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TO: James P. Sloughter, Hanford K Basins Closure Project

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SUBJECT: **Potential for Flammable Atmosphere Above the K-Basin Pool During Grouting**

1.0 SUMMARY AND SUGGESTIONS

The present work describes how reaction rate data measured by PNNL (Fisher et al., 2004) may be used to conclude that large amounts of residual aluminum on the basin floor may be tolerated at the time of grouting. Basic methodology used here is as follows:

- We cast results in terms of allowed reactive area of Al per unit area of basin floor, which can be compared with estimates of residual Al,
- Results are obtained up to 90 °C by creating and extrapolating a rate law from reference data,
- Potential for flammability is governed by the rate of gas production and its rate of mixing above the basin pool up to the level of the grating,
- The model for hydrogen generation simply uses the rate law and reaction area,
- The model for hydrogen mixing invokes turbulent diffusion and is based on FAI laboratory data and analyses to address flammability potential at the Hanford tank farms, and
- By setting the maximum hydrogen concentration equal to the flammability limit (4% in air) at the basin pool surface, the allowed Al reactive area is found and plotted versus temperature.

The worst case result (90 °C) allows nearly 100 times the average aluminum loading, and allows slightly greater than the assumed peak loading, corresponding to an 8 inch canister.

Suggestions to better document and use these results for K Basins Closure are:

- Create a self-contained report by combining the present work with up-front information about the present state of the basins including amounts of residual Al.
- Address uncertainty and assertions of conservatism. Experimental data at temperatures likely to be attained during grouting would be useful. The FAI model could be expanded to include concentrated sources of Al, to show that the present work is indeed bounding.
- Apply this work to grout in containers. A container model would consider other waste reactions, radiolysis, venting of the container headspace, and groups of containers in a storage vault.
- Calculate the aerosol source in the K basins due to bubble release during grouting, and use this as part of the authorization basis to select appropriate controls.
- Incorporate current techniques into the HANSF computer code already licensed to the K Basins Closure Project and use a HANSF calculation in the authorization basis.

2.0 INTRODUCTION AND PURPOSE

During grouting of the K Basin after fuel and sludge are removed, hydrogen gas will be generated as a result of the chemical reaction between residual aluminum and high pH grout. The gas will rise to the surface of the basin pool in the form of bubbles. The bubbles will burst at the pool surface releasing their H_2 gas to the otherwise stagnant air layer between the surface of the pool and the grating suspended above the pool. There is a concern that if the rate of hydrogen gas generation is too high, a flammable H_2/air atmosphere will develop above the surface of the pool.

An important question that arises in this regard is how much aluminum can be left behind in the basin without creating a flammability hazard condition above the basin pool during grouting? This question is addressed in this memo by formulating a kinetic law for H_2 production as a function of grout temperature that is suggested by recent scoping experiments (Fisher et al., 2004) and combining it with an available successful model (Epstein and Burelbach, 2000) of vertical turbulent diffusion of a light fluid (H_2) through a heavier miscible fluid medium (air).

Since the rate of generation of H_2 reaction product gas is proportional to the surface area of residual aluminum in the basin, the aluminum concentration is usually expressed as an Al surface area-to-basin floor surface area ratio (hereafter referred to as the Al area ratio; see Whyatt et al., 2004). The analysis presented here demonstrates that the residual Al area ratios that can be tolerated without creating a flammability hazard above the basin pool are much higher than the Al area ratio based on the actual aluminum inventory in the basin.

3.0 TURBULENT NATURAL CONVECTION DIFFUSION COEFFICIENT

The upward transport of light H_2 gas through the dense air layer above the pool may be regarded as a process analogous to Fickian (molecular) diffusion. However the diffusion coefficient for this process is several orders of magnitude larger than the molecular diffusion coefficient for the H_2/air mixture, because vertical diffusion of the light H_2 gas is caused by buoyancy rather than molecular motion.

The concept of a vertical turbulent diffusion coefficient has been widely applied in modeling the upward transport of a lighter fluid through a heavier and miscible fluid (Baird and Rice, 1975; Gardner, 1977; Epstein, 1988; Baird and Ramo Rao, 1991; Holmes et al., 1991; Baird et al., 1992; and Epstein and Burelbach, 2000, 2001). Baird and Ramo Rao (1991) and Holmes et al. (1991) measured the turbulent diffusion (dispersion) coefficient E under steady-state conditions and found that E can be correlated by an equation of the form

$$E = \ell^2 \left(\frac{g}{\rho} \frac{\partial \rho}{\partial z} \right) \tag{1}$$

where ρ is the local density of the mixture at vertical location z, ℓ is a characteristic mixing length and g is the gravitational constant. Most of the experiments on density-gradient-driven vertical diffusion were carried out in high aspect ratio tubes and, as might be anticipated, the mixing length ℓ in Eq. (1) was found to be a constant value proportional to the column diameter.

Experimental work conducted at FAI and supported by the flammable gas risk assessment program at Hanford focused on gravitational diffusion layers that are much broader than they are tall (Epstein and Burelbach, 2000). These are the kinds of layers that apply when Al is distributed over a large basin floor area. This work showed that ℓ is proportional to the thickness (depth) of the diffusion layer and that the proportionality constant β has the value 0.164. Denoting the vertical distance between the pool surface and the grating by the symbol H, the pertinent mixing length for steady-state, upward H_2 transport above the pool is

$$\ell = \beta H \qquad , \qquad \beta = 0.164 \tag{2}$$

4.0 H_2/AIR DIFFUSION PROBLEM: CRITICAL HYDROGEN GENERATION RATE FOR FLAMMABLE ATMOSPHERE ABOVE BASIN POOL

Epstein and Burelbach (2000) developed the diffusion equation and boundary conditions for a brine/water turbulent diffusion layer. There exists a simple analogy between mixing in the brine/water system and mixing in a heavy gas/light gas system so that their equations may be readily converted to allow useful prediction of the H_2 transport rate above the basin pool. The conversion equations, which can be found in a later paper by Epstein and Burelbach (2001), result in the following steady-state diffusion equation for the H_2/air system:

$$\frac{d}{dz}\left[\left(-\frac{dX_L}{dz}\right)^{3/2}\right] = 0 \tag{3}$$

where X_L is the volume fraction of the light gas (H_2) at height z above the pool surface. The boundary condition at the pool surface is

$$u_0 = \frac{2}{3} H^2 K \left(-\frac{\partial X_L}{\partial z}\right)^{3/2} \qquad ; \qquad \text{at } z = 0 \tag{4}$$

where

$$K = \frac{3}{2} \beta^2 \left[g \left(1 - \frac{M_L}{M_H}\right)\right]^{1/2} \tag{5}$$

and M_L, M_H are, respectively, the molecular weights of the light gas and heavy gas (air). Equation (4) expresses the condition that the light gas generation rate (superficial velocity u_0) is equal to the turbulent upward diffusion velocity just above the pool surface; it is derivable for small light gas volume fractions. At the pool surface the light gas volume fraction is designated by the symbol $X_L(0)$; so that

$$X_L = X_L(0) \qquad \text{at} \qquad z = 0 \tag{6}$$

Finally at the grating level H the light gas concentration is zero:

$$X_L = 0 \quad \text{at} \qquad z = H \tag{7}$$

Solving Eq. (3) subject to boundary conditions Eqs. (6) and (7) gives the linear concentration profile

$$X_L = X_L(0)\left[1 - \frac{z}{H}\right] \tag{8}$$

Substituting Eq. (8) into Eq. (4) and identifying $X_L(0)$ with the light gas LFL concentration X_{LFL} results in the sought expression for the hydrogen generation velocity required to raise the H_2 concentration at the pool surface to its LFL value

$$u_0 = b^2\left[gH\left(1 - \frac{M_L}{M_H}\right)X_{LFL}^3\right]^{1/2} \tag{9}$$

Inserting the appropriate parameter values into Eq. (9), namely $\beta = 0.164$, $H = 1.45$ m, $M_L = 2$, $M_H = 29$, the predicted superficial H_2 generation velocity that produces $X_{LFL} = 0.04$ at the pool surface is

$$u_0 = 7.83 \times 10^{-4} \text{ m s}^{-1} \tag{10}$$

5.0 PROPOSED ARRHENIUS RATE LAW FOR H_2 GENERATION

Measurements of H_2 generation off aluminum coupons submerged in calcium hydroxide [$Ca(OH)_2$] solutions and in a portland cement mixture have been reported by Fischer et al. (2004). The experiment with portland cement was performed at 27.1°C and the initial (maximum) rate of H_2 generation was 0.3 $cm^3\ min^{-1}$. The aluminum sample dimensions were 7.62 cm x 2.54 cm x 0.47 cm and, therefore, had a total surface area of 48.3 cm^2. Thus the H_2 volumetric gas generation rate per unit area of Al was

$$\dot{Q}''_{H_2} = 1.04 \text{ x } 10^{-6} \text{ m}^3 \text{ H}_2 \text{ m}^{-2} \text{ s}^{-1} \qquad \text{at T} = 27.1°\text{C} \tag{11}$$

The data on H_2 generation in $Ca(OH)_2$ solutions showed a factor of five increase when the solution temperature was increased from 23°C to 52°C. Using this observation, assuming that the temperature (T) dependence of the reaction in portland cement is the same as that in $Ca(OH)_2$ and assuming Arrhenius behavior, gives

$$\dot{Q}''_{H_2} = \dot{Q}''_0 \exp\left(-\frac{T_{act}}{T}\right) \tag{12}$$

where the activation temperature T_{act} = 5339K. The numerical value of the pre-exponential coefficient in Eq. (12) is readily obtained by incorporating the experimental measurement given by Eq. (11) and is $\dot{Q}''_0 = 55.68 \text{ m}^3 \text{ H}_2 \text{ m}^{-2} \text{ s}^{-1}$.

6.0 CRITICAL ALUMINUM SURFACE AREA RATIO FOR ONSET OF FLAMMABLE ATMOSPHERE ABOVE BASIN POOL

The incipient flammability condition can now be readily formulated, being identified with the condition that the H_2 gas-chemical-generation rate becomes equal to the upward H_2 turbulent diffusion rate through air when the H_2 concentration at the pool surface is equal to its LFL value:

$$\dot{Q}''_{H_2} A_{Al} = u_0 A_{floor} \tag{13}$$

where the value of u_0 is given by Eq. (10) and A_{Al} and A_{floor} are the surface areas of the aluminum and basin floor, respectively.

Solving Eq. (13) for A_{Al}/A_{floor} and using Eq. (12) gives the desired, explicit flammability relation

$$\frac{A_{Al}}{A_{floor}} = \frac{u_0 \exp(T_{act}/T)}{\dot{Q}_0''} \tag{14}$$

This A_{Al}/A_{floor} versus grout temperature T relation is plotted in Fig. 1. The figure enables the distinct question of interest to be answered: how much aluminum can be left behind and therefore grouted before a flammable atmosphere appears above the surface of the pool. Also shown in Fig. 1 is the average aluminum area ratio 0.76 if the total inventory of aluminum surface area (596 m^2) in K Basin were spread uniformly across the basin floor (780 m^2). As pointed out by Whyatt et al. (2004) local concentrations of aluminum will exceed the average value. Several examples of this are noted in Fig. 1, very conservatively assuming that the local high concentrations are floor-wide averages. Clearly, all the aluminum area ratios indicated in the figure do not lead to a flammable atmosphere at the surface of the K Basin pool.

7.0 CONCLUDING REMARKS

The possibility of flammable mixtures of hydrogen and air collecting above the basin pool during grouting activities in K-Basin was assessed. The analysis fully accounted for the efficient mixing of H_2 and air by buoyancy driven turbulent diffusion. The permissible aluminum area ratios were predicted to be orders of magnitude above the actual (estimated) average aluminum surface area ratio of 0.76, even for grout temperatures as high as 90°C.

It is important to mention that, while the gas phase diffusion analysis exploited here has a firm theoretical and experimental foundation, there is considerable uncertainty associated with the hydrogen generation rate law used in the analysis. The rate law was based on only one relevant gas generation data point for aluminum covered by cement paste. Temperature extrapolation was made using data on H_2 generation during aluminum/calcium hydroxide solution reactions. However, the hazard implications of the rate law uncertainty are probably not significant considering the wide margin between the Al area ratio flammability curve and the actual average Al area ratio in the basin.

Concentrated regions of aluminum having above-average Al area ratios were not treated in this memo. A concentrated source produces a bubble plume which spreads laterally as it rises through the pool. Upon breaking through the pool surface the hydrogen gas plume is diluted by inward, lateral entrainment of air as well as turbulent vertical diffusion (see Epstein and Burelbach, 2001). Accordingly, the H_2 concentration at the pool surface due to a localized region of concentrated aluminum would be less than that if the high Al concentration existed over the entire basin floor. Therefore, since the Al area ratios of local concentrated sources based on actual aluminum hardware (Whyatt et al., 2004) even when assumed to exist over the entire basin floor do not exceed the Al area ratio flammability curve (see Fig. 1), there appears to be little incentive from a safety point of view to pursue the problem of concentrated regions of aluminum.

8.0 REFERENCES

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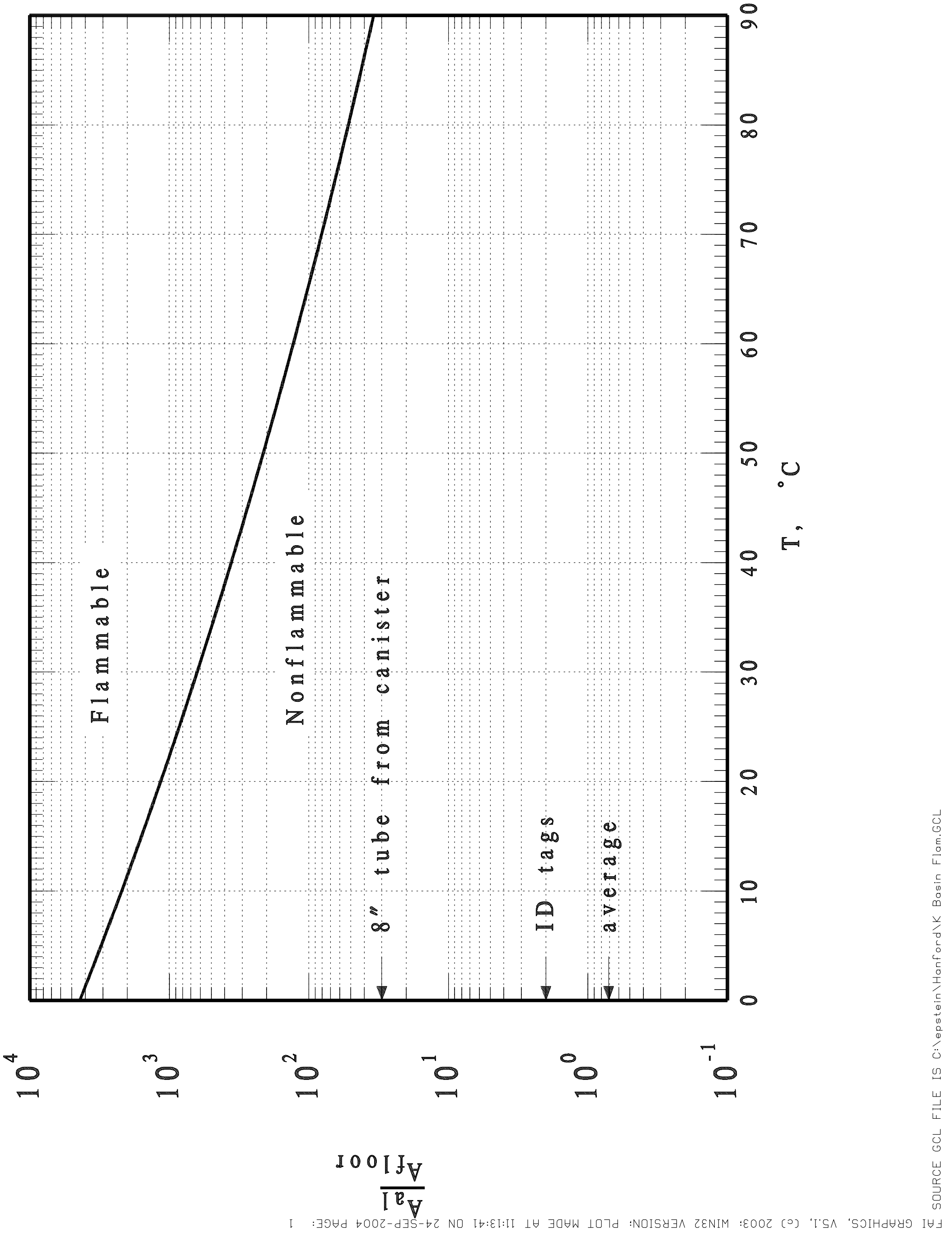

Figure 1 Critical aluminum surface area ratio for flammable condition at surface of K Basin pool versus grout temperature.