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# A Model to Estimate Volume Change due to Radiolytic Gas Bubbles and Thermal Expansion in Solution Reactors

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## Introduction

Aqueous homogeneous solution reactors have been proposed for the production of medical isotopes, such as $^{99}$Mo. Commercial production of $^{99}$Mo in solution reactors requires steady-state operation at about 200 kW during a five-day week period to meet the 16500 Ci ($6.1\times10^{14}$ Bq) per week demand in the United States [Chopelas and Ball, 1993, p. 6]. This amount is about 50% of the world's demand of $^{99}$Mo. However, previous experiments with solution reactors suggest that radiolytic gas bubble formation may impede steady-state operation above a certain power threshold and, therefore, commercial production of $^{99}$Mo may not be accomplished in solution reactors without mitigation of the effects of radiolytic gas bubbles.

The main coefficients of reactivity observed in transient experiments in aqueous homogeneous solution reactors are due to temperature (thermal expansion) and radiolytic gas bubble formation [Kimpland and Kornreich, 1996, p. 208]. Both effects result in volumetric expansion of the fuel solution, which decreases the reactor core surface-to-volume ratio (geometrical effect) and decreases the fuel density.

The specific effect of radiolytic gas bubbles on the volumetric expansion reactivity coefficient has been observed in several burst or transient experiments, such as the KEWB [Dunenfeld, *et al.*, 1962, pp.19-20] and SHEBA experiments [Cappiello, *et al.*, 1997, p. 29]. In particular, these experiments show that shorter initial reactor periods dramatically increase the effect of radiolytic gas bubbles. In contrast, these experiments show that radiolytic gas bubbles do not have a significant effect during long initial period transients at relatively low power, suggesting even the possibility of no reactivity effects at all due to radiolytic gas bubbles in case of steady-state operation.

The SUPO solution reactor, for example, was operated at any steady-state power between ~0.1 W and 25 kW [Bunker, 1963, p. 38]. Note that these solution reactors encompass three fuel solutions, i.e., uranyl nitrate, uranyl sulfate, and uranyl fluoride, as well as high and low $^{235}U$ enrichments, i.e., ~90% and 5%, respectively. It is not clear, however, under which specific conditions and for how long the steady-state operation was achieved in these cases. It is of interest, therefore, to investigate the conditions that allow steady-state operation of solution reactors.

To investigate the effects of radiolytic gas bubbles and thermal expansion on the steady-state operation of solution reactors at the power level required for the production of medical isotopes, a calculational model has been developed. To validate this model, including its principal hypotheses, specific experiments at the Los Alamos National Laboratory SHEBA uranyl fluoride solution reactor were conducted.

The following sections describe radiolytic gas generation in solution reactors, the equations to estimate the fuel solution volume change due to radiolytic gas bubbles and thermal expansion, the experiments conducted at SHEBA, and the comparison of experimental results and model calculations.

## Radiolytic Gas Generation in Solution Reactors

The fission process in a solution reactor produces radiolytic gas molecules, primarily $H_2$ gas molecules. A corresponding amount of oxygen, either hydrogen peroxide or oxygen gas, is produced along with the hydrogen [Lane, *et al.*, 1958, p. 105], [ORNL, 1958, p. 5]. According to Henry's law, uranium aqueous solutions can accommodate $H_2$ and $O_2$ molecules up to the point at which the so-called *critical concentration* is reached. This critical concentration characterizes the saturation limit for $H_2$ and $O_2$ molecules in solution in the reactor. A gas bubble in a liquid-gas solution will grow or shrink according as the solution is over-saturated or under-saturated.

The amount of hydrogen gas in a solution reactor depends on the fission rate and the uranium concentration in the fuel solution. Considering that the time required to recombine radiolytic products back into water is very long [Lane, *et al.*, 1958, p. 104], the rate of formation of hydrogen gas molecules per unit volume of solution, $H_2$, is given by:

$$\frac{dH_2}{dt} = G_{(H2)}\,\varepsilon_0\,\varepsilon_f\,S(t)\,, \tag{1}$$

where $G_{(H2)}$ is the hydrogen yield, $\varepsilon_f$ is the energy release per fission of $^{235}U$, $\varepsilon_0$ is the fraction of the energy release per fission that results in hydrogen production[1] and $S(t)$ is the fission rate per unit volume.

From Equation (1), and assuming that initially there is no radiolytic gas in the reactor, the production of hydrogen and oxygen gas in stoichiometric proportions is given by:

$$M_{RG}(t) = \frac{3}{2}\frac{G_{(H2)}}{N_A}E(t), \tag{2}$$

where $M_{RG}$ is the total quantity of radiolytic gas (*i.e.*, $H_2$ and $O_2$ moles) produced when the reactor has generated energy $E$ over time $t$, and $N_A$ is Avogadros's constant.

**Equivalent Void Volume due to Radiolytic Gas Bubbles**

An ensemble of bubbles may be described in terms of several weighted averages of bubble radius. The most useful average is one weighted by the number of moles of gas in each radius interval [Dunenfeld, *et al.*, 1962, p. 26]. Consider an ensemble of gas bubbles characterized by a size distribution function $\xi(r)$, where $r$ is the radius of the bubble. In the following discussion, it will be assumed that that this size distribution is a continuous function of the bubble radius from a minimum bubble radius, $r_o$, up to a maximum bubble radius denoted by $r_{max}$.

The internal pressure of a gas bubble, $p_g$, is given by:

$$p_g = \frac{2\sigma(T)}{r} + p_l, \tag{3}$$

where $\sigma$ is the surface tension of the liquid-gas interface[2], T is the fuel solution temperature, $p_l$ is the liquid pressure and $r$ is the bubble radius.

Assuming that the hydrostatic pressure, $p_l$, is negligible compared with the internal gas pressure, $p_g$, the number of moles of gas per bubble, $n_M$, is given by:

$$n_M = \frac{8\sigma\pi r^2}{3RT_g}, \tag{4}$$

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[1] Reported values for this fraction are 0.04 [Dunenfeld, *et al.*, 1962, p. 25] and 0.05 [King, 1972, p. 18]. Note, however, that the values for the hydrogen yields reported already include this fraction and, therefore, $\varepsilon_o = 1$ [Lane, *et al.*, 1958, p. 106].

[2] The surface tension of inorganic compound solutions is proportional to the solute concentration and decreases with the solution temperature. For a concentration of 900 kg/m$^3$, an increase in temperature from 293 to 313 K decreases the surface tension by less than 10%. (See, for example, [Hosoma, *et al.*, 2000, pp. 230-231]). Since this is the temperature range of interest in this analysis, the surface tension of the fuel solution will be considered constant.

where $R$ is the gas constant and $T_g$ is the internal temperature of the gas bubble, which is independent of the bubble radius.

The total number of gas moles in the bubble ensemble is then given by integrating Equation (4):

$$M = \frac{8\sigma\pi}{3RT_g}\int_{r_o}^{r_{\max}} r^2\,\xi(r)\,dr\,. \tag{5}$$

The mole-weighted average bubble radius is:

$$\langle r\rangle_{mol} = \frac{\int r\,dM}{\int dM} = \frac{\int_{r_o}^{r_{\max}} \frac{8\sigma\pi r^3\,\xi(r)\,dr}{3RT_g}}{\int_{r_o}^{r_{\max}} \frac{8\sigma\pi r^2\,\xi(r)\,dr}{3RT_g}} = \frac{\frac{2\sigma}{RT_g}\int_{r_o}^{r_{\max}} \frac{4}{3}\pi r^3\xi(r)\,dr}{M}\,. \tag{6}$$

This mole-weighted average represents the characteristic size of the ensemble of radiolytic gas bubbles in the solution reactor and it is particularly useful because it can be inferred from experimental data by noting that the integral in the numerator of Equation (6) is the total volume occupied by radiolytic gas in the solution, referred as $V_B$. Hence, the average bubble radius can be expressed as:

$$\langle r\rangle_{mol} = \frac{2\sigma V_B}{M\,RT_g}\,. \tag{7}$$

Note that, if the thermal expansion of the fuel solution is known, $V_B$ and therefore $\langle r\rangle_{mol}$, can be determined by measuring the increase in the fuel solution level during the operation of the solution reactor.

The model for volume expansion due to radiolytic gas considers that radiolytic gas bubbles can be described by a void of characteristic size equivalent to the volume of radiolytic gases generated in the fuel solution during the free run. The volume of radiolytic gas, after the critical concentration is reached, is estimated from Equation (7):

$$V_B(t) = \frac{M_{RGr}(t)\,RT_g}{2\sigma}\langle r\rangle_{mol}\,, \tag{8}$$

where $M_{RGr}$ is the number of moles of radiolytic gas in excess of the quantity of gas equivalent to the critical concentration:

$$M_{RGr} = M_{RG} - m_f \left( \frac{\chi_{H2}}{\mu_{H2}} + \frac{\chi_{O2}}{\mu_{O2}} \right), \tag{9}$$

where $m_f$ is the fuel solution mass, $\chi_{H2}$ and $\chi_{O2}$ are the critical concentrations of $H_2$ and $O_2$ in the fuel solution, respectively, and $\mu_{H2}$ and $\mu_{O2}$ are the molecular weights of $H_2$ and $O_2$, respectively.

The internal temperature of the radiolytic gas bubble is estimated from the radiolytic gas sensible energy $Q$:

$$Q = \left( c_{H2}\, m_{H2} + c_{O2}\, m_{O2} \right) \Delta T_g , \tag{10}$$

where $c_{H2}$ and $c_{O2}$ are the specific heats, at constant volume, of $H_2$ and $O_2$, respectively, $\Delta T_g$ is the temperature increase of the radiolytic gas bubble, $m_{H2}$ and $m_{O2}$ are the masses of $H_2$ and $O_2$, respectively. The radiolytic gas sensible energy is proportional to the energy generated by the solution reactor:

$$Q = \varepsilon \; E ,$$

where $\varepsilon$ is the fraction of the reactor energy that results in an increase in the internal temperature of the radiolytic gas bubble. Parameter $\varepsilon$ can be estimated from the increase in the cover gas temperature observed experimentally.

The internal temperature of the radiolytic gas bubble is thus obtained by substituting $\Delta T_g = T_g - T_o$, where $T_o$ is the initial fuel solution temperature, $m_{H2}$, $m_{O2}$ and $Q$ in Equation (10):

$$T_g = T_o + \frac{\varepsilon \; N_A}{G_{(H2)} \left( c_{H2}\, \mu_{H2} + c_{O2}\, \mu_{O2} / 2 \right)} . \tag{11}$$

Equation (11) indicates that the radiolytic gas bubbles are not in thermal equilibrium with the fuel solution. A high internal temperature of the radiolytic gas bubble may be expected by realizing that most of these bubbles are formed during the fission process. Once a bubble is formed, little interaction is expected between the internal gas molecules (created directly by the interaction of fission fragments and water molecules) and the liquid molecules surrounding the bubble. Hence, an internal temperature of the radiolytic gas bubble higher than the average fuel solution temperature is not surprising. Note also that the internal temperature of the radiolytic gas bubbles does not depend directly upon the power history, the energy released, the bubble size or the quantity of radiolytic gas. It depends only on the type of fuel solution (through the hydrogen yield),

and on the parameter $\varepsilon$, i.e., the fraction of the energy due to fissions that results in an increase in the internal temperature of the radiolytic gas bubble.

**Equivalent Void Volume due to Fuel Solution Thermal Expansion**

The thermal expansion of the fuel solution is given by:

$$\Delta V = V_o \left[ e^{\int_{T_o}^{T} \gamma(T)\, dT} - 1 \right], \tag{12}$$

where $\Delta V$ is the fuel solution volume increase due to a temperature increase $\Delta T$, $V_o$ is the initial volume of the fuel solution in the reactor vessel, and $\gamma$ is the coefficient of thermal expansion of the fuel solution.

The temperature increase, considering adiabatic conditions, is given by:

$$\Delta T = \frac{E}{c_{fuel}\ m_f}, \tag{13}$$

where $c_{fuel}$ is the specific heat of the fuel solution.

**SHEBA Specific Experiments**

The model for the equivalent void volume due to radiolytic gas and thermal expansion in solution reactors is implemented for the specific conditions of the Solution High-Energy Burst Assembly, SHEBA, commissioned at Los Alamos National Laboratory in 1993. SHEBA is a cylindrical, bare assembly that uses a uranyl fluoride ($UO_2F_2$) solution with uranium enriched to 5% $^{235}U$. The solution is stored in four stainless-steel tanks and transferred to the critical assembly vessel (CAV) by pumping the solution at predetermined rates. Reactivity control is carried out by varying the solution level.

Several experiments at the SHEBA solution reactor have been conducted and their data is available to validate the proposed model to estimate the fuel solution volume change due to radiolytic gas bubbles and thermal expansion in solution reactors, i.e., Equations (8) and (12), respectively.

The power and energy observed during these experiments are illustrated in Figure 1 for the free run conducted on 3 August 2000.

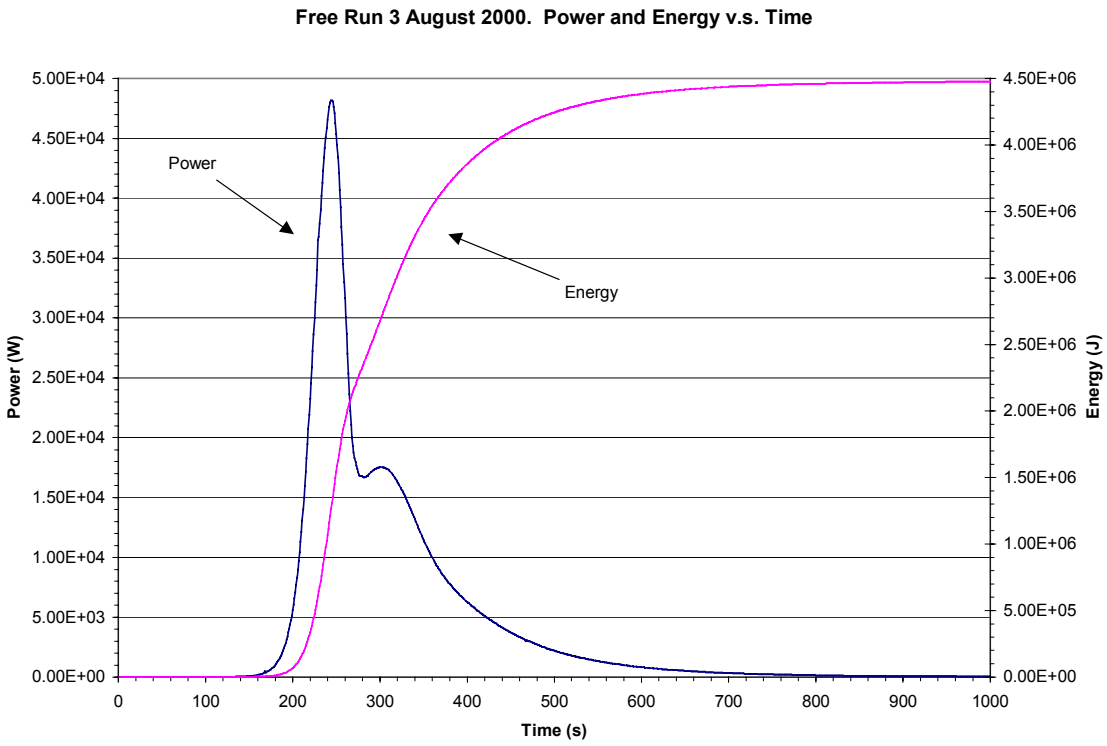


**Figure 1.** Power and energy during a typical free run (3 August 2000).

As indicated in Figure 1, the power initially increases exponentially with an initial reactor period of about 11 s. The power increase slows down, resulting in a power peak of about $4.8\times10^4$ W approximately 247 s into the free run. At this time, the power decreases for about 40 s and then increases again to reach a second smaller peak, of about $1.7\times10^4$ W, approximately 314 s into the free run. From this time on, the power decreases to practically zero at about 1000 s into the free run. The slow down in the initial power increase is due to the negative reactivity introduced by the fuel solution volume increase due to thermal expansion and formation of radiolytic gas bubbles. The smaller power peak occurs when the bulk of radiolytic gas bubbles is released from the fuel solution into the cover gas plenum, indicating that there was enough positive reactivity in the reactor to overcome the thermal expansion of the fuel solution at that time. The power decrease after this second power peak is due to thermal expansion of the fuel solution, which reaches a quasi steady-state value at about 480 s into the free run. As indicated in Figure 1, the reactor energy generated during this free run was approximately $4.47\times 10^6$ J.

Figure 2 shows the fuel solution level, its temperature, and the cover gas temperature for the reactor conditions of the free run conducted on 3 August 2000. During a free run, once the initial reactor period has been established, no more fuel solution is added into the reactor. Then, the observed increase in the fuel solution level during free runs is caused by the fuel solution volume increase due to radiolytic gas bubbles and thermal expansion.

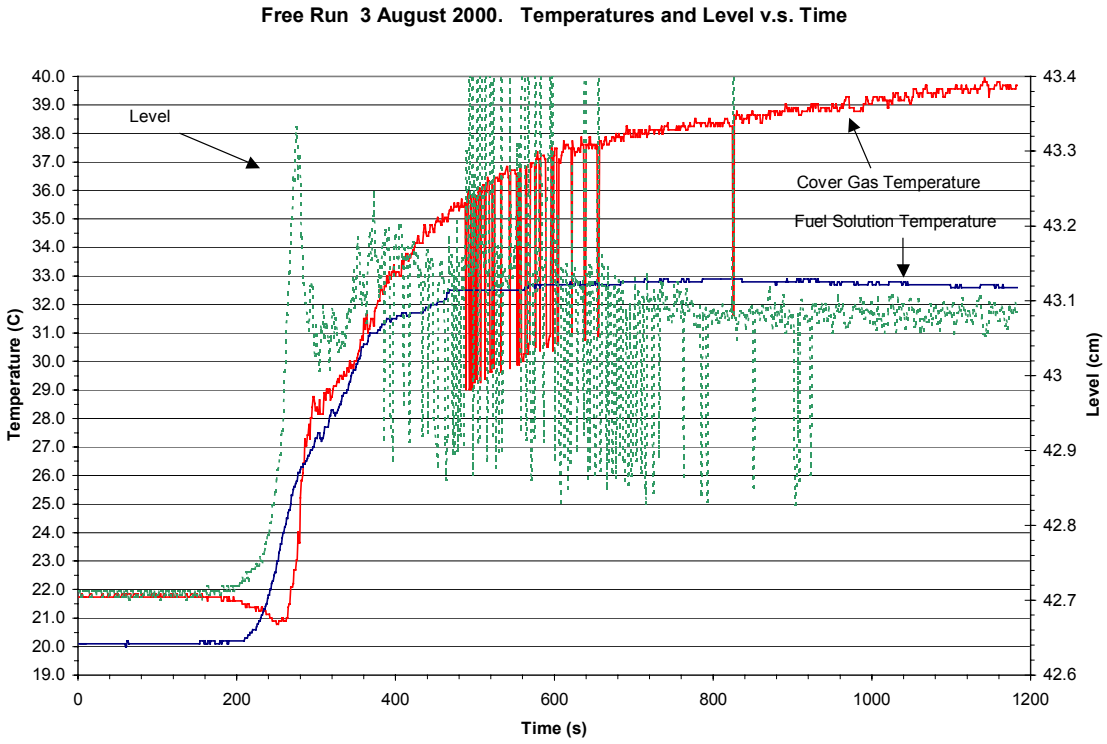


**Figure 2.** Cover gas temperature, fuel solution temperature and fuel solution level during Free Run 3 August 2000.

Figure 2 shows that the fuel solution level increases during the free run due to radiolytic gas bubbles and thermal expansion, and suddenly decreases when most of the radiolytic gas bubbles escape from the fuel solution. The fuel solution temperature increases steadily as the free run progresses, reaching a steady state value by the end of the power transient. The cover gas temperature is higher than the fuel solution after the radiolytic gas bubbles escape from the fuel solution into the cover gas plenum, confirming that radiolytic gas bubbles are not in thermal equilibrium with the fuel solution. Note that the cover gas temperature increases well after the end of the power transient, suggesting that there may be a time lag to heat the cover gas with radiolytic gas due to the relatively low thermal conductivity of the mixture of gases in the cover gas. Right before the release of radiolytic gas bubbles, at about 270 s into the free run, there is a reduction of approximately 1°C in the cover gas temperature. This dip is because, as the fuel solution expands before the release of radiolytic gas, the cover gas volume decreases. Since the pressure and number of moles in the cover gas plenum are constant at this time, the cover gas temperature decreases.

## Model Results for the SHEBA Specific Experiments

The fuel solution volume change due to radiolytic gas bubbles and thermal expansion was estimated using the model with the characteristic values presented in Table 1.

**Table 1.** Characteristic values used to estimate fuel solution volume change due radiolytic gas and thermal expansion in SHEBA.

| Parameter | Value | Description |
|---|---|---|
| $G_{(H2)}$ | $6\times10^{-3}$ molecules/eV | Hydrogen yield in the fuel solution. |
| $\sigma$ | $1.00\times10^{-1}$ N/m | Uranyl fluoride surface tension. |
| $\chi_{H2}$ , $\chi_{O2}$ | 0.1 and 0.13 of critical concentration of $H_2$ and $O_2$, respectively, in water. | Critical concentration of concentration of $H_2$ and $O_2$, respectively, in the fuel solution |
| $\rho_f$ | $2.11\times10^{3}$ kg/m$^3$ | Fuel solution density. |
| $c_f$ | $2.16\times10^{3}$ J/Kg°C | Fuel solution specific heat. |
| $\mu_f$ | $1.85\times10^{-2}$ Pa-s | Fuel solution viscosity. |

Equations (8) and (12) estimate the total fuel solution volume increase due radiolytic gas bubbles and thermal expansion, respectively. The corresponding fuel solution level increase estimated for the free run conducted is presented, together with the actual fuel solution level measured during the experiment, in Figure 3.

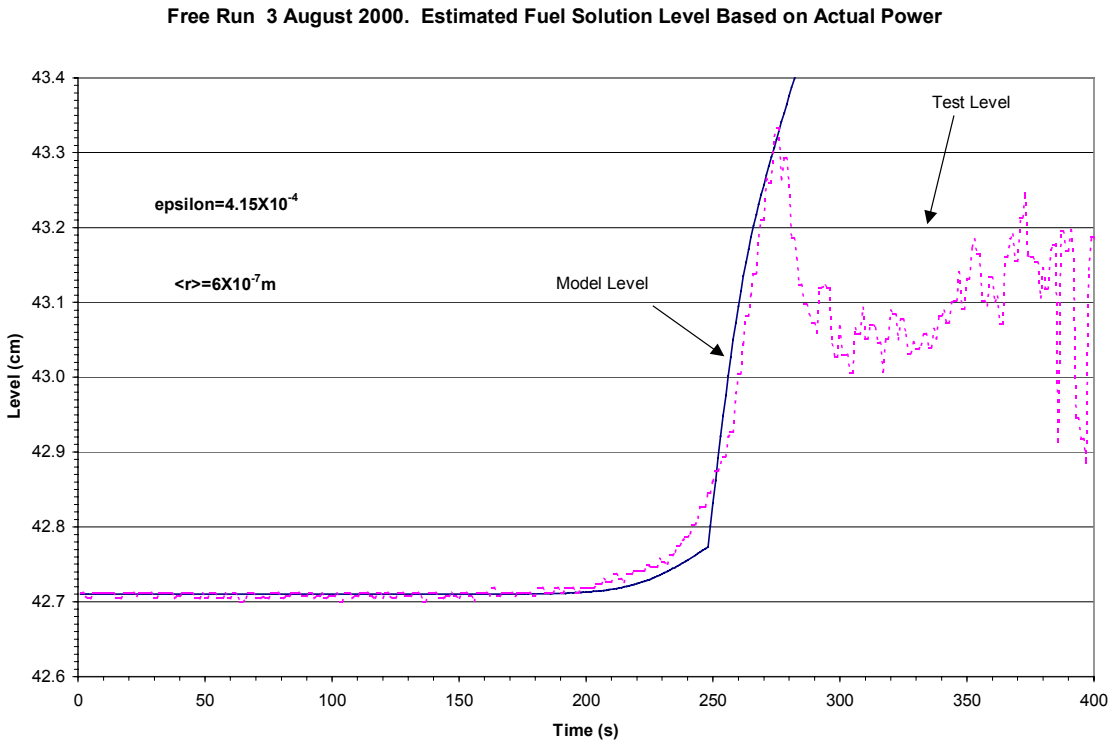


**Figure 3.** Comparison between the actual fuel solution level measured during Free Run 3 August 2000 and the fuel solution level increase estimated from Equations (8) and (12).

As indicated in Figure 3, the fuel solution level increase estimated from Equations (8) and (12) for radiolytic gas bubbles and thermal expansion, respectively, accurately

simulates the observed fuel solution level behavior during the free run. From about 200 s up to approximately 250 s into the free run, the fuel solution level increase is due to thermal expansion only. When the critical concentration is reached, at about 250 s, radiolytic gas bubbles grow fairly rapidly, as indicated by the rapid increase in the fuel solution level at about 250 s. In case of the free run conducted on 3 August 2000, the fraction of reactor energy that results in increase of the radiolytic gas bubble temperature, i.e., parameter $\varepsilon$ in Equation (11), is estimated to be $4.15\times10^{-4}$. The mole-weighted average radius of the ensemble of radiolytic gas bubbles, estimated from the actual fuel solution level increase measured during the experiment, is about 1 μm.

During these experiments, the fuel solution in SHEBA was not cooled. Hence, the fuel solution temperature increased as a result of the operation of the reactor. The increase in the fuel solution temperature estimated with Equation (13), together with the actual fuel solution temperature measured during the experiment, are presented in Figure 4 for the free run.

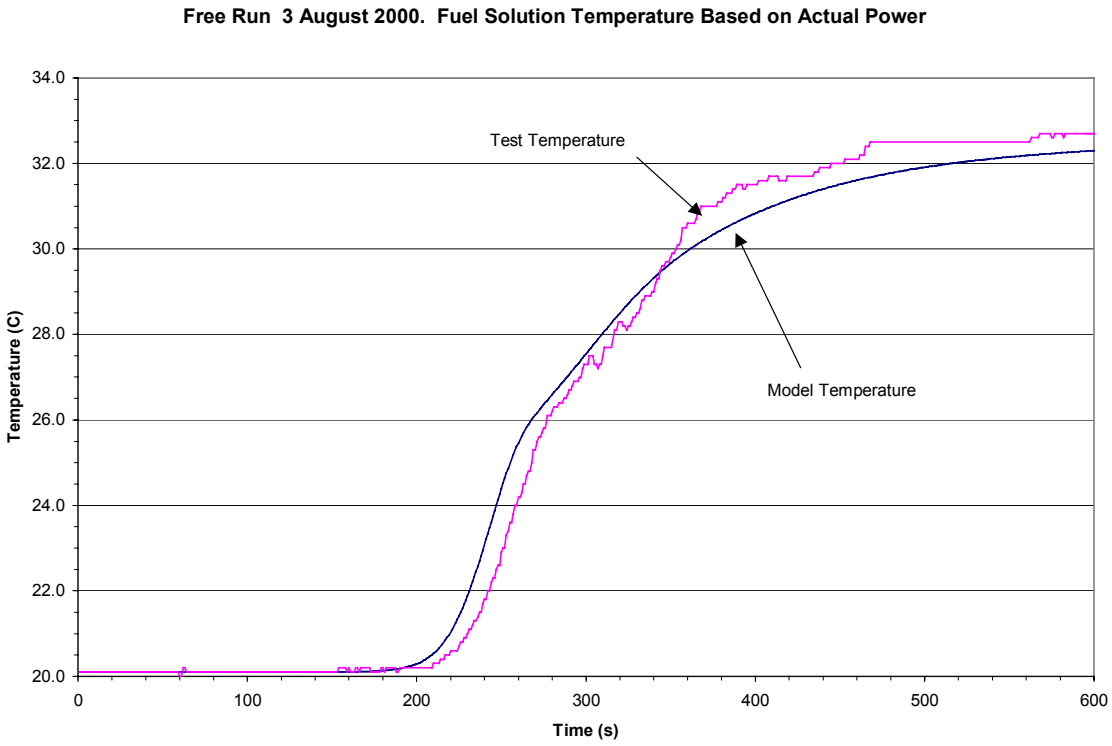


**Figure 4.** Comparison between the fuel solution temperature estimated with Equation (13) and the actual temperature measured during Free Run 3 August 2000.

As indicated in Figure 4, the fuel solution temperature increase estimated with Equation (13) accurately simulates the observed fuel solution temperature observed during the free run. The results in Figure 4 show that the fuel solution temperature is proportional to energy generated during the free run.

## Conclusions

Aqueous homogeneous solution reactors have been proposed for the production of medical isotopes. However, the reactivity effects of fuel solution volume change, due to formation of radiolytic gas bubbles and thermal expansion, have to be mitigated to allow steady-state operation of solution reactors. The results of the free run experiments analyzed indicate that the proposed model to estimate the void volume due to radiolytic gas bubbles and thermal expansion in solution reactors can accurately describe the observed behavior during the experiments. This void volume due to radiolytic gas bubbles and fuel solution thermal expansion can then be used in the investigation of reactivity effects in fissile solutions. In addition, these experiments confirm that the radiolytic gas bubbles are formed at a higher temperature than the fuel solution temperature. These experiments also indicate that the mole-weighted average for the radiolytic gas bubbles in uranyl fluoride solutions is about 1 μm.

Finally, it should be noted that another model, currently under development, would simulate the power behavior during the transient given the initial fuel solution level and density. The model is based on Monte Carlo simulation with the MCNP computer code [Briesmeister, 1997] to obtain the reactor reactivity as a function of the fuel solution density, which, in turn, changes due to thermal expansion and radiolytic gas bubble formation.

## References


Briesmeister, J. F., Editor, *MCNP™ A General Monte Carlo N-Particle Transport Code*, Los Alamos National Laboratory, Report LA-12625-M, March 1997.

Bunker, M., *Status Report on the Water Boiler Reactor*, Los Alamos National Laboratory, LA-2854, October 1963.

Cappiello, C., K. Butterfield, R. Sanchez, J. Bounds, R. Kimpland, R. Damjanovich, P. Jaegers, *Solution High-Energy Burst Assembly (SHEBA) Results from Subprompt Critical Experiments with Uranyl Fluoride Fuel*, Los Alamos National Laboratory, LA-13373-MS, October 1997.

Chopelas, A and R. Ball, "The Passive Safety of the Medical Isotope Production Reactor (MIPR)", Babcock & Wilcox, Handout distributed during the ANS Winter Meeting, November 17, 1993.

Dunenfeld, M., D.L. Hetrick, D.P. Gamble, A. Norman, E.R. Cohen, R.E. Wimmer, and A. Schwarz, *Kinetic Experiments on Water Boilers. "A" Core Report. Part II, Analysis of Results*, Atomics International, NAA-SR-5416, February 1962.

Hosoma, T., M. Aritomi, and T. Kawa, "Formulas to Correct Excess Pressure and Pressure Shift to be Used in Volume Measurement for Plutonium Nitrate Solution", *Nuclear Technology*, **129**, 218-235, 2000.

Kimpland, R. H. and D. E. Kornreich, “A Two-Dimensional Multiregion Computer Model for Predicting Nuclear Excursions in Aqueous Homogeneous Solution Assemblies”, *Nuclear Science and Engineering*, **122**, 204-211, 1996.

King, L. D. P., *Status of Work Related to the King Reactor*, Los Alamos National Laboratory, LA-4926-MS, 1972.

Lane, J. A., H. G. MacPherson and F. Maslan, *Fluid Fuel Reactors*, Addison-Wesley Publishing Company, Inc., Reading, MA, 1958.

ORNL (Oak Ridge National Laboratory), “Aqueous Homogeneous Reactor Fuel Technology”, in *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy*, Volume 7, Reactor Technology, United Nations, Geneva, 1958.