one of the anion concentrations.

Thermally altered fluids, definition and selection

Placement of waste in Yucca Mountain will heat the repository for many centuries (ANL-EBS-HS-00003 Rev 00, and Fig. 1 of this report). This will create chemical potential gradients for water vapor that will dry certain sections of the repository while condensation forms elsewhere. High-temperature fluids may also initiate rock-water interactions that alter solution compositions. The YMP program has considered these issues in some detail so it is possible to obtain water chemistries for a variety of thermally driven scenarios.

One study evaluated what happened when different "normal formation waters" ("initial" in the top half of Table 6) fall onto a hot drip shield and partially evaporate. In this study evaporation continued until the salinity was high enough to produce a relative humidity of ~60% over the brine ("evaporated" in the bottom half of Table 6). To provide a minimum number of test solutions we started by computing an average composition for each component (e.g., over all 11 bins). The charge imbalance inherent in all such averaging processes was then corrected by adjusting the sodium concentration (see "Invert Average" in Table 7).

Table 6: Starting and final fluid chemistries (molal) for the various bins used to compute drip shield brine chemistries (taken from: Table 2 in ANL-EBS-MD-00037 Rev 03B, p. 21, April 2004, *also see*: CRWMS M&O 2004. Engineered Barrier System: Physical and Chemical Environment Model. ANL-EBS-MD-000033 REV 03. Las Vegas, Nevada.)

Bin	1	2	3	4	5	6	7	8	9	10	11
T	111.9	109.1	104.3	104.9	95.62	65.13	56.34	40.18	91.78	56.34	95.61
Initial											
pH	7.407	7.583	7.615	7.896	7.634	7.695	7.768	7.94	8.139	7.815	7.759
	Molal	Molal	Molal	Molal	Molal	Molal	Molal	Molal	Molal	Molal	Molal
Ca^{++}	1.75E-02	6.49E-03	2.14E-03	1.08E-03	1.36E-03	4.20E-04	4.46E-04	5.73E-04	7.24E-05	3.52E-04	3.34E-04
Mg^{++}	1.70E-05	2.95E-06	4.13E-06	5.75E-07	1.13E-05	4.82E-05	5.52E-05	8.51E-05	2.54E-07	4.31E-05	6.34E-06
Na^{+}	3.89E-03	2.63E-03	2.67E-03	1.26E-03	5.53E-03	8.09E-03	7.65E-03	7.31E-03	4.27E-03	6.82E-03	4.80E-03
Cl^{-}	2.01E-02	5.02E-03	3.35E-03	1.03E-03	3.28E-03	3.32E-03	7.44E-04	5.61E-04	7.34E-04	6.00E-04	1.30E-03
$SiO_2(aq)$	9.42E-03	7.42E-03	6.96E-03	7.38E-03	1.22E-02	2.90E-03	2.46E-03	1.79E-03	4.15E-03	2.47E-03	1.19E-02
HCO_3^{-}	5.57E-05	9.06E-05	1.95E-04	1.64E-04	4.18E-04	2.93E-03	6.72E-03	6.92E-03	2.04E-03	5.74E-03	1.13E-03
$SO_4^{=}$	8.87E-03	4.89E-03	1.50E-03	5.88E-04	1.77E-03	1.21E-03	4.12E-04	3.55E-04	1.18E-04	3.80E-04	7.29E-04
K^{+}	8.68E-04	5.40E-04	5.00E-04	2.38E-04	8.68E-04	6.25E-04	4.67E-04	2.76E-04	5.02E-04	4.17E-04	7.50E-04
F^{-}	1.93E-04	2.46E-04	3.48E-04	4.28E-04	1.00E-03	8.26E-04	7.81E-04	6.43E-04	9.77E-04	8.61E-04	1.38E-03
NO_3^{-}	1.30E-03	5.46E-04	1.83E-04	1.33E-04	2.22E-04	1.04E-04	6.87E-05	3.97E-05	3.10E-04	4.25E-05	1.26E-04
Evaporated											
pH	5.59	5.69	5.88	7.13	7.60	9.01	8.73	8.58	9.15	8.75	9.17
	Molal	Molal	Molal	Molal	Molal	Molal	Molal	Molal	Molal	Molal	Molal
Ca^{++}	3.58E+00	2.38E+00	1.10E+00	2.66E-03	8.57E-04	8.47E-06	1.00E-05	1.14E-05	2.57E-06	5.64E-07	2.65E-06
Mg^{++}	9.16E-04	1.32E-03	1.26E-03	2.32E-06	9.30E-07	6.72E-08	1.30E-06	2.54E-06	3.28E-08	4.08E-07	3.91E-08
Na^{+}	1.63E+00	3.41E+00	4.24E+00	5.57E+00	6.22E+00	6.63E+00	6.81E+00	8.05E+00	7.51E+00	7.32E+00	7.06E+00
Cl^{-}	8.43E+00	8.30E+00	8.42E+00	7.17E+00	7.71E+00	6.36E+00	5.83E+00	4.57E+00	5.37E+00	5.33E+00	6.58E+00
$SiO_2(aq)$	1.48E-03	2.20E-03	2.29E-03	3.45E-03	5.51E-03	4.45E-02	8.04E-03	4.15E-03	9.34E-02	1.02E-02	8.12E-02
HCO_3^{-}	5.54E-04	5.74E-04	4.55E-04	4.23E-04	1.53E-03	5.03E-01	3.51E-01	2.08E-01	1.14E+00	4.12E-01	1.16E+00
$SO_4^{=}$	1.84E-03	1.93E-03	2.07E-03	3.76E-01	1.02E+00	8.53E-01	1.24E+00	1.64E+00	7.31E-01	1.09E+00	6.51E-01
K^{+}	3.64E-01	9.28E-01	3.00E+00	5.64E+00	4.67E+00	4.30E+00	4.90E+00	4.63E+00	3.93E+00	4.60E+00	3.84E+00
F^{-}	6.31E-05	5.20E-05	3.79E-05	7.53E-04	2.29E-03	8.67E-02	4.42E-02	2.30E-02	2.39E-01	2.07E-01	2.42E-01
NO_3^{-}	5.45E-01	7.62E-01	1.02E+00	3.64E+00	1.20E+00	1.45E+00	2.81E+00	3.86E+00	2.34E+00	3.37E+00	5.58E-01

The other published account of thermally perturbed repository fluids considers formation waters that enter a cooling repository (MDL-NBS-HS-000018 REV 00). Fluids compositions were computed for several locations around the drift but what seemed most pertinent was the information classified as "Front Base (fractures)". Because of their complex history the provenance of the dissolved components in these fluids cannot be readily ascribed to single processes or sources. However, in examining the time-composition histories of these fluids several regularities do appear. The early history can be quite variable but typically the chemistry stabilizes after several centuries. Then, at around "2000 years", most components exhibit a sharp spike in concentration. Within a few centuries, however, this declines back to more modest values, after which not much additional change occurs out to the end of the simulation (100,000 years).

In abstracting information from the document two conditions were evaluated, the peak concentration values at 2,000 years and the (more or less) steady-state long-term concentrations at 100,000 years. The actual concentrations in Table 7 were read from the rather small figures in the body of the report. Thus, they are not as accurate as could be obtained from an EQ3/6 output but still can provide the kinds of "ball park" estimates needed for this report. In the 2,000-year case (Table 7) it was also necessary to adjust the sodium (the most abundant cation) concentration downward to maintain the charge balance while, for the 100,000-year case, the initial composition contained excess negative charge so bicarbonate (the most abundant anion)

was adjusted downward. Original cation and anion concentrations (prior to the charge balance correction) are shown at the bottom of table 7

Table 7: Comparison of formation fluids at two times with the invert average chemistry and the composition of the primary suggested test fluid.

	Peak at 2000 years	Final at 1E5 years	Drip Shield Average	Test Fluid
pH	7.63	8.25	7.75	7 to 8
	molal	molal	molal	molal
HCO_3^-	1.91E-03	*4.86E-03*	3.43E-01	3.43E-01
Ca^{++}	1.66E-02	1.00E-03	6.42E-01	see note
Cl^-	1.58E+00	3.16E-03	6.73E+00	4.45E+00
F^-	1.26E-03	5.62E-04	7.69E-02	7.69E-02
K^+	8.91E-01	2.00E-04	3.71E+00	1.71E+00
Mg^{++}	6.31E-05	1.26E-04	3.19E-04	see note
NO_3^-	7.24E-02	2.63E-04	1.96E+00	9.59E-01
Na^+	*2.74E+00*	8.91E-03	*5.50E+00*	5.50E+00
$SO_4^=$	1.00E+00	1.26E-03	6.91E-01	6.91E-01
$SiO_2(aq)$	6.61E-03	1.26E-03	2.33E-02	see note
TDS g/kg H_2O	2.56E+02	8.88E-01	7.48E+02	4.99E+02
original values	*2.82E+00*	*9.77E-03*	*5.86E+00*	**Charge balance**
before charge	Na^+	HCO_3^-	Na^+	**on chloride**
balance				

*Calcium and magnesium are not compatible with the fluoride and bicarbonate in this recipe; inclusion of silica should be optional.

Recipe Development: Tabulation of the available information on thermally perturbed fluids resulted in the identification of three classes: (1) fluids that evaporated on the drift shield, (2) "2000 year" fluids that gained entry as the repository cooled to below the boiling point of the brine and (3) waters infiltrating over the very long term through a modestly heated block of rock around the repository. Not surprisingly, the fluid returning to the repository after 100,000 years is so dilute as to be reminiscent of the formation waters discussed previously (and, hence, not warranting further evaluation in the context of developing new test fluid recipes). The average fluid that evaporated on the drip shield differs from the 2000-year peak fluid in its higher concentrations of calcium, bicarbonate, nitrate and fluoride, and its higher overall ionic strength. A cursory examination of the drip shield fluid shows that averaging the fluids from bins 1 to 11 clearly resulted in incompatible combinations of calcium fluoride and bicarbonate: fluorite and calcite would immediately precipitate from such a mix. Referring to Table 5 reveals that that the bin fluid chemistries were, initially, *either* high in alkali earth metals or fluoride plus bicarbonate - *but not both*. Hence, this incompatibility is not reflected in any real groundwater and may, therefore, be avoided by preparing recipes that reflect the original distinction between the two types of bin waters. In contrast, a REACT simulation of the 2,000-year formation fluid indicates only a small amount of fluorite should precipitate so the basic incompatibility is not nearly as acute in this mix.

Solutions high in F^- and HCO_3^- and $SO_4^=$, are most relevant because these anions may interfere with iodide and iodate sorption. Consequently, the first thermally derived reference brine preserves elevated concentrations of these constituents (Table 7 "test fluid") while deleting the (incompatible) Ca and Mg. The other constituents in this recipe were then defined *initially* by averaging the 2000-year and the average drip shield brine. Having done this, it was then calculated (using REACT) that K_2SO_4 would also precipitate in considerable quantities (another result of the averaging process, this time the lumping of high and low sulfate solutions with high and low potassium solutions). Taking 1 mole of KNO_3 and 1 mole of KCl out of the mix resolved this issue while preserving the desired high sulfate concentration.

One of the drawbacks of developing brine recipes based on purely theoretical computations is that one cannot anticipate the precipitation of phases not included in the database supporting the program. When this recipe was actually mixed it was found that a mineral not in the REACT database did, in fact, precipitate (kogarkoite, Na_3FSO_4). To prevent this it was also necessary to remove 30 g/kg of NaCl from the recipe defined by the Table 7 "test fluid". In total, these considerations led to the test brine recipe presented in the top half of table 8.

It is not unreasonable to suggest that a situation might arise (addition of substantial amounts of concrete in the construction) where elevated calcium or magnesium concentrations dominated rather than the anions addressed in the preceding mix. To cover such an eventuality a second recipe was formulated from which incompatible fluoride and carbonate and sulfate containing salts were removed, and appropriate amounts of calcium chloride and magnesium nitrate added, as per the levels specified in the test fluid in Table 7. KCl was also substituted for the K_2SO_4, in order to maintain an appropriate potassium concentration (also from Table 7) while avoiding calcium sulfate precipitation. If a chloride level appropriate to the test fluid in Table 7 is to be maintained (in spite of adding calcium and potassium chlorides) it follows that the amount of NaCl added will only result in a total Na level that is about 44% of the Table 7 test fluid concentration. However, this value is still quite "reasonable" as this amount of Na only marginally less than the value actually predicted for the 2000-year brine also shown in Table 7.

In short, two possible recipes might be developed based on a review of the literature and the averaging processes described above. The most interesting option (Table 8, top) places emphasis on achieving an overall salinity near NaCl saturation together with significant bicarbonate, sulfate and fluoride concentrations; while omitting the alkaline earth cations. To test still higher ionic strengths, assess the importance of alkaline earth cations (principally Ca^{++}), and assess the impact of leaving out sulfate, bicarbonate and fluoride, a second recipe was provided (Table 8, bottom). Unlike the other fluids discussed in this section it is not necessary to prepare stock solutions since the concentrations are high enough that the salts can be easily weighed out and added directly.

Table 8: Recipes for testing potential getters in thermally altered fluids

Thermally Altered Fluid with F⁻, HCO₃⁻, SO₄⁼

No Mg++, Ca++	Molal	Formula Wt	Grams per 1 kg H_2O	Grams per 25 kg H_2O
$NaHCO_3$	3.43E-01	82.01	2.81E+01	7.03E+02
$NaCl$ **&**	3.42E+00	58.44	2.00E+02	5.00E+03
NaF **#**	7.69E-02	41.99	3.23E+00	8.07E+01
KNO_3	3.27E-01	101.11	3.31E+01	8.27E+02
K_2SO_4	6.91E-01	147.27	1.02E+02	2.54E+03
$NaNO_3$	6.32E-01	84.99	5.37E+01	1.34E+03

Thermally Altered Fluid With Mg^{++}, Ca^{++}

No F⁻, HCO₃⁻, SO₄⁼	Molal	Formula Wt	Grams per 1 kg H_2O	Grams per 25 kg H_2O
$NaCl$	1.79	58.44	105E+02	2.62E+03
KNO_3	3.27E-01	101.11	3.31E+01	8.27E+02
$NaNO_3$	6.32E-01	84.99	5.37E+01	1.34E+03
$CaCl_2.6H_2O$*	6.42E-01	219.08	1.41E+02	3.52E+03
$Mg(NO_3)_2.6H_2O$	3.19E-04	256.41	8.17E-02	2.04E+00
KCl **	1.38	74.56	1.02E+02	2.57E+03

Adding this level of NaF, with the other sodium and sulfate containing salts, still results in a slightly milky fluid because a little kogarkoite (Na_3FSO_4) precipitates. It readily settles overnight so one option is simply to decant off the clear fluid that will contain the fluoride concentration that is naturally established in the brine. (REACT contains no data for kogarkoite so brine recipes developed using this code cannot anticipate precipitation of this phase.) Secondly, if fluoride is not of concern, then NaF may be omitted from the recipe - which only causes a trivial perturbation in the overall sodium level in the brine. In that case it is also permissible to use the initial NaCl entry that is consistent with Table 7 (see note below, "&"). Finally, in one trial synthesis the kogarkoite actually re-dissolved after a few days so the problem may be temporary.

& The entry for NaCl consistent with Table 7 initially appeared as follows:

NaCl	4.45E+00	58.44	2.60E+02	6.50E+03

However, to minimize kogarkoite precipitation the current entry was substituted.
* Use 7.14E+1 g per kg and 1.79E+3 g per 25 kg if $CaCl_2$ (anhydrous) is available instead of $CaCl_2·6H_2O$.
** KCl was substituted for the K_2SO_4 tabulated in the F⁻-HCO₃⁻-SO₄⁼ -free recipe in the lower half of Table 8. However, if low levels of sulfate are desired then, once the basic mix has been prepared, one may add excess calcium sulfate, shake the slurry for (at least) a day, allow the residual calcium sulfate to settle, and decant (or filter) off the clear supernate.

Waste package leach fluids, definition and selection

Discussion: The leaching of waste packages has been modeled (using the EQ3/6 reaction path program) in some considerable detail (ANL-EBS-MD-000037 REV 03B). Starting fluids for these calculations were based on three fluid chemistries (Table 3); "J-13", "Ca pore water" and

"Na pore waters". These fluid chemistries were then modified to accommodate the somewhat higher CO_2 level in the subsurface, along with some thermal effects. For the first few centuries after a canister breaches (the package is assumed to be breached at the start of the modeling interval) the pH remains low since sulfuric and chromic acids are released by the relatively rapid corrosion of A516 alloy, along with slower corrosion of the 316 and 304 stainless steel components. Once the A516 alloy has been (mostly) consumed the pH raises about one unit. The identity of the waste package contents is important because glass leach fluids are significantly more basic than fluids that leach spent fuel. For the sake of simplicity the following discussion is restricted to considering only the more abundant waste packages containing spent fuel.

The first step was to extract results from the EQ3/6 outputs for different starting fluids ("J-13", "Ca pore water" and "Na pore waters") at an early-low pH-time (~200 years) and a later, more moderate, pH time (10,900 years). The early fluids might alter the phase chemistry of the getters, while the later fluid is the chemical matrix from which iodine would be scavenged. Next, averages were computed for the three ~ 200 year interaction results and, separately, for the three 10,900 interaction study results (Table 9). At this point radioisotopes and trace components were also eliminated from further consideration as neither is relevant to developing simple surrogate fluid recipes for use outside of hot cell facilities. Finally, the electrical neutrality of both averages was restored by adjusting sodium concentrations.

Recipe Development (rust absent): In moving from hypothetical fluids to something that can actually be mixed it is first necessary to eliminate combinations of ions that might cause precipitates to form. CaF_2 and $CaMoO_4$ precipitation both seemed like potential problems so Ca was eliminated from the fluid recipes. (It was a minor constituent, anyway, so it seemed unlikely that this change would affect iodine scavenging.). Next, a modal analysis was made of the solution chemistries to develop tabulations of commercially available salts that might be dissolved to formulate these solutions (Table 10). $NiMoO_4$ is costly and it may prove advantageous to make it in house; see Dury et al., 2003 for a synthesis that sounds relatively straightforward. However, in attempting to prepare a mix from this material it was found it to be relatively insoluble (see following discussion dealing with stock solution preparation) so obtaining this constituent is probably unnecessary. Similarly, the use of CuF_2 is eliminated because its use is problematic; small amounts must be weighed, it is very hygroscopic, and it, too, is not very soluble. Finally, note must be taken of the fact that **CrO_3** is particularly nasty. It forms a strong acid when dissolved in water, is a powerful oxidizing agent, most importantly it is a ***serious carcinogen***. Its use, therefore, requires ***special administrative procedures*** (check with your in-house health organization for guidance in meeting these regulation) because it appears on the ***EPA list of "Particularly Hazardous Chemicals"***.

An additional problem inherent in interpreting Table 9 is that the identity of the dissolved chromate species is not immediately obvious. The obstacle presented by this can be illustrated by considering how to formulate a recipe for the 200-year average fluid. It can be started by mixing (per liter) 0.0172 moles of magnesium sulfate, 0.0184 moles of nickel sulfate and 0.0110 moles of nickel chromate, but this then leaves a deficit of ~0.038 moles of chromium. Since no other cations are present in sufficient quantity to counterbalance this constituent the only way to complete the mix is to add CrO_3, - which promptly reacts with water to form H^+ and $HCrO_4^-$. This suggests a pH around 1.5, while pH values range from 2.1 to 2.5

are what is found when the full recipes are mixed based on using CrO_3 to make up the missing Cr (appendix 3).

A better approach is developed based on the complete composition for such fluids (Table 9). When this is done it becomes evident that the only way to achieve reasonable charge balances (and pH values) is to assume the effective valence of the Cr(VI) species is close to -1 per chromium (-1.005 for the 200-year average, and -1.07 for the 10.900-year average). The Cr(VI) anions with this property are $HCrO_4^-$ and $Cr_2O_7^=$, both of which are predicted by REACT model speciation to exist in about equal amounts in such solution. On the other hand, $CrO_4^=$ is predicted to be a factor of 10 (or more) less abundant, which is consistent with the slight deviations from a -1 chromium species needed to actually achieve a charge balance on the Table 9 inventories. Thus, to develop an appropriate recipe one first uses Na2Cr2O7 to compensate for the charge imbalance inherent in having omitted cationic radionuclides (and other trace constituents) from the recipe. Then, the remainder of the missing chromium could, in theory, be added as either $NiCr_2O_7$ or $Ni(HCrO_4)_2$. Unfortunately, neither constituent can be purchased commercially but nickel bichromate can be prepared in the laboratory by mixing one mole of nickel carbonate, two moles of CrO_3, and a bit of water - and then placing the mix (not too tightly capped) in a drying oven overnight (see detailed instructions below).

As with the surrogate J-13 fluid preparation (described above) it was found that much time could be saved by preparing stock solutions that could then be added together to prepare the final test fluid. In addition, such procedures avoid the transient high concentrations, and subsequent precipitation of metabstable phases, that resulted when all the dry salts were placed together and then dissolved together when water was added.

Table 9: Fluid chemistry after waste package interactions (times after canister breaches "rust absent"):

Element	194.7 years C22C25B Molal	197.6 years C22j25B Molal	225.2 years C22N25B Molal	~200 years Average Molal	Element	10,900 years C22C25B Molal	10900 years C22j25B Molal	10900 years C22N25B Molal	10,900 years Average Molal
pH	4.35	4.44	4.53	4.44E+00	pH	5.67	5.66	5.67	5.67E+00
O	5.59E+01	5.59E+01	5.59E+01	5.59E+01	O	5.62E+01	5.62E+01	5.62E+01	5.62E+01
Al	8.76E-05	5.98E-05	1.22E-04	8.99E-05	Al	6.97E-06	2.85E-06	2.21E-05	1.06E-05
B	1.02E-02	1.04E-02	1.17E-02	1.08E-02	B	3.26E-02	3.26E-02	3.26E-02	3.26E-02
Ba	5.31E-08	5.36E-08	5.68E-08	5.45E-08	Ba	8.80E-07	8.99E-07	8.76E-07	8.85E-07
Ca	9.67E-04	3.41E-04	6.50E-04	6.53E-04	Ca	6.66E-05	5.23E-05	6.35E-05	6.08E-05
Cl	6.22E-04	2.12E-04	7.24E-04	5.20E-04	Cl	5.93E-04	2.02E-04	6.81E-04	4.92E-04
Co	2.41E-04	2.51E-04	1.64E-04	2.18E-04	Co	1.17E-06	1.20E-06	1.16E-06	1.17E-06
Cr	4.65E-02	4.71E-02	5.33E-02	4.90E-02	Cr	1.43E-01	1.43E-01	1.43E-01	1.43E-01
Cs	1.17E-03	1.22E-03	2.08E-03	1.49E-03	Cs	2.75E-06	2.47E-06	4.26E-08	1.75E-06
Cu	1.88E-03	1.91E-03	2.16E-03	1.98E-03	Cu	7.78E-04	7.96E-04	7.71E-04	7.82E-04
F	1.88E-04	1.21E-04	3.39E-04	2.16E-04	F	1.79E-04	1.15E-04	3.18E-04	2.04E-04
Fe	1.61E-10	1.64E-10	1.28E-10	1.51E-10	Fe	9.27E-12	9.37E-12	9.23E-12	9.29E-12
Gd	2.91E-03	3.06E-03	1.53E-03	2.50E-03	Gd	2.51E-07	2.31E-07	2.97E-07	2.60E-07
H	1.11E+02	1.11E+02	1.11E+02	1.11E+02	H	1.11E+02	1.11E+02	1.11E+02	1.11E+02
C	5.70E-05	5.73E-05	9.86E-05	7.10E-05	C	4.50E-05	4.45E-05	4.10E-05	4.35E-05
P	1.42E-08	1.43E-08	1.42E-08	1.42E-08	P	2.36E-08	2.35E-08	2.36E-08	2.36E-08
I	7.36E-17	7.33E-17	7.08E-17	7.26E-17	I	9.79E-26	9.86E-26	9.12E-26	9.59E-26
K	3.54E-06	3.38E-06	7.17E-06	4.70E-06	K	1.95E-04	1.29E-04	1.57E-04	1.60E-04
Li	7.36E-17	7.33E-17	7.08E-17	7.26E-17	Li	9.79E-26	9.86E-26	9.12E-26	9.59E-26
Mg	1.87E-02	1.82E-02	1.47E-02	1.72E-02	Mg	5.64E-04	1.85E-05	2.24E-05	2.02E-04
Mn	3.16E-08	3.29E-08	2.12E-08	2.86E-08	Mn	1.16E-10	1.19E-10	1.15E-10	1.16E-10
Mo	4.44E-04	4.28E-04	6.40E-04	5.04E-04	Mo	7.56E-03	9.70E-03	7.94E-03	8.40E-03
N	2.75E-04	3.83E-04	2.72E-04	3.10E-04	N	7.77E-04	8.77E-04	7.42E-04	7.99E-04
Na	1.78E-03	2.10E-03	5.59E-03	3.15E-03	Na	1.70E-03	1.99E-03	5.25E-03	2.98E-03
Ni	2.79E-02	2.83E-02	3.20E-02	2.94E-02	Ni	8.28E-02	8.50E-02	8.20E-02	8.33E-02
Np	2.18E-04	2.22E-04	1.79E-04	2.06E-04	Np	1.36E-05	1.38E-05	1.36E-05	1.36E-05
Pb	7.36E-17	7.33E-17	7.08E-17	7.26E-17	Pb	9.79E-26	9.86E-26	9.12E-26	9.59E-26
Pu	2.43E-03	2.53E-03	4.32E-03	3.09E-03	Pu	5.71E-06	5.12E-06	8.91E-08	3.64E-06
Ru	3.07E-13	3.08E-13	3.02E-13	3.06E-13	Ru	2.90E-13	2.90E-13	2.90E-13	2.90E-13
S	3.64E-02	3.61E-02	3.43E-02	3.56E-02	S	4.96E-04	3.12E-04	4.45E-04	4.18E-04
Si	1.03E-04	1.04E-04	1.03E-04	1.03E-04	Si	9.29E-05	1.08E-04	1.07E-04	1.03E-04
Tc	7.19E-04	7.49E-04	1.28E-03	9.16E-04	Tc	1.69E-06	1.52E-06	2.62E-08	1.08E-06
Ti	2.18E-47	2.18E-47	2.18E-47	2.18E-47	Ti	2.17E-47	2.17E-47	2.17E-47	2.17E-47
U	1.35E-03	1.38E-03	9.17E-04	1.22E-03	U	1.36E-05	1.18E-05	1.74E-05	1.43E-05
Zn	1.66E-03	1.68E-03	1.90E-03	1.75E-03	Zn	1.05E-10	1.05E-10	9.72E-11	1.02E-10
Zr	8.73E-12	8.88E-12	7.48E-12	8.36E-12	Zr	3.61E-12	3.61E-12	3.62E-12	3.61E-12
Fe_2O_3 moles	3.94E+01	3.94E+01	3.94E+01	3.94E+01	Fe_2O_3 moles	4.38E+01	4.37E+01	4.37E+01	4.37E+01

Table 10: Synthetic water chemistries for waste package leach fluids (**rust absent**):

Composition and recipe for 200 year waste package leachate

	Molal Recipe	Molal Target	Modal Salt Amounts	Moles/kg H_2O	Formula Weight	g per 1 liter	g per 25 liter
B	1.08E-02	1.08E-02	Na_2SO_4	5.57E-03	142.04	7.91E-01	1.98E+01
Co	2.18E-04	2.18E-04	$MgSO_4$	1.72E-02	120.37	2.07E+00	5.17E+01
Cl	4.37E-04	5.20E-04	Cs_2SO_4	7.44E-04	361.87	2.69E-01	6.73E+00
Mg	1.72E-02	1.72E-02	$CuSO_4.5H_2O$	1.98E-03	249.68	4.95E-01	1.24E+01
Cr	4.89E-02	4.90E-02	$Gd_2(SO_4)_3.8H_2O$	1.25E-03	746.81	9.34E-01	2.33E+01
Cu	1.98E-03	1.98E-03	$NiSO_4.6H_2O$	6.34E-03	262.86	1.67E+00	4.17E+01
NO₃	6.04E-04	3.10E-04	$Ni(HCrO_4)_2$*	2.30E-02	292.71	6.74E+00	1.69E+02
Ni	2.94E-02	2.94E-02	$Zn(HCrO_4)_2$*	1.45E-03	299.37	4.34E-01	1.08E+01
SO₄	3.55E-02	3.56E-02	$Zn(NO_3)_2.6H_2O$	3.02E-04	297.47	9.00E-02	2.25E+00
Zn	1.75E-03	1.75E-03	$Na_2MoO_4.2H_2O$	5.04E-04	241.95	1.22E-01	3.05E+00
Na *	**1.21E-02**	**1.21E-02**	H_3BO_3	1.08E-02	61.83	6.68E-01	1.67E+01
K	2.16E-4	4.70E-06	**Minor Constituents**				
Gd	2.50E-03	2.50E-03	$CoCl_2.6H_2O$	2.18E-04	237.93	5.19E-02	1.30E+00
F	2.16E-04	2.16E-4	KF	2.16E-04	58.1	1.25E-02	3.14E-01
Mo	5.04E-04	5.04E-04	* In-house preparation				
Cs	1.48E-03	1.49E-03	required.				

*required for charge balance

Ca deleted to prevent $CaMoO_4$ and CaF_2 precipitation

Composition and recipe for 10,900 year waste package leachate

	Recipe	Target	Modal Salt Amounts	Moles/kg H_2O	Formula Weight	g per 1 liter	g per 25 liter
B	0.03255169	0.03255169	$CrO3$	1.41E-01	99.99	1.41E+01	3.52E+02
Cl	0.00049179	0.00049179	$Ni(OH)_2$	7.49E-02	92.73	6.94E+00	1.74E+02
Mg	0.00020155	0.00020155	H_3BO_3	3.26E-02	61.83	2.01E+00	5.03E+01
Cr	0.14286437	0.14286437	$NiMoO_4$	8.40E-03	218.63	1.84E+00	4.59E+01
Cu	0.00051958	0.00078182	$Na_2Cr_2O_7.2H_2O$	8.45E-04	298	2.52E-01	6.30E+00
NO₃	0.00079867	0.00079867	**Minor Constituents**				
Ni	0.08329005	0.08329005	$CuSO_4.5H_2O$	4.18E-04	249.68	1.04E-01	2.61E+00
SO₄	*0.00041764*	*0.00041764*	$NaNO_3$	7.99E-04	84.99	6.79E-02	1.70E+00
Na	0.00318636	0.00298061	$MgCrO_4.5H_2O$	2.02E-04	230.38	4.64E-02	1.16E+00
K	0.00016018	0.00016018	$Na_2SiO_3.9H_2O$	1.03E-04	284.2	2.92E-02	7.31E-01
Si	0.00010287	0.00010287	NaCl	4.92E-04	57.96	2.85E-02	7.13E-01
F	0.00020388	0.00020388	$K_2Cr_2O_7$	8.01E-05	294.19	2.36E-02	5.89E-01
Mo	0.0084017	0.0084017	CuF_2 @	1.02E-04	101.54	1.04E-02	2.59E-01
			{ @ Substitute **NaF** for CuF_2 }	{ 2.04E-4 }	(41.99)	{ 8.57E-3 }	{ 2.14E-1 }

Recipe for mixing the 200-year fluid (rust absent)

1. Use **all (~ 20 ml)** to make 1 liter of fluid
   2.07 g of **MgSO₄**
   0.791 g of **Na₂SO₄** (increase to 0.897 g if neither Cs₂SO₄ or K₂SO₄ are to be employed)
   0.269 g of **Cs₂SO₄** (or, 0.130 g of **K₂SO₄** if Cs is not of importance)
   0.495 g of **CuSO₄.5H₂O**
   1.67 g of **NiSO₄.6H₂O**
   20 g of **deionized water**

2. Use **1 ml** to make 1 liter of fluid
   2.25 g of **Zn(NO₃)₂.6H₂O;**
   If the slightly elevated level of nitrate resulting from this selection presents problems an exact match with the recipe can be obtained by decreasing the amount of zinc nitrate to 1.152 g, while slightly incrementing the amount of ZnO added (see step 7).
   1.30 g of **CoCl₂.6H₂O**
   25 g of **deionized water**

3. Use **1 ml** to make 1 liter of fluid
   3.05 g of **Na₂MoO₄.2H₂O**
   25 g of **deionized water**

4. Use **just 20 ml** to make 1 liter of test fluid
   0.0625 g of **KF**
   3.34 g of **H₃BO₃**
   100 g of **deionized water**

5. Use **all (~ 50 ml)** to make 1 liter of test fluid
   0.935g of **Gd₂(SO₄)₃.8H₂O** (0.755 g of **Gd₂(SO₄)₃** – no water, or 0.772 grams of **Nd₂(SO₄)₃** – no water, or 0.902 g of **Nd₂(SO₄)₃.8H₂O**)
   50 g of **deionized water**

6. Use **all (~ 50 ml)** to make 1 liter of test fluid
   6.74 g of **Ni(HCrO₄)₂**, made with 2.73 g of **NiCO₃** and 4.60 g of **CrO₃** plus
   50 g of **deionized water**

7 Use **2 ml** to make 1 liter of test fluid
   "0.434 g of **Zn(HCrO₄)₂*"**, made with 0.118 g of **ZnO** (or 0.182 g **ZnCO₃**) and 0.290 g of **CrO₃,** (0.130 g ZnO, or 0.200 g ZnCO₃, to achieve an exact match for the nitrate in the recipe; note also the reduction in zinc nitrate described in step 2.)
   20 g of **deionized water**

Recipe for mixing the 10900-year fluid (rust absent)

1. Use **all (100 ml)** to make 1 liter of fluid
   39.0 g of **Ni(HCrO$_4$)$_2$**; prepared from 15.8g **NiCO$_3$** and 13.3 g of **CrO$_3$.**
   100 g of **deionized water**

2. Use **all (~ 20 ml)** to make 1 liter of fluid
   0.0419 g of **MgCl$_2$·6H$_2$O**
   0.888 g of **Na$_2$Cr$_2$O$_7$·2H$_2$O**
   0.104 g of **Cu$_2$SO$_4$·5H$_2$O**
   0.0847 g of **Cu(NO$_3$)$_2$·2.5 H$_2$O**
   3.970 g of **NiCl$_2$·6H$_2$O** [#&]
   20 g of **deionized water**

3. Use **all (20 ml)** to make 1 liter of fluid
   1.33 g of **Na$_2$CrO$_4$** [#]
   2.03 g of **Na$_2$MoO$_4$·2H$_2$O** [#]
   0.0093 g of **KF**
   20 g of **deionized water**

4. Use **all (20 ml)** to make 1 liter of fluid
   2.01 g of **H$_3$BO$_3$**
   20 g of **deionized water**

[#] Prior to adding these components the preparation had a proportionally smaller nickel deficit that would be charge-balanced with molybdate and chromate (not dichromate or bichromate). NiCrO$_4$ is not commercially available and mixing Na$_2$CrO$_4$ and Ni(NO$_3$)$_2$·6H$_2$O produces a red orange precipitate. Thus, even if the compound were commercially available it might still have such a low solubility that it would not be useful in preparing (relatively concentrated) stock solutions. In contrast, NiMoO$_4$ can either be prepared or purchased (at a relatively high cost) but, both materials proved to be quite insoluble. In keeping with the philosophy of trying to define recipes that are easily mixed these deficits are, instead, made up using salts that are, inexpensive, readily available, and soluble: sodium chromate, nickel chloride and sodium molybdate. This fix is, effectively, the same as adding a small amount of excess sodium chloride to the mix. Since Table 9 was compiled from models that had almost certainly overlooked some potential NaCl sources this approach should not be seriously flawed.

[&] If excess sulfate is deemed preferable to excess chloride then 4.39g of **NiSO$_4$·6H$_2$O** may be substituted for the nickel chloride hydrate.

.

Impact of rust on waste package leach fluid chemistry

One shortcoming of the EQ3/6 computations in Table 9 (and one that is acknowledged in ANL-EBS-MD-000037 REV 03B) is that the code did not evaluate the effects of surface complexation reactions with the rust. Rust is both chemically active and will be present in considerable amounts because the massive waste packages will corrode (see Table 9; bottom line: moles Fe_2O_3 as tabulated is per liter of fluid). Additional calculations were, therefore, carried out to account for this factor (Appendix 1) using REACT, which does have a surface complexation database derived from the approach developed by Dzombak and Morel, 1990. Custom alterations were also made to the commercially available database to account for actinide sorption (see Appendix 2).

With these additions it was possible to model the resulting fluid chemistry starting with the complete (averaged) analyses from Table 9, rather than the simplified composition extracted into Table 10. And, again, charge balance was maintained by adjusting the sodium level. Both the early and late (average) waste package leach fluids were reacted with the appropriate amounts of iron oxide (also from Table 9) assuming that goethite would be the principle iron corrosion product. This choice turns out to not be critical to the outcome since most of the important changes occurred before even 10% of the rust inventory was (computationally) "added" to the fluid.

It was noted earlier that after 2000 years there was still a potential for producing highly evaporated (and concentrated) brines, but by the time 10^5 years had elapsed the expected salinity of fluids entering the repository was so low as to resemble the unperturbed groundwater(s) initially added to the model (similar to Table 3). It is likely that some of the containers will be breached in the intervening time and that some intermediate degree of evaporation may influence the chemistry of the fluids coming in contact with the waste. Fortunately, REACT also has the option of reacting "negative" water, which concentrates solutes and simulates evaporation. Such calculations are not as elegant as those described earlier (regarding fluids from the invert) since the ionic strength is high enough that using Pitzer activity coefficients would be preferential but the YMP-developed extended Pitzer activity coefficient database is not (yet) available in a form that can be used with the Geochemist's Workbench codes. However, the REACT results should still provide some perspective on the expected fluid chemistries. Thus, in all, Table 11 provides five fluid chemistries for both the early and late time fluids:

     a. The initial "average" fluids for the two times *from Table 9 – not Table 10* (with charge balances achieved by adjusting Na levels);

     b. The fluid chemistries that resulted when these two fluids were equilibrated using the Geochemist's Workbench database (e.g. after insoluble combinations of ions were, computationally, removed from the recipe – similar to the manual process described earlier which led to the decision to eliminate calcium from the recipes in table 10);

     c. The fluid chemistries that result when the fluids were evaporated by 90% with no goethite present (Scenario 1);

     d. The chemistries that result when the fluids both react with goethite and lose 90% of the water to evaporation (Scenario 2);

     e. The chemistries that result when these fluids react with appropriate amounts of goethite but are not subject to evaporation (Scenario 3).

In Table 11 it is **important to note** that the values given for the individual components are the **number of moles that remain in the fluid at the end of the run (not the molal concentration!).** The weights of water, and solution, present at the end of the run are given at the top of the table and computing molal concentrations involves nothing more than moving a decimal point appropriately. Data were tabulated in this form because: (1) simplicity; REACT outputs appear in this form so assembling the table only required conducting multiple cut and paste operations and, (2) this format facilitates the ready identification of constituents that are removed from solution as a consequence of the processes modeled in scenarios 1-3.

Table 11: Waste package leach fluid chemistries calculated for early and late time periods – *moles remaining in the fluid, not molal concentartions.*

	~200 Years	~200 Years	~200 Years	~200 Years	~200 Years
Goethite	No	No	No	Yes	Yes
Evaporation	No	No	90% evap.	90% evap.	No
	Initial Fluid	Equilibrated	Scenario 1	Scenario 2	Scenario 3
Solvent Mass - kg	1.00	1.00	0.10	0.10	1.00
Solution Mass - kg	1.02	1.02	0.12	0.10	1.00
pH	4.44	2.56	2.23	8.12	8.16
Aluminum	8.99E-05	8.99E-05	8.99E-05	1.27E-07	1.15E-06
Boron	1.08E-02	1.08E-02	1.08E-02	2.95E-05	2.41E-04
Calcium	6.53E-04	6.02E-04	6.02E-04	8.31E-09	3.87E-08
Carbon	7.10E-05	7.10E-05	7.10E-05	1.29E-05	7.10E-05
Cesium	1.49E-03	1.49E-03	1.49E-03	1.49E-03	1.49E-03
Chlorine	5.20E-04	5.20E-04	5.20E-04	5.20E-04	5.20E-04
Chromium	9.80E-02	9.80E-02	9.47E-02	9.34E-06	4.62E-05
Cobalt	2.18E-04	2.18E-04	2.18E-04	7.34E-15	6.61E-14
Copper	1.98E-03	1.98E-03	1.98E-03	3.18E-13	2.34E-12
Europium	2.50E-03	2.50E-03	2.50E-03	3.81E-08	1.31E-07
Fluorine	2.16E-04	2.16E-04	2.16E-04	2.16E-04	2.16E-04
Hydrogen	1.11E+02	1.11E+02	1.12E+01	1.12E+01	1.11E+02
Iron	1.51E-10	1.51E-10	1.51E-10	3.29E-13	3.22E-12
Magnesium	1.72E-02	1.72E-02	1.72E-02	1.71E-02	1.72E-02
Neptunium	2.06E-04	2.06E-04	2.06E-04	2.17E-14	1.70E-13
Nickel	2.94E-02	2.94E-02	2.94E-02	1.36E-10	6.38E-10
Nitrogen	3.10E-04	3.10E-04	3.10E-04	3.10E-04	3.10E-04
Oxygen	5.61E+01	5.60E+01	6.07E+00	5.62E+00	5.56E+01
Plutonium	3.09E-03	1.17E-05	2.21E-05	3.18E-13	3.25E-13
Potassium	4.70E-06	4.70E-06	4.70E-06	4.70E-06	4.70E-06
Silicon	1.03E-04	5.91E-18	4.77E-18	4.29E-23	4.16E-22
Sodium	5.17E-02	5.17E-02	5.17E-02	5.17E-02	5.17E-02
Sulfur	3.56E-02	3.45E-02	3.45E-02	8.20E-04	2.18E-03
Technetium	9.16E-04	9.16E-04	9.16E-04	9.16E-04	9.16E-04
Uranium	1.22E-03	5.64E-05	1.02E-05	2.04E-12	4.93E-12
Zinc	1.75E-03	1.75E-03	1.75E-03	1.87E-12	7.92E-13

	10,900 Years	10,900 Years	10,900 Years	10,900 Years	10,900 Years
Goethite	No	No	No	Yes	Yes
Evaporation	No	No	90% evap.	90% evap.	No
	Initial Fluid	Equilibrated	Scenario 1	Scenario 2	Scenario 3
Solvent Mass - kg	1.00	1.00	0.10	0.10	1.00
Solution Mass - kg	1.04	1.04	0.14	0.11	1.01
pH	5.67	5.66	5.94	8.13	8.18
Aluminum	1.06E-05	1.06E-05	1.06E-05	1.33E-07	1.22E-06
Boron	3.26E-02	3.26E-02	3.26E-02	6.69E-05	6.48E-04
Calcium	6.08E-05	5.37E-05	1.63E-05	7.52E-10	3.07E-09
Carbon	4.35E-05	4.35E-05	4.35E-05	4.35E-05	4.35E-05
Cesium	1.75E-06	1.75E-06	1.75E-06	1.75E-06	1.75E-06
Chlorine	4.92E-04	4.92E-04	4.92E-04	4.92E-04	4.92E-04
Chromium	2.86E-01	2.86E-01	2.86E-01	2.74E-05	1.42E-04
Cobalt	1.17E-06	1.17E-06	7.83E-07	7.67E-15	7.04E-14
Copper	7.82E-04	7.82E-04	3.14E-05	1.30E-13	8.98E-13
Europium	2.60E-07	2.60E-07	2.60E-07	7.14E-08	9.54E-08
Fluorine	2.04E-04	2.04E-04	1.29E-04	2.04E-04	2.04E-04
Hydrogen	1.11E+02	1.11E+02	1.12E+01	1.15E+01	1.11E+02
Iron	9.29E-12	9.29E-12	1.34E-14	3.37E-13	3.24E-12
Magnesium	2.02E-04	2.02E-04	2.02E-04	2.02E-04	2.02E-04
Neptunium	1.36E-05	1.36E-05	1.25E-05	1.51E-15	1.08E-14
Nickel	8.33E-02	8.31E-02	8.31E-02	3.96E-10	1.66E-09
Nitrogen	7.99E-04	7.99E-04	7.99E-04	7.99E-04	7.99E-04
Oxygen	5.66E+01	5.66E+01	6.68E+00	5.76E+00	5.57E+01
Plutonium	3.64E-06	6.88E-09	6.40E-08	2.86E-12	3.14E-14
Potassium	1.60E-04	1.60E-04	1.60E-04	1.60E-04	1.60E-04
Silicon	1.03E-04	9.33E-04	6.60E-10	1.70E-06	1.80E-05
Sodium	1.39E-01	1.39E-01	1.39E-01	1.39E-01	1.39E-01
Sulfur	4.18E-04	4.18E-04	4.18E-04	6.97E-06	2.10E-05
Technetium	1.08E-06	1.08E-06	1.08E-06	1.08E-06	1.08E-06
Uranium	1.43E-05	2.22E-25	1.81E-23	1.04E-26	1.65E-28
Zinc	1.02E-10	1.02E-10	1.02E-10	1.10E-19	4.56E-19

Several aspects of this modeling exercise are noteworthy. When rust is added the acidic waste package corrosion fluids (discussed in the last section) are replaced by mildly basic solutions (as the originators of ANL-EBS-MD-000037 REV 03B noted repeatedly). Secondly, assuming the equilibrium constants in the sorption database are roughly correct (Appendix 2), the elevated actinide concentrations initially present in the acidic (rust free) leach fluids are no longer present. In part, this reflects sorption onto the iron oxide, and partly the precipitation of phases such as uranophane and PuO2(c) that is favored by the elevated pH that resulted from adding goethite to the system. Parenthetically, even if all the solid forms of Pu(IV) in the database are suppressed the code still predicts low dissolved Pu concentrations (less than 10-10 molal) because the

PuO2++ is then quantitatively scavenged from solution by sorption onto goethite. Eliminating PuO2(c) precipitation also raises the equilibrium pH of the rust-free, unevaporated, fluid of the ~200 year time from 2.56 (Table 11, column 2) to 3.63 (resulting solution chemistry is not tabulated). When rust is present most of the boron (from the borated steel - added as a neutron poison to the waste packages) also sorbs onto the rust where, fortuitously, it would remain in close proximity to the actinides.

The remaining dissolved constituents responded to evaporation in two distinct ways (Table 11). Some major constituents (bicarbonate, Cs, Cl, F, Mg, nitrate, K, Na, and TcO4-) were merely concentrated, while others (borate, chromate and sulfate) were partially removed by further sorption onto the rust as their concentrations increased. Several minor or trace constituents were also removed by sorption progressively during evaporation in both solutions: Al, Ca, Co, Cu, Eu, Fe, Np, Ni and silicate. However, trace levels of Pu, U and Zn remaining in solution behaved differently, depending on which fluid evaporated.

It is the predicted major element chemistries that are of greatest importance (and most immediate interest) in developing surrogate test solutions. The principle anions present in the late leach solution are:

NO_3^- (7.99E-4 m) > borate (6.48E-4 m) > Cl (4.92E-4 m) > F (2.04E-4 m) > $CrO_4^=$ (1.42E-4 m) > HCO_3^- (4.25E-5 m) > $SO_4^=$ (2.10E-5 m) > Silicate (1.80E-5 m) .

The principle anions in the early leach solution in contact with the rust are:

$SO_4^=$ (2.18E-3 m) > TcO4- (9.16E-4 m) > Cl (5.20E-4 m) > HCO_3^- (3.10E-4 m) > borate (2.41E-4 m) > F (2.16E-4 m) > HCO_3^- (7.10E-5 m) > $CrO_4^=$ (4.62E-5 m).

An interesting result is that when the early leach solution evaporates additional sulfate is sorbed onto the rust. This produces a fluid in which (at least formally) *pertechnetate becomes the dominant anion*! This same computation process would also predict significantly elevated levels of other soluble, non-sorbing radionuclides, *including iodide*. ORIGIN run results indicate that after 10,000 years the relative abundances (in a PWR spent fuel assembly) of the readily soluble fission products are (on a molar basis): [99]Tc: 1.00, [127]I: 0.0744, [129]I: 0.240, [133]Cs: 1.51, and [135]Cs: 0.400 (Croff and Alexander, 1980). It follows that a Tc concentration of 9.16x10^{-3} molar (Table 13) implies an iodine concentration of 2.91x10^{-3} molar [129>127]I (or about 375 ppm I). This clearly constitutes an exception to the overall perspective of this document that getters will only have to scavenge radionuclides at tracer levels, and at concentrations much below those of the (presumably dominant) non-radioactive constituents in solution.

There is no immediate way of resolving this contradiction, but is worth noting that other S&T programs are in the process of trying to develop a better understand of the "real" mobility of technetium in repository-relevant environments (Brady, et al., 2006). At issue is the question of whether the large amounts of spent fuel and metallic iron (plus Cr and Ni) will impact Tc mobility during the early stages of fuel leaching (when most of the soluble radionuclides would probably go into solution). In this setting it seems likely that transient, localized, reducing environments may exist (inside partly degraded waste packages) where Tc(VII) will be reduced

to Tc(IV). In this reduced state it is reasonable to postulate that Tc may be permanently immobilized in the massive amounts of rust that are forming simultaneously. Consequently, the best choice for our purposes may not be a test solution recipe in which ReO_4^- (the best non-radioactive surrogate for TcO_4^-) is the dominant anion. Instead, a more forward-looking approach would involve testing with a reduced level of Tc, for simplicity set at a level commensurate with the amount of Cs presumed to be present. This arbitrary, "fix" "solves" the problem of developing test fluid recipes, but leaves unaddressed how a getter would be tested (and function) in settings where iodine (and other radionuclides) are actually the dominant components in a waste-leach solution.

A second odd aspect of these calculations is that it turns out that one cannot actually directly tabulate the cation content of the fluids using the REACT output. This happens because adding rust to the computational system also adds a large excess positive charge (as compared to the dissolved anion concentrations in the same listing). This, then, is compensated for by the dissolved anions, leaving an apparent excess of positive charge in the solution. When these surface effects are accounted for (calculation not shown) the overall ratio of positive to negative charges (e.g., in the total system) is essentially 1.

Physically, the apparent large positive charge excess reflects contributions from both freely dissolved cations (counterbalancing dissolved anions) and those cations residing in the double layer at the goethite surface (counterbalancing negative surface charges). Cations bound in the double layer are no more mobile than the iron oxide particles with which they are associated. And, in particular, they are not free to travel with a solution that leaves the rust and drips onto the invert.

The problem of developing a drip-solution chemistry can be resolved by referring back to the solutions that were input into the model (prior to making any corrections for sorption). In particular, in the 10,900 year fluid simple, mass balance arguments show that only Na and Mg could be present in sufficient amounts to potentially counterbalance the dissolved anions, while for the ~200 year fluid, Cs is also a minor player. Further, if one examines how REACT models the behavior Mg relative to Ca one finds, rather surprisingly, that most of the calcium is sorbed onto the rust – but none of the magnesium behaves in this way. The explanation for this oddity lies in the fact that the database used to compute metal sorption simply contains no data on Mg sorption (nor, for that matter, does the original database advanced by Dzombak and Moral, 1990).

The few existing studies on Mg sorption suggest that interactions with rust are quite weak, and probably resemble the behavior of Sr^{++} (see, for example, Kinniburgh et al., 1976). Running REACT using Sr^{++} (which is represented in the sorption database) as a surrogate for Mg^{++} (while suppressing celestite and strontianite precipitation) shows that, that, like Ca^{++}, any Sr^{++} should also be quantitatively removed by sorption. By inference, one can also conclude that in the "real world" Mg should also be essentially gone from such solutions. Thus, by a process of elimination, sodium, with minor Cs and traces of K, are the only cations left to charge-balance anion content of the solution that drips onto the invert.

As these constituents are not sorbed onto iron oxides they should be available to maintain charge balance in the freely moving fluid in approximately the same ratios as they occurred in the initial input fluids (Table 12). Since sodium greatly outweighs the other cations a pragmatic approach to making up test solutions would also involve simply adding the major anionic constituents using readily available sodium salts. Further, since the amount of Na greatly outweighs that of potassium, it would also be pragmatic to not worry about explicitly adding this component at some pre-specified level. (However, options that implicitly add K are, in fact, included in the recipe section that follows.).

Table 12: Initial concentrations of non-sorbing cations (from Table 12) and molar ratios of minor constituents to initial sodium concentrations.

Input Fluid	Na-Molal	Cs-molal	K-molal	Cs/Na molal	K/Na molal
200 years	5.17E-02	1.49E-03	4.70E-06	2.88E-02	9.09E-05
10,900 years	1.39E-01	1.75E-06	1.60E-04	1.26E-05	1.15E-03

Recipe Development (rust present): So far, the discussion has considered input fluids from two times, as well as the impacts of evaporation and sorption onto "goethite" corrosion products. The variability in major fluid constituents resulting from these deliberations is summarized on the left side of Table 13. To be useful, however, it is necessary to abstract the "important" chemistry from all these calculations and develop a test fluid recipe. In general, given the massive size and presumed longevity of the waste containers, it is more likely that the getters will have to perform in a fluid having the 10,900-year chemistry, than in one with the 200-year fluid chemistry.   It is, noteworthy, that this contradicts the current YMP-PA position that presumes (unrealistic) early canister failure and high Cs and Tc concentrations in the 200-year fluid (Tables 11, 12).   However, the first fluid that actually encounters the waste will still leach out most of the soluble Cs, I and some Tc. Consequently, some accommodation needs to be made even when the remainder of a recipe being developed reflects a later-stage fluid chemistry. It also seems reasonable, from the standpoint of establishing credible over-test conditions (commensurate with our short-term perspective on testing) that an accommodation be made for at least a modest degree of evaporative concentration.

As a basis for defining the major constituents in the test fluid it was decided to use the 90% evaporated case for the 10,900-year fluid and simply mix the principle non-radioactive constituents using sodium salts.   The amount of Cs to be added was, then, determined by multiplying the (higher) Cs: Na ratio found in the 200 year - 90% evaporation recipe by the level of Na from the 10,900 - 90% evaporation year recipe (e.g., the sodium concentration that results from adding the principle anionic components, except boric acid, as sodium salts). As stated above, the amount of ReO_4^- (the TcO_4^- surrogate) added was then *arbitrarily chosen* to be comparable to the amount of Cs. Parenthetically, the higher levels of Re/TcO_4^- (and corresponding iodine concentrations), can – if needed – be deduced from the Tc concentrations associated with the individual fluid compositions in Table 12, in conjunction with the Tc:I ratios tabulated above for the PWR fuel elements (from which the radionuclides are, ultimately, derived).

Since $CsReO_4$ is not readily available commercially there is a question of which salts to use in adding Cs and Re. One could choose to add Cs_2SO_4 and $KReO_4$, with the objective of

incrementally increasing the concentrations of constituents (K^+ and $SO_4^=$) that probably are at unrealistically low levels in the 10,900-year formalism anyway. Alternatively, the use of CsCl and $NaReO_4$ would only result in trivial increments in the amounts of Na and Cl already present in the recipe.   The first option was arbitrarily chosen as the standard because it seems to present a (marginally) more appropriate fluid to experiment with. Finally, both Cs^+ or ReO_4^- are trace constituents in the current formulation. It follows that a second pragmatic choice (given availability and cost concerns) might also be to simply leave them out and substitute potassium sulfate ($\sim 2.32 \times 10^{-4}$ molar K_2SO_4).

Overall sulfate levels are also worth discussing since, other than the elevated radionuclide concentrations just addressed, this is only major difference between the 90% evaporated 200 and 10,900 year fluids. If a scenario arises where testing with an early fluid chemistry becomes important, then the only adjustment needed would be an increase in sulfate (added as sodium sulfate; from 6.98×10^{-5} to 8.20×10^{-3} molar).

*Recipe for "late" waste package corrosion test fluid assuming that **rust is present**:*

    1. Add 2 ml to make up 1 liter of test solution:
        0.248 g of **Na_2SO_4** [##]
        2.10 g of **Cs_2SO_4** [#]
        3.36 g **KReO4** [#]
        ([#] 1.01 g of **K_2SO_4** may be used if Cs^+ and ReO_4^- are not needed.)
        ([##] Use 1.32 g of **K_2SO_4** if the Na_2SO_4 is left out of the recipe along with the Cs^+ and ReO_4^- salts. This results in a trivial change in the total sodium, helps to restore a plausible level of potassium to the fluid, and avoids weighing out a small amount of still another component.)
        0.914 g of **$NaHCO_3$**
        7.19 g of **NaCl**
        17.0 g of **$NaNO_3$;** $NaNO_3$ dissolution is highly endothermic and will significantly cool the solution which - in turn - temporarily suppresses the solubility of other components. It is advisable to let the solution warm before adding the additional constituents:
        50 g of **deionized water**.

    2. Add 1 ml to make up 1 liter of test solution:
        1.03 g of **H_3BO_3**; adding this component to mix #1(above) resulted in a small amount of initial bubble production, presumably from interactions with bicarbonate. Since long term stability is important a better strategy seemed to be to prepare this additional stock solution.
        1.11 g of **Na_2CrO_4**; since Na in this recipe is elective, e.g. it just balances anions, 1.02 grams of $Na_2C_2O_7$ can be substituted. It is noteworthy that when a trial was carried out by adding dichromate to mix #1 (above) vigorous bubbling resulted. This, presumably, results from exposing bicarbonate to acid generated by: $Cr_2O_7^= + H_2O \rightarrow 2CrO_4^= + 2\ H^+$. Hence, this component was shifted to the second stock solution.
        25 g of **deionized water**

2. Add 3 ml to make up 1 liter of test solution:

    2.14 g of **NaF**

    0.121g of **$Na_2Si_3O_8 \cdot 9H_2O$**

    75 g of **deionized water**; the salts all essentially dissolve in 50 ml of water (in which case then just add 2ml per liter of test solution) but the extra 25 ml greatly facilitates the dissolution process, as does gentle heating.

    To increase the sulfate level by an amount appropriate to the 200 year fluid dissolve 1.11 g or **Na_2SO_4** in 25 g of **deionized water**, and add the complete amount to 1 liter of fluid.

Table 13: Reference test solution chemistry and recipe for waste leachate that has interacted with waste package corrosion products (rust present).

	10,900 Years 90% evap. Scenario 2 **Molal**	~200 Years 90% evap. Scenario 2 **Molal**	10,900 Years No evap. Scenario 3 **Molal**	~200 Years No evap. Scenario 3 **Molal**	**Test Soln. Chemistry Molal**
H_3BO_3	**6.69E-04**	2.95E-04	6.48E-04	2.41E-04	**6.69E-04**
HCO_3^-	**4.35E-04**	1.29E-04	4.35E-05	7.10E-05	**4.35E-04**
Cl-	**4.92E-03**	5.20E-03	4.92E-04	5.20E-04	**4.92E-03**
$CrO_4^=$	**2.74E-04**	9.34E-05	1.42E-04	4.62E-05	**2.74E-04**
F^-	**2.04E-03**	2.16E-03	2.04E-04	2.16E-04	**2.04E-03**
NO_3^-	**7.99E-03**	3.10E-03	7.99E-04	3.10E-04	**7.99E-03**
$SO_4^=$	**6.97E-05**	8.20E-03	2.10E-05	2.18E-03	**6.97E-05**
$SiO_2(aq)$	**1.70E-05**	4.29E-22	1.80E-05	4.16E-22	**1.70E-05**
Na^+ *	**1.61E-2**	3.24E-2			**1.61E-2**
Cs^+	2.03E-7	9.33E-4			**4.64E-4**[#]
K^+					Variable
TcO_4^-	1.08E-05	9.16E-03	1.08E-06	9.16E-04	**4.64E-4**[&]
pH	8.13	8.12	8.18	8.16	

[#] from Cs: Na ratios at 200 years times Na concentration at 10,900 years

*Na charge balances major anions

[&] Assumed to equal Cs, see text

BOLD values indicate selections for test solution recipe, see text

Modal addition of salts	Formula Weight	Moles per liter	grams salt per liter	grams salt per 25 liters
H_3**BO**$_3$	61.83	6.69E-04	4.14E-02	1.03E+00
Na**HCO**$_3$	84	4.35E-04	3.65E-02	9.14E-01
Na**Cl**	58.44	4.92E-03	2.88E-01	7.19E+00
Na$_2$**Cr**O$_4$	161.97	2.74E-04	4.44E-02	1.11E+00
Na**F**	41.99	2.04E-03	8.57E-02	2.14E+00
Na**NO**$_3$	84.99	7.99E-03	6.79E-01	1.70E+01
Na$_2$**SO**$_4$	142.04	6.97E-05	9.90E-03	2.48E-01
Na$_2$**SiO**$_3$·9H$_2$O	284.2	1.70E-05	4.83E-03	1.21E-01
Cs$_2$SO$_4$	361.87	2.32E-4	8.40E-2	2.10E+00
K**ReO**$_4$ [for KTcO$_4$]	298.3	4.64E-4	1.35E-1	3.36E+00
[K_2SO_4, for **Cs**$_2$SO$_4$, K**ReO**$_4$]	174.27	2.32E-4	4.04E-2	1.01E+00
[Na$_2$SO$_4$, 200 year value]	142.04	8.20E-03	1.16E+00	2.91E+01

V.   SUMMARY

The overall purpose of this document is to define a standardized screening procedure to identify potential iodine getters for eventual placement in the YMP-repository invert. Simplicity in implementation was a priority, as was the objective of eliminating unpromising materials with minimal effort. The different tests were prioritized in such a way that the plan could be presented in a single table (Table 1) at the start of the document. Recipes for the requisite test fluids are also supplied, along with some rather lengthy documentation relating to the choices made in defining these mixes. However, sorting through these arguments is unnecessary if the reader merely wants to proceed with the task of screening getters. This additional documentation does, however, provide the background needed for updating the protocol should the getter program be revived in the future. Other findings of this work, the apparent impact of including sorption by rust on the fluid chemistry of waste package leach fluids (Table 13), and the appropriate substitution of surrogates (Table 2) may also be of informative to the Project, but they still need to be evaluated in the context of a rigorous YMP quality assurance process.

The reader is also cautioned that the fact that the program ended unexpectedly after just one year may have some undesirable consequences. In order to conclude on schedule we had neither the opportunity to verify the long-term stability of the proposed test solutions, or to double-check the numerous computations that went into developing the recipes in the first place. However, as is amply demonstrated, a diverse range of fluids can be used and the results obtained will still be meaningful. It follows that small miscalculations or adjustments in fluid chemistry will not diminish the utility of the recipes or the screening protocol in general.

Both the thermal and chemical environments of the repository were considered in formulating this protocol. Although the thermal environment is relatively well constrained much ambiguity remains in defining the types and timing of fluids that might enter the invert and impact getter performance.   The first set of screening tests focuses on room-temperature performance in the extremely dilute formation waters that are indigenous to the region. These tests eliminate materials that, in some gross sense, are simply unsuitable - either because of chemical/thermal instability, or because they simply have no ability to scavenge iodine. Later testing is related to evaluating performance envelopes in different thermal and chemical environments that may develop over time in the YMP facility. Basically, these settings can be divided into scenarios where the fluid originated at elevated temperatures by evaporation of indigenous groundwaters, or where fluid chemistry is dominated by waste package corrosion and leaching processes.

Much uncertainty in assembling this document also resulted from our poor understanding of the impact(s) of the waste package corrosion. The "state of the art" at the time of the getter program (2004-2005) suggested that corrosion produces relatively acidic solutions containing significant concentrations of components not normally found in groundwater (Ni, Cr, Mo from corrosion of metals and fission products plus actinides from the waste). However, models which include the surface chemistry of the rust present a different picture. Then, the model predicts fluids that are mildly basic, have a low ionic strength, and differ from normal groundwaters principally by virtue of having slightly elevated levels of cesium, pertechnetate, chromate, *and iodine*.

What this document explicitly *does not provide* is acceptance criteria for deciding whether a getter will actually perform, as needed, over the long-term under repository conditions. Nor can the data derived from this protocol be incorporated in any meaningful way into performance assessment (PA) models. Separate, much larger, programs, *with the full YMP-QA process in place*, would be required to accomplish either of these objectives.

VI.   REFERENCES

ANL-EBS-HS-000003 Rev.00, April, 2000, "Abstraction of NFE Drift Thermodynamic Environment and Percolation Flux, Fig. 1, 36, and 37.

ANL-EBS-MD-000033 REV 03, 2004, "Engineered Barrier System: Physical and Chemical Environment Model" CRWMS M&O, Las Vegas, Nevada.

ANL-EBS-MD-00037 Rev 03B, April 2004, "In-Package Chemistry Abstraction", p. 21.

Bethke, C.M., 1998, The Geochemist's Workbench; Release 3.0, A Users' Guide to Rxn, Act2, Tact, React, and Gtplot, Hydrology Program, University of Illinois, p.91-146.

Bontchev, R.P., 2005, BiOX-Based Solid Radionulide (Tc) Getters, in OST&I Annual Report 2005, DOE/RW-0851, p. 135-136.

Bontchev, R.P., Bonhomme, F., Krumhansl, J.L., and Moore, R.C., 2005, Structural relations and phase transformations in the system BiOX (X = Cl-, BO3-3, NO3- CO3= and CH3COO-), 229th ACS National Meeting, INOR 866, San Diego, CA March 13-17, 2005.

Brady, P.V., Anderson, B.E., and K.B. Helean, 2005, Waste Package Corrosion Studies Using Small Mockup Experiments, in OST&I Annual Report 2005, DOE/RW-0851, p. 39-40.

Croff, A.G. and Alexander, C.W., 1980, Decay characteristics of once-through LWR and LMFBR spent fuels, high-level wastes, and fuel-assembly structural material wastes, ORNL/TM 7431, p. 41, Table A.18

Dury, F., Centeno, M.A., Gaigneaux, E.M., and Ruiz, P., 2003, Interaction of NO2 (as gas dope) with nickel molybdate catalysts during the oxidative dehydrogenation of propane to propylene, Applied Catalysis A: General v. 247, p. 231-246.

Dzombak, D.A., and Morel, F.M.M., 1990, Surface Complexation Modeling, Hydrous Ferric Oxide, Wiley, New York, 398p.

Harrar, J.E., Carley, J.F., Isherwood, W.F., and Raber, E., 1990, Report of the Committee to Review the Use of J-13 Well Water in Nevada Nuclear Waste Storage Investigations, UCID-21867.

Johnson, J., 2004, DOE Defends "Hot" Repository Design, Chemical and Engineering News, v. 82(22), p.19-20.

Kinniburgh, D.G.,Jackson, M.L., and Syers, J.K., 1976, Adsorption of Alkaline Earth, Transition, and Heavy Metal Cations by Hydrous Oxide Gels of Iron and Aluminum, Soil Sci. Soc. Am. J., v. 40, pp. 796-799.

Krumhansl, J.L., 1986, Observations Regarding the Stability of Bentonite Backfill in a High-Level Waste (HLW) Repository in Rock Salt, SAND83-1293.

Krumhansl, J.L., Pless, J.D. and J.B. Chwirka, 2005, Iodine Getter Development, in OST&I Annual Report 2005, DOE/RW-0851, p. 133-134.

Krumhansl, J.L., Pless, J.D., Chwirka, J.B. and Holt, K.C., 2006, Yucca Mountain Project Getter Program Results; 129I and other anionic radionculides, SAND06-3869.

MacNeil, K., Thiers, T.G., Zarrabi, K.,McKenzie, D.G., and Saunders, R.S., 1999, Diffusive Barrier and Getter Under Waste Packages VA Reference Design Feature Evaluations, B00000000-01717-2200-00213 Revision 00(C), MOL 199902525.0399, YMP program design document.

MDL-NBS-HS-000018 REV 00, December, 2003, "Abstraction of Drift-Scale Coupled Processes, Fig. 6.3-2, "Waste Package" and Fig. 6.3-3(c), "Base".

Pless, J.D., Chwirka, J.B., and Krumhansl, J.L., 2006, Iodine Sequestration using Delafossites and Layered Hydroxides, Environmental Chemistry Letters – on line journal; DOI 10.1007/s10311, 4 pp.

Rosenberg, N.D., Gdowski, G.E. and Knauss, K.G., 2001, Evaporative chemical evolution of natural waters at Yucca Mountain, Applied Geochemistry, V. 16(9-10), p. 2131-1240.

APPENDICES

Appendix 1

REACT set-up files used in modeling the interaction of waste package leachate with goethite ("rust")

Note: **Eu+++ substituted for Gd+++**; MoO_4^{--} = 5.04E-04 molal deleted*,*

200 year fuel leachate	10,900 year fuel leachate
reset	reset
go	go
pH = 4.44	pH = 5.67
Cl- = 5.20E-04 molal	Na+ = .0001 molal
Na+ = 3.15E-03 molal	balance on Na+
balance on Na+	Cl- = 4.92E-04 molal
Al+++ = 8.99E-05 molal	Al+++ = 1.06E-05 molal
B(OH)3 = 1.08E-02 molal	B(OH)3 = 3.26E-02 molal
Ca++ = 6.53E-04 molal	Ca++ = 6.08E-05 molal
Co++ = 2.18E-04 molal	Co++ = 1.17E-06 molal
Swap Cr2O7-- for Cr+++	Swap Cr2O7-- for Cr+++
Cr2O7-- = 4.90E-02 molal	Cr2O7-- = 1.43E-01 molal
Cs+ = 1.49E-03 molal	Cs+ = 1.75E-06 molal
Swap Cu++ for Cu+	Swap Cu++ for Cu+
Cu++ = 1.98E-03 molal	Cu++ = 7.82E-04 molal
F- = 2.16E-04 molal	F- = 2.04E-04 molal
Swap Fe+++ for Fe++	Swap Fe+++ for Fe++
Fe+++ = 1.51E-10 molal	Fe+++ = 9.29E-12 molal
Eu+++ = 2.50E-03 molal	Eu+++ = 2.60E-07 molal
HCO3- = 7.10E-05 molal	HCO3- = 4.35E-05 molal
K+ = 4.70E-06 molal	K+ = 1.60E-04 molal
Mg++ = 1.72E-02 molal	Mg++ = 2.02E-04 molal
NO3- = 3.10E-04 molal	NO3- = 7.99E-04 molal
Ni++ = 2.94E-02 molal	Ni++ = 8.33E-02 molal
Np++++ = 2.06E-4 molal	Np++++ = 1.36E-05 molal
PuO2++ = 3.09E-3 molal	PuO2++ = 3.64E-06 molal
SO4-- = 3.56E-02 molal	SO4-- = 4.18E-04 molal
SiO2(aq) = 1.03E-04 molal	SiO2(aq) = 1.03E-04 molal
TcO4- = 9.16E-04 molal	TcO4- = 1.08E-06 molal
Swap UO2++ for U++++	Swap UO2++ for U++++
UO2++ = 1.22E-03 molal	UO2++ = 1.43E-05 molal
Zn++ = 1.75E-03 molal	Zn++ = 1.02E-10 molal
Swap O2(g) for O2(aq)	Swap O2(g) for O2(aq)
f O2(g) = 1.94984E-01	f O2(g) = 1.94984E-01
fix f O2(g)	fix f O2(g)
react 78.8 moles Goethite	React 87.4 moles Goethite
surface_data feohupu.dat	surface_data feohupu.dat
Suppress Hematite	Suppress Hematite
Delxi = .005	Delxi = .005
Itmax = 1000	Itmax = 1000
go	go
react -900 g H2O	react -900 g H2O
go	go

Appendix 2

Surface complexation constants used in predicting the uptake of constituents by goethite ("rust"):

Goethite
surface area=   600.0000 m2/g
2 sorption sites
>(s)FeOH   site density=   0.0050 mol/mol mineral
>(w)FeOH   site density=   0.2000 mol/mol mineral

- 53 surface species

>(s)FeO-
   1.000 >(s)FeOH   -1.000 H+
   log K= 8.9300
>(w)FeO-
   1.000 >(w)FeOH   -1.000 H+
   log K= 8.9300
>(s)FeOH2+
   1.000 >(s)FeOH   1.000 H+
   log K= -7.2900
>(w)FeOH2+
   1.000 >(w)FeOH   1.000 H+
   log K= -7.2900
>(s)FeOAg
   1.000 >(s)FeOH   1.000 Ag+   -1.000 H+
   log K=   1.7200
>(s)FeOHBa++
   1.000 >(s)FeOH   1.000 Ba++
   log K= -5.4600
>(s)FeOHCa++
   1.000 >(s)FeOH   1.000 Ca++
   log K= -4.9700
>(w)FeOCa+
   1.000 >(w)FeOH   -1.000 H+   1.000 Ca++
   log K=   5.8500
>(s)FeOCd+
   1.000 >(s)FeOH   -1.000 H+   1.000 Cd++
   log K= -0.4700
>(w)FeOCd+
   1.000 >(w)FeOH   -1.000 H+   1.000 Cd++
   log K=   2.9000
>(s)FeOCrOH+
      1.000 >(s)FeOH   -2.000 H+   1.000 Cr+++   1.000 H2O
   log K= -2.0600

>(s)FeOCo+
    1.000 >(s)FeOH   -1.000 H+   1.000 Co++
   log K= 0.4600
>(w)FeOCo+
    1.000 >(w)FeOH   -1.000 H+   1.000 Co++
   log K= 3.0100
>(s)FeOCu+
    1.000 >(s)FeOH   -1.000 H+   1.000 Cu++
   log K= -2.8900
>(s)FeONi+
    1.000 >(s)FeOH   -1.000 H+   1.000 Ni++
   log K= -0.3700
>(s)FeOHg+
    1.000 >(s)FeOH   -1.000 H+   1.000 Hg++
   log K= -7.7600
>(w)FeOHg+
    1.000 >(w)FeOH   -1.000 H+   1.000 Hg++
   log K= -6.4500
>(s)FeOPb+
    1.000 >(s)FeOH   -1.000 H+   1.000 Pb++
   log K= -4.6500
>(s)FeOHSr++
    1.000 >(s)FeOH   1.000 Sr++
   log K= -5.0100
>(w)FeOSr+
    1.000 >(w)FeOH   1.000 Sr++   -1.000 H+
   log K= 6.5800
>(w)FeOSrOH
    1.000 >(w)FeOH   1.000 Sr++   -2.000 H+   1.000 H2O
   log K= 17.6000
>(s)FeOZn+
    1.000 >(s)FeOH   -1.000 H+   1.000 Zn++
   log K= -0.9900
>(w)FeOZn+
    1.000 >(w)FeOH   -1.000 H+   1.000 Zn++
   log K= 1.9900
>(w)FeH2AsO3
   1.000 >(w)FeOH   1.000 As(OH)3   -1.000 H2O
   log K= -5.4100
>(w)FeH2AsO4
    1.000 >(w)FeOH   1.000 AsO4---   -1.000 H2O   3.000 H+
   log K= -29.3100
>(w)FeHAsO4-
   1.000 >(w)FeOH   1.000 AsO4---   2.000 H+   -1.000 H2O
   log K= -23.5100
>(w)FeOHAsO4---

```
      1.000 >(w)FeOH      1.000 AsO4---
      log K= -10.5800
>(w)FeH2BO3
      1.000 >(w)FeOH      1.000 B(OH)3      -1.000 H2O
      log K=  -0.6200
>(w)FeCrO4-
      1.000 >(w)FeOH      1.000 H+      1.000 CrO4--      -1.000 H2O
      log K= -10.8500
>(w)FeH2PO4
      1.000 >(w)FeOH      1.000 PO4---      3.000 H+      -1.000 H2O
      log K= -31.2900
>(w)FeHPO4-
      1.000 >(w)FeOH      2.000 H+      1.000 PO4---      -1.000 H2O
      log K= -25.3900
>(w)FePO4--
      1.000 >(w)FeOH      1.000 H+      1.000 PO4---      -1.000 H2O
      log K= -17.7200
>(w)FeSO4-
      1.000 >(w)FeOH      1.000 H+      1.000 SO4--      -1.000 H2O
      log K=  -7.7800
>(w)FeOHSO4--
      1.000 >(w)FeOH      1.000 SO4--
      log K=  -0.7900
 >(w)FeOHS2O3--
      1.000 >(w)FeOH      1.000 S2O3--
      log K=  -0.4900
>(w)FeSeO4-
      1.000 >(w)FeOH      1.000 SeO4--      -1.000 H2O      1.000 H+
      log K=  -7.7300
>(w)FeOHSeO4--
      1.000 >(w)FeOH      1.000 SeO4--
      log K=  -0.8000
>(w)FeSeO3-
      1.000 >(w)FeOH      1.000 SeO3--      -1.000 H2O      1.000 H+
      log K= -12.6900
>(w)FeOHSeO3--
      1.000 >(w)FeOH      1.000 SeO3--
      log K=  -5.1700
>(w)FeOHVO4---
      1.000 >(w)FeOH      1.000 VO4---
      log K= -13.5700
>(s)FeOUO2+
      1.000 >(s)FeOH      -1.000 H+      1.000 UO2++
      log K=  -5.200
>(w)FeOUO2+
      1.000 >(w)FeOH      -1.000 H+      1.000 UO2++
```

log K= -2.8

>(s)FeOPuO2+
    1.000 >(s)FeOH   -1.000 H+   1.000 PuO2++
    log K= -5.4

>(w)FeOPuO2+
    1.000 >(w)FeOH   -1.000 H+   1.000 PuO2++
    log K= -3.0

>(s)FeOPuO2
    1.000 >(s)FeOH   -1.000 H+   1.000 PuO2+
    log K= -0.5

>(w)FeOPuO2
    1.000 >(w)FeOH   -1.000 H+   1.000 PuO2+
    log K= +2.5

>(s)FeOPu+++
    1.000 >(s)FeOH   -1.000 H+   1.000 Pu++++
    log K= -11.5

>(w)FeOPu+++
    1.000 >(w)FeOH   -1.000 H+   1.000 Pu++++
    log K= -9.3

>(s)FeOPu++
    1.000 >(s)FeOH   -1.000 H+   1.000 Pu+++
    log K= -3.4

>(w)FeOPu++
    1.000 >(w)FeOH   -1.000 H+   1.000 Pu+++
    log K= +0.1

>(s)FeONpO2+
    1.000 >(s)FeOH   -1.000 H+   1.000 NpO2++
    log K= -5.9

>(w)FeONpO2+
    1.000 >(w)FeOH   -1.000 H+   1.000 NpO2++
    log K= -3.6

>(s)FeONpO2
1.000 >(s)FeOH   -1.000 H+   1.000 NpO2+
    log K= -1.6

>(w)FeONpO2
    1.000 >(w)FeOH   -1.000 H+   1.000 NpO2+
    log K= +1.1

EXTERNAL DISTRIBUTION

.

Deborah Barr (1)
Physical Scientist
RW-631/ HL 1551 Hillshire Drive, Suite A
Las Vegas, NV 89134

Bo Bodvarsson (1)
Lawrence Berkeley National Laboratories
1 Cyclotron Road Mail Stop 90R1116
Berkeley, CA 94720

Robert J. Budnitz (1)
Lawrence Livermore National Laboratories
Mail Stop L-632
Livermore, CA 94551

Rod Ewing (1)
University of Michigan,
425 E. University Ave.
Ann Arbor, MI 48109

Andrew R. Felmy (1)
PNNL
P.O. Box 999 / K8-96
Richland, WA 99352

Glen Fryxell (1)
PNNL
P.O. Box 999/K2-44
Richland, WA 99352

Diane Graziano (1)
Argonne National Laboratories
9700 South Cass Avenue
Building 205 Room 128
Argonne, Illinois 60439

Mic Griben (5)
Science & Technology Consulting Group, LLC
10153 Vantage Point Court, Suite 100
New Market, MD 21774-6843

Stephen Hanauer (1)
General Engineer
RW-63/ HL 1551 Hillshire Drive, Suite A
Las Vegas, NV 89134

David T. Hobbs (3)
Westinghouse Savannah River Company
773-A Building
 Aiken, S.C. 29898

Michael Hochella (2)
Virginia Polytechnic and State University
Geosciences 5049 Derring Hall
Blacksburg, VA 24061

Jun Liu (2)
PNNL
P.O. Box 999 / K2-50
Richland, WA 99352

Shas Mattigod (3)
PNNL
P.O. Box 999/ K6-81
Richland, WA 99352

Lester Morss (1)
DOE Office of Basic Energy Science, Chemist, SC-22.1/ GTN
1000 Independence Ave., S.W.
Washington, DC 20585-1290

Joe Payer (1)
The Case School of Engineering Materials Science and Engineering,
10900 Euclid   Avenue
Cleveland OH 44106-7204

Mark Peters (1)
Los Alamos National Laboratories
P.O. Box 1663 P21 Mail Stop D454
Las Alamos, New Mexico 87545

Jason Pless (3)
Catalytic Solutions Inc
1620 Emerson St
Oxnard, CA 93033

Choon Quan (1)
OST&I, Physical Scientist, RW-40/ Fors Building
US. Dept. of Energy 1000 Independence Ave.
S.W. Washington, DC 20585

Kevin M. Rosso (1)
PNNL
P.O. Box 999 / K8-98
Richland, WA 99352

Paige Russell (1)
General Engineer
RW-631/ HL, 1551 Hillshire Drive, Suite A
Las Vegas, NV 89134.

Abe VanLuik (1)
Senior Policy Advisor, RW-63/ HL,
1551 Hillshire Drive, Suite A
Las Vegas, NV 89134

Jeffrey Walker (1)
OST&I,
General Engineer
RW-40/ Fors Building US. Dept. of Energy
1000 Independence Ave., S.W.
Washington, DC 20585

Dawn Wellman (1)
PNNL, P.O. Box 999/K6-81
Richland, WA 99352

John Wengle (5)
OST&I, Supervisory Program Analysis
RW-40/ Fors Building
1000 Independence Avenue SW
Washington, DC 20585

INTERNAL DISTRIBUTION