Update of R&D at BNL for Gd-Loaded Liquid Scintillator (Gd-LS)

1 Recent Progress at BNL

The BNL Group has made considerable progress with its work on Gd-LS since the Braidwood R&D proposal was submitted in September 2004. We have focused on several properties of the Gd-LS that are key for the successful operation of a high- precision theta-13 experiment: chemical stability, optical transparency (large attenuation length), high light output, and ultra-low concentrations of radioactive and of chemical contaminants. "Chemical stability" means that we cannot tolerate the formation over time of anything in the liquid that will change its optical properties or its composition, e.g., development of color, or gels, or precipitates, or colloids, or hydrolysis, etc. The Gd-LS must also be chemically compatible with the containment vessel; for example, it is known that an organic solvents such as pseudocumene (PC) can attack acrylic plastic but is benign in nylon.

The common wisdom is that poor quality Gd-LS can be a show stopper for the new theta-13 experiments. New developments that have been achieved by the BNL Group in synthesizing the Gd-LS can be applied equally well to the different experiments that are being proposed. As is discussed below, we have made excellent progress in our R&D towards controlling the kinds of chemical and optical deterioration of their Gd-LS formulations that had plagued the CHOOZ and Palo Verde reactor experiments.

As had been noted previously, the Solar-Neutrino/Nuclear-Chemistry Group in the BNL Chemistry Department has been involved since 2000 in R&D of chemical techniques for synthesizing metal-loaded organic liquid scintillators. The original motivation of that work was a proposed new low-energy solar-neutrino experiment, the LENS-Sol project, where metal concentrations of $\sim$10% by weight are needed in the LS to serve as targets for neutrino capture. We had excellent results with the elements that we focused on, ytterbium, Yb^{3+} ion and especially indium, In^{3+} ion. It was immediately clear to us that it should be relatively straightforward to extend our program to reactor antineutrino experiments, to prepare Gd-LS with Gd^{3+} ion at the much lower concentration required for neutron detection, $\sim$0.1%, a factor $\sim$1/100 of the In-LS concentrations.

A common thread in our R&D at BNL has been the application of decades of experience, relating to chemical syntheses and separations and to chemical analyses, that was gained in nuclear fuel cycle R&D with the multivalent actinide and lanthanide elements. Our goal is to produce a metal-organo-chemical complex that is soluble in an organic solvent, which also acts as a liquid scintillator (LS). There are many different chemical approaches to synthesis of the metal-loaded LS (M-LS), using many different organic complexing agents. We have focused on using carboxylic acids (RCOOH) as organic complexants (a) to form soluble metal carboxylates that (b) can be

introduced into the LS by solvent-solvent extraction. Some advantages of the carboxylic acids are that a variety of them are produced by industry in bulk amounts at low cost, with relative ease of disposal (as chemical waste) because they contain only C, H, and O. Other known approaches using solvent extraction include: (i) organo-phosphorus extractants, which we have also studied, or (ii) other oxygenated complexants, for example, diketones such as acetyl acetonate. A slightly different approach (iii) is to try to prepare a solid organo-Gd compound that is directly soluble in the LS. We have also tried this method with carboxylates at BNL, but did not observe significant advantages over the solvent-extraction method. It should be noted that the formation of an organo-Gd solid compound requires days of preparation while the solvent-extraction method only takes few hours.

We have developed procedures at BNL for the purification and the synthesis of the M-LS. The best carboxylic acid found to date is the six-carbon carboxylic acid, methylvaleric acid, "HMVA". We have also perfected many methods, instrumental and chemical, to analyze the resulting M-LS samples, e. g., for pH and for concentrations of Gd, $RCOO^-$, undissociated RCOOH (HMVA), Cl^-, and H_2O . To date, we have prepared a few hundred samples.

Another of our key steps for obtaining high-quality Gd-LS has been to purify all of the starting chemical ingredients, to remove chemical contaminants that can negatively affect the optical properties or the long-term stability of the Gd-LS. It must be realized that most of the purification steps have to be applied before and during the synthesis of the Gd-LS. These chemical separation schemes cannot be applied once the final Gd-LS has been formulated because they would likely remove the Gd. Even vacuum techniques for removing Rn may cause problems by changing the concentrations of the volatile components in the LS.

In 2004 we began to apply our procedures for In-LS to the preparation of Gd-LS. Our approach so far has been to prepare and purify relatively concentrated samples of Gd-LS, with ∼1% Gd dissolved in the organic solvent, which to date has primarily been 1,2,4-trimethylbenzene (or pseudocumene, PC), and subsequently to dilute the samples by a factor ∼10 with PC or other organic solvents to get large volumes at the desired Gd concentration, ∼0.1%. By late 2004 we had successfully shown that it is rather straightforward to use our methods to obtain Gd-LS in the range of 0.1-0.2% Gd, with consistently excellent properties that meet the stringent demands for an antineutrino detector. For example, the values of the optical absorbance of these samples were measured in 10-cm optical cells with a variable wavelength spectrophotometer (UV-visible) and extrapolated to give attenuation lengths ∼11 meters at a wavelength of 430 nm. We subsequently bettered these values with measurements of the same samples in a 100-cm cell with a 442-nm blue laser. The larger the attenuation length the better, if one is to do a high-precision neutrino oscillation experiment.

We have instituted a Quality Control program at BNL to monitor the quality of our M-LS preparations with the passage of time. The QC parameters that we periodically monitor are the visible appearance of the samples (looking for any apparent color, or precipitate formation.), the measured light absorbance, and the measured light yield (produced by excitation with a radioactive ^{137}Cs source, in apparatus that we have built). We are very encouraged by the facts that (a) many of the samples of the ∼10% In-LS that we prepared for the LENS-Sol project have been stable since their synthesis 20 months ago, (b) our recently prepared 0.1% Gd-LS samples in PC have been stable for the 7 months since they were synthesized, and (c) our recently prepared samples of 0.2% Gd-LS in a mixture of 20% PC and 80% dodecane have been stable for the ≥2 months since

they were prepared. We have begun to study such mixtures of organic solvents to ascertain if we could prevent or retard the possible chemical attack of acrylic plastic, which is a prime candidate for the construction material of the antineutrino detector vessel.

Figs. 1 - 3 show representative data for some BNL Gd-LS samples.

1. Fig. 1 shows values of Abs, the optical absorbance values at 430 nm , measured in a 10-cm optical cell in a UV-visible spectrophotometer, for Gd-LS samples with different Gd concentrations, up to 1.1% by weight.

2. As part of our QC monitoring program, we have made periodic measurements of the Abs values for several Gd-LS samples, with different Gd concentrations. These data are pesented in Fig. 2. Most of the Gd-LS samples shown are in PC, although one is a recent sample prepared in 20% PC - 80% dodecane. It is noteworthy that the properties of all of these samples have not changed over the several months since they were synthesized, and that the Abs values do not vary strongly with changing Gd concentration . All of these samples meet our requirements of long optical attenuation lengths: an absorbance value of 0.004 leads to an extrapolated value of the 1/e attenuation length of $\sim$11 meters; 0.008, to $\sim$5.5 m.

3. Fig. 3 shows the variation of light yields, relative to pure PC, of different Gd concentrations in PC, up to 1.1% Gd (these Gd-LS samples have been doped with wavelength-shifting fluors). For the 0.1% and 0.2% Gd-LS, the relative light yields are 97% and 95% of pure PC. As expected, the light yield decreases as the metal concentration increases.

2 Future R&D at BNL, and Expected Results

Even though our procedures already give satisfactory, consistent results, much more remains for us to do on the R&D of Gd-LS. We intend to perfect our methods of synthesis and purification (both chemical and radioactive) to make them reliable and reproducible, especially when we scale them up to large volumes. A list of the tasks that we have begun or will undertake during the next year includes:

1. We will continue our QC program of long-term stability for periods >1 year.

2. We have begun to construct an optical system with variable pathlengths up to $\sim$2 m to measure optical attenuation and scattering lengths of liquids over a range of wavelengths, using different colored LED's.

3. We will build a closed synthesis system that excludes air, since we suspect that O_2may degrade the Gd-LS over time.

4. We will continue testing a broad selection of candidate organic solvents in addition to PC to serve as the LS, such as PCH (phenylcyclohexane), dodecane (a single aliphatic compound containing twelve C atoms), mineral oil (a variable mixture of aliphatic compounds), and mixtures of these solvents with PC.

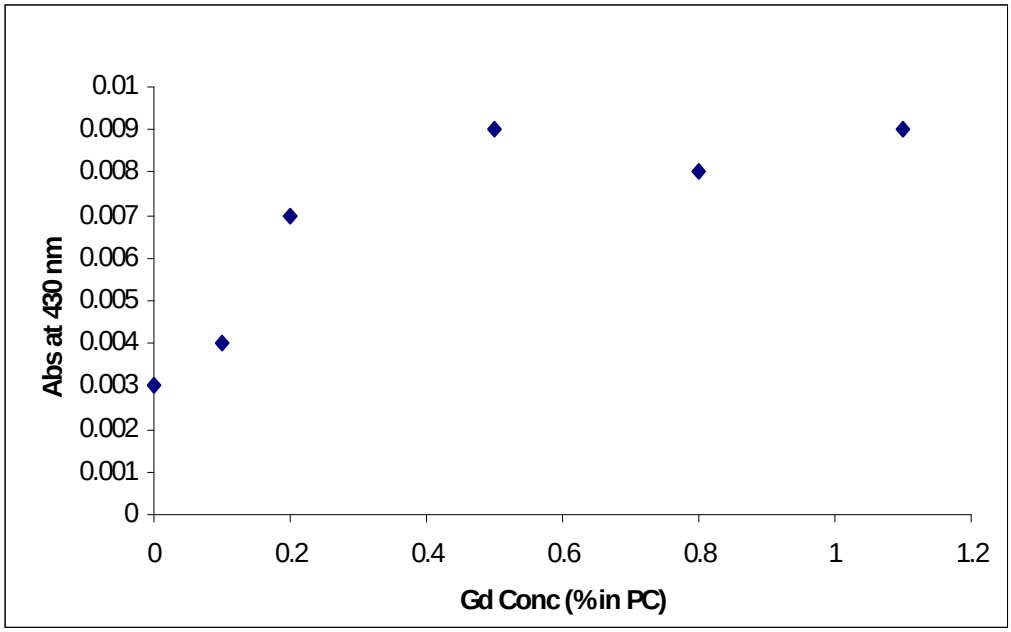

Figure 1: The optical absorbance of the BNL Gd-LS (in PC), measured at 430 nm in 10-cm cells for several Gd concentrations up to 1.1%. An absorbance value of 0.004 leads to an extrapolated value of the attenuation length of ∼11 meters; 0.008, to ∼5.5 m.

5. We will study the chemical compatibility of these organic LS with the materials that will be used to construct the detector vessel, e.g., acrylic or nylon. For this work, we have arranged to obtain samples of the acrylic that was used to construct the SNO detector vessel, that we will use in ASTM-type standardized tests of chemical attack.

6. We will strictly control the concentrations of impurities in the Gd-LS, e. g., of non-radioactive chemical species that can adversely affect the optical properties.

7. We are also beginning to develop methods to remove and assay radioactive contaminants, mainly from the naturally occurring ^{238}U and ^{232}Th decay chains, and ^{40}K. We require the radiopurity of these radionuclides in the ∼0.1% Gd-LS to be $\leq 10^{-13}$g/g, which implies $\leq 10^{-10}$g/g in the Gd, a value that is within striking distance.

8. We will utilize existing or develop new analytical chemistry methods for the accurate determination of the concentrations of H and Gd in the Gd-LS, which represent the numbers of target atoms for antineutrino interactions (H) and neutron interactions (Gd). These values will have to be determined with a precision ∼0.1%. We are also considering methods, such as mixing of different production batches, to ensure that these concentrations in the near and far detectors are "identical".

9. We will automate our chemical procedures for Gd-LS synthesis and construct apparatus to scale them up from the current scale of a few liters to volumes ∼100 L, as a prelude to industrial-scale production on the level of tons. An important goal for us in FY-2006

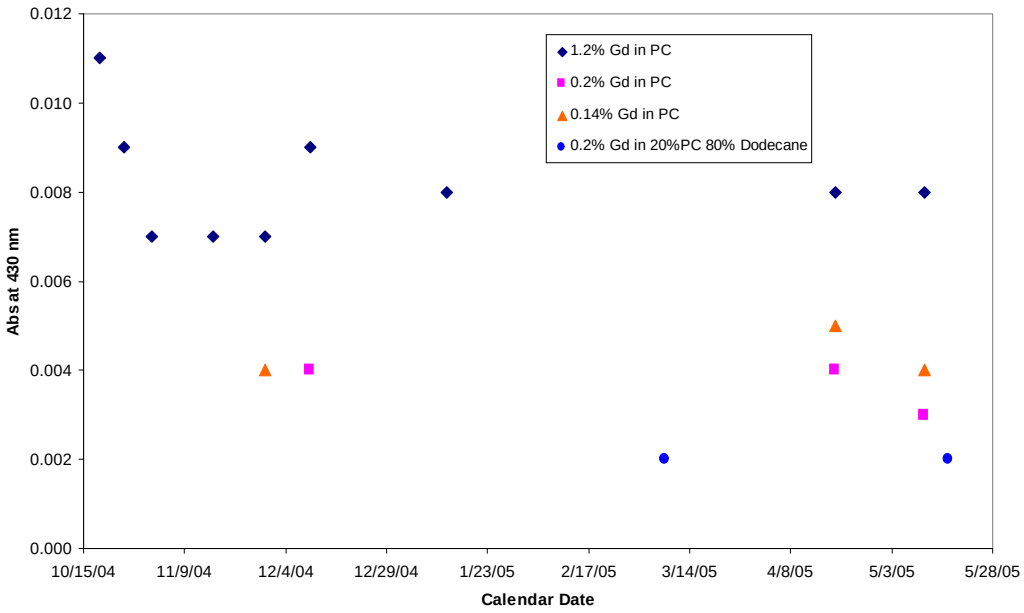

Figure 2: Stability over time of the BNL Gd-LS at different Gd concentrations and compositions, as measured by the optical absorbance at 430 nm in 10-cm cells. The measurements for the 0.2% and 0.14% samples cover a time span of ∼200 days. An absorbance value of 0.004 leads to an extrapolated value of the attenuation length of ∼11 meters; 0.008, to ∼5.5 m.

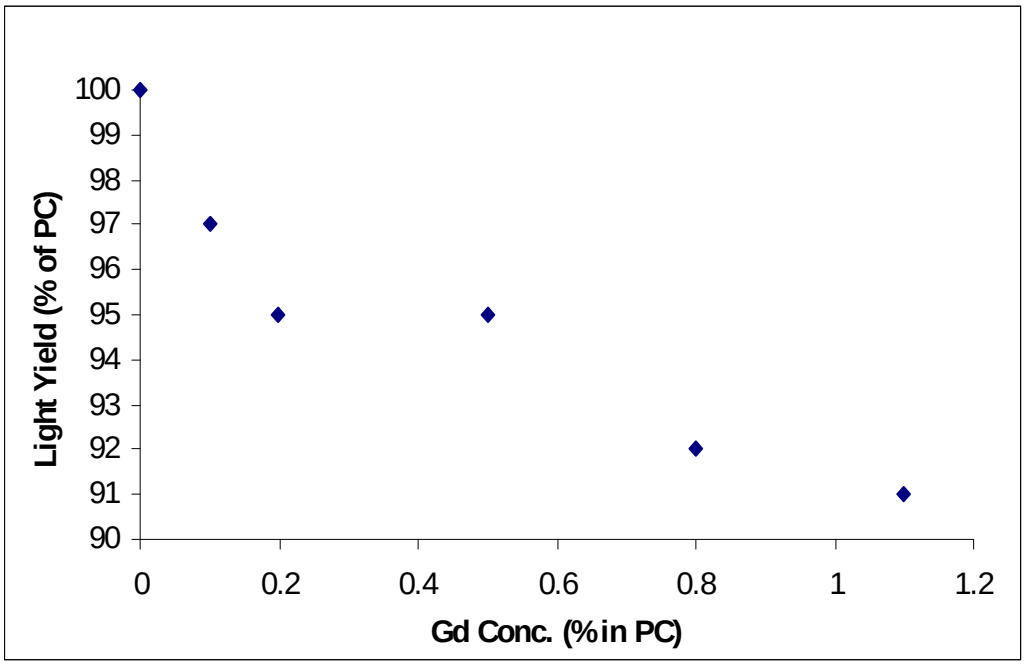

Figure 3: Variation of the measured light yield vs. Gd concentrations up to 1.1% of the BNL Gd-LS (dissolved in PC). The light yield values are relative to 100% for pure PC. As expected, the light yield decreases as the metal concentration increases.

is to produce hundreds of liters of ∼0.1% Gd-LS for our collaboration colleagues at other institutions to test in prototype detector modules that they are constructing.

3 Scaling Up Gd-LS Production for a full-size Detector Module

To prepare 1 ton of 1% Gd-LS, we would ideally use 10 kg of Gd (at present we use the solid compound, $GdCl_3{\cdot}6H2O$), 35 kg of HMVA, and 960 kg of PC (or other organic solvent). In the procedure we also use 50 kg of NH_4OH (as 28% NH_3 in H_2O) to neutralize the HMVA and 200 kg of H_2O (purified to a resistivity of 18 MegOhms). We add fluors to the Gd-LS as wavelength shifters; for example, 0.3 g/L PBD and 15 mg/L bis-MSB. Other possible chemicals for purification steps include silica gel, alumina, and various ion-exchange resins.

Let us assume that one detector module will contain 60 tons of 0.1% Gd-LS. With an approximate density of 1 kg/L, the volume will be 60,000 L at 0.1% Gd., or 6,000 L of a Gd concentrate at 1% Gd. We could then do the synthesis at BNL in a practical manner by doing 20 batches of 300 L at 1% Gd. We have not yet investigated the equipment that would be needed for this production scale, nor the price. However, we note that at SNO a distillation rig with 200 L capacity was recently assembled. It is a simpler system than what we would need; its approximate cost was ∼$70k. Such a large system is essentially a small chemical factory. It will likely be an automated closed system, and will incorporate apparatus for distillation, solvent extraction, mixing, ion exchange, and centrifugation. Its construction may well require the services/advice of chemical engineers.

One can envisage shipping the 1% Gd concentrate to the Braidwood reactor site, where additional equipment will be needed for the factor $\times 10$ dilution to get the 0.1% Gd , and possibly also storage tanks.

An alternative approach that we might consider exploring would be to try to cooperate with private industry to prepare the 1% Gd-LS (according to the BNL recipe). The Palo Verde antineutrino collaboration used such an approach; its Gd-LS, BC-521, was developed by the Bicron Co. for their experiment, and was purchased in industrial-scale amounts. It has been reported that the BC-521 is a carboxylate complex of Gd in PC (an analogous approach to the BNL synthesis procedure). The signal from the Palo Verde Gd-LS deteriorated over time; the Gd-LS "aged" at a slow but measurable rate, 0.03% per day or $\sim$10% per year. We note that we have purchased samples of BC-521, which contains 1% Gd in PC, and of another Gd-LS, BC-525, which contains 0.5% Gd in mineral oil, and have used them to make our standard QC measurements. We found that the light yields of the BNL and Bicron samples were roughly comparable, but that the attenuation lengths of the BNL Gd-LS were approximately twice as large as the Bicron values. As we stated earleir, the larger the attenuation length the better.

No matter the final choice of how to obtain the needed Gd-LS, either by having BNL scientists do the syntheses or by purchasing it from industry, it is clear that BNL will want to set acceptance specifications for the Gd-LS, and do analyses and measurements of the Gd-LS to determine the suitability of the properties from one production batch to another, i.e., in general to set up and maintain a QC program.