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# ASSESSMENT OF THE POTENTIAL FOR HYDROGEN GENERATION DURING GROUTING OPERATIONS IN THE R- AND P-REACTOR VESSELS

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**TITLE: Assessment of the Potential for Hydrogen Generation During Grouting Operations  
in the R- and P- Reactor Vessels**

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**Record of Revisions**

Rev.	Date	Description
2	May 2010	<p>An error in the calculation of a constant was corrected. This resulted in a change in the calculated numbers that appeared in the tables, figures and the appendix.</p> <p>Some of the assumptions that were made for the calculations were clarified.</p> <p>The risk of utilizing Portland cement grout in the R-reactor vessel was discussed in more detail.</p>
1	December 2009	<p>Walk-down inspections determined that there were no USH's present in the R-reactor vessel. As a result, the surface area of aluminum exposed to the grout for this reactor vessel is less than that which was assumed in the previous revision of this document. The calculations for the R-reactor vessel were performed again based on this information. No changes were made to the calculations for the P-reactor vessel.</p>
0	October 2009	Initial issue

## Assessment of the Potential for Hydrogen Generation During Grouting Operations in the R- and P-Reactor Vessels

### Executive Summary

The R- and P-reactor buildings were retired from service and are now being prepared for deactivation and decommissioning (D&D). D&D activities will consist primarily of immobilizing contaminated components and structures in a grout-like formulation. Aluminum corrodes very rapidly when it comes in contact with the alkaline grout materials and as a result produces hydrogen gas. To address this potential deflagration/explosion hazard, the Materials Science and Technology Directorate (MS&T) of the Savannah River National Laboratory (SRNL) has been requested to review and evaluate existing experimental and analytical studies of this issue to determine if any process constraints on the chemistry of the fill material and the fill operation are necessary.

Various options exist for the type of grout material that may be used for D&D of the reactor vessels. The grout formulation options include ceramicrete (pH 6-8), low pH portland cement + silica fume grout (pH 10.4), or Portland cement grout (pH 12.5). The assessment concluded that either ceramicrete or the silica fume grout may be used to safely grout the P-reactor vessel. The risk of accumulation of a flammable mixture of hydrogen between the grout-air interface and the top of the reactor is very low. Portland cement grout, on the other hand, for the same range of process parameters does not provide a margin of safety against the accumulation of flammable gas in the reactor vessel during grouting operations in the P-reactor vessel. It is recommended that this grout not be utilized for this task.

The R-reactor vessel contains significantly less aluminum based on current facility process knowledge, surface observations, and drawings. Therefore, a Portland cement grout may be considered for grouting operations as well as the other grout formulations. For example, if the grout fill rate is less than 1 inch/min and the grout temperature is maintained at 70 °C or less, the risk of hydrogen accumulation during fill operations in the R-reactor vessel is low for the Portland cement. Alternatively, if the grout fill rate is less than 0.5 inch/min and the grout is maintained at a temperature of 80 °C, the risk is again low.

Although these calculations are conservative, there are some measures that may be taken to further minimize the potential for hydrogen evolution.

1. Minimize the temperature of the grout as much as practical. Lower temperatures will mean lower hydrogen generation rates. For P-reactor, grout temperatures less than 100 °C should provide an adequate safety margin for the pH 8 and pH 10.4 grout formulations. For R-reactor, grout temperatures less than 70 °C or 80 °C

- will provide an adequate safety margin for the Portland cement. The other grout formulations are also viable options for R-reactor.
2. Minimize the grout fill rate as much as practical. Lowering the fill rate takes advantage of passivation of the aluminum components and hence lower hydrogen generation rates. For P-reactor, fill rates that are less than 2 inches/min for the ceramicrete and the silica fume grouts will reduce the chance of significant hydrogen accumulation. For R-reactor, fill rates less than 1 inch/min will again minimize the risk of hydrogen accumulation.
  3. Ventilate the building as much as practical (e.g., leave doors open) to further disperse hydrogen. The volumetric hydrogen generation rates in the P-reactor vessel, however, are low for the pH 8 and pH 10.4 grout, (i.e., less than 0.97 ft<sup>3</sup>/min).

If further walk-down inspections of the reactor vessels suggest an increase in the actual areal density of aluminum, the calculations should be re-visited.

## Introduction

The R- and P-reactor buildings were retired from service and are now being prepared for deactivation and decommissioning. D&D activities will consist primarily of immobilizing contaminated components and structures in a grout-like formulation. This report specifically addresses the grouting of the reactor vessels along with the aluminum components that are contained with the vessel [1].

The aluminum components contained in the reactor pose a concern in that aluminum will corrode very rapidly when it comes in contact with the very alkaline grout materials, and as a result produce hydrogen gas. To address this potential deflagration/explosion hazard, the Materials Science and Technology Directorate (MS&T) of the Savannah River National Laboratory (SRNL) has been requested to review and evaluate existing experimental and analytical studies of this issue to determine if any process constraints on the chemistry of the fill material and the fill operation are necessary. This report does not address hydrogen generation after the reactor has been filled with grout. Further analysis, perhaps laboratory testing, would be needed to assess the behavior in grouts that have cured.

Various options exist for the type of grout material that may be used for D&D of the reactor vessels. The grout formulation options include ceramicrete (pH 6-8), low pH portland cement + silica fume grout (pH 10.4), or portland cement grout (pH 12.5). As part of this task, the rate of hydrogen generation in the vessels for grouts with a pH range from 8 to 13 will be calculated. The calculations considered such factors as temperature, the rate at which the grout fills the vessel, the surface area of the components present, the surface area of the reactor vessel and the void volume of the reactor vessel. The principles utilized in calculating the hydrogen generation rate from the R- and P-reactor disassembly basins were employed [2]. The objective of these calculations was to

provide input as to which grout formulation is appropriate for the operations so that the risk of hydrogen gas accumulation is minimized.

### Approach

Pacific Northwest National Laboratory (PNNL) performed a similar analysis for the K basins at the Hanford Site [3]. This analysis was reviewed and applied to the situation for the R- and P- reactor vessels. The process is as follows:

- 1) Aluminum corrodes upon exposure to the grout.
- 2) Hydrogen is generated as a consequence of the corrosion reaction.
- 3) The gas rises to the surface of the grout in the form of bubbles.
- 4) The bubbles will burst at the grout surface releasing H<sub>2</sub> gas into the stagnant air layer.

This process was modeled by formulating a kinetic law for hydrogen production as a function of the grout temperature, pH, fill rate and combining it with a model for vertical turbulent diffusion of a light fluid (H<sub>2</sub>) through a heavier miscible fluid medium (air). Vertical turbulent diffusion is a process analogous to molecular diffusion. However, the diffusion coefficient is several orders of magnitude larger than the molecular diffusion coefficient for the H<sub>2</sub>/air mixture, because vertical diffusion of the lighter gas is due to buoyancy rather than molecular motion. This model has been confirmed experimentally and has been shown to be effective for predicting diffusion layers that are broader than they are tall [4].

The assumptions used in the analysis were:

- The aluminum is exposed to wet cement while the reactor vessel is being filled. Corrosion and hydrogen generation rates associated with this condition were assumed.
- There are openings in the reactor vessel that allow hydrogen to escape the vessel.
- Once the hydrogen reaches the top of the reactor vessel, there is sufficient advection to disperse the hydrogen within the building superstructure.

Based on these assumptions the only place that hydrogen could potentially accumulate is in the region between the grout layer and the top of the reactor vessel.

The first part of the model involved developing a kinetic expression for the generation of hydrogen due to aluminum corrosion. This kinetic expression can be represented by the following relationship:

$$Q = f(\text{pH}, T, h) \quad (1)$$

Where Q is the hydrogen generation rate in cm<sup>3</sup>/cm<sup>2</sup>/min, T is the grout temperature in °K, and h is the level of the grout as a function of time t in inches. The derivation of this relationship is shown in the Appendix. The final explicit relationship was:

$$Q = \frac{Q_0 * m * [1 - \exp(-0.00385 * H/m)]}{0.00385 * H} \quad (2)$$

where,

$$Q_0 = 3 * 10^{-14} * \exp(2.0952 * \text{pH}) * \exp[-5339 * (1/T - 1/303)] \quad (3)$$

Where  $Q_0$  is the hydrogen generation rate as a function of pH and temperature,  $m$  is the rate at which the grout fill level increases with time, and  $H$  is the fill level at a given time,  $t$ .

Laboratory tests performed at PNNL to measure the hydrogen generation rate of a non-corroded aluminum metal coupon immersed in either grout or saturated  $\text{Ca}(\text{OH})_2$  solution provided part of the technical basis for the parameters that go into the equation. The key results from the tests were:

- The initial hydrogen generation rate of non-corroded aluminum metal in a grout mixture at 25 °C is 0.3 cm<sup>3</sup>/min.
- The hydrogen generation rate of non-corroded aluminum metal in grout decreases to approximately 0.15 cm<sup>3</sup>/min after 2 to 3 hours of exposure to the grout mixture at 25 °C. The decrease in corrosion rate is due to the formation of a corrosion product (principally tricalcium aluminum hydroxide and hydrocalumite) layer on the surface of the aluminum metal.
- The hydrogen generation rate for aluminum metal in grout was performed at 27 °C. Extrapolation of this result to hydrogen generation rates for higher grout temperatures was made using the test results from aluminum exposed to  $\text{Ca}(\text{OH})_2$  solution (i.e., similar to the pore solution in the grout). However, the five-fold increase in hydrogen generation rate with a 30 °C increase in the  $\text{Ca}(\text{OH})_2$  solution temperature is consistent with literature values for hydrogen generation in grout. Matsuo et al. observed a 3 fold increase in hydrogen generation rate with a 30 °C increase in an inhibited grout mixture [5].
- Literature data was also used to obtain the corrosion rate as a function of pH [6, 7]. The corrosion rate was then converted to a hydrogen generation rate assuming that 1.5 moles of hydrogen are generated for every one mole of aluminum that corrodes.

The following conservatisms and uncertainties were considered when applying the data to the R- and P- reactor vessel situation.

- The experimentally measured hydrogen generation rate was determined on clean or non-corroded aluminum metal. The surface of the aluminum metal in the reactor vessels is corroded. The aluminum metal in the reactors has been there for many years and the surface is protected by an oxide film. In either case, the rate of hydrogen generation from corrosion would be lower than that measured for the non-corroded aluminum metal coupons in the laboratory tests.

- The hydrogen generation rate due to aluminum metal corroding in grout is based on only one relevant gas generation test. However, four tests were conducted in a  $\text{Ca}(\text{OH})_2$  solution and the results were consistent based on chemical engineering fundamentals (i.e., mass transfer conditions in the grout are poorer than those in the  $\text{Ca}(\text{OH})_2$  solution). Additionally, the hydrogen gas generation rate for the aluminum in grout was also comparable to other values in the literature. Matsuo et al. measured a rate of  $0.105 \text{ cm}^3/\text{min}$  for aluminum exposed to Portland cement at room temperature [8, 9].
- There are no additional species present in the Portland cement grout or in the lower pH grouts, that significantly accelerate the corrosion reaction.

While the first two bullets do indicate that there is uncertainty in the experimental data due to the few number of laboratory tests, it is unlikely that this is significant relative to other conservatisms in the analysis.

The second part of the model involves the mass transport of the hydrogen gas from the surface of the grout to the top of the reactor. The derivation of the mass transport equation is also shown in the Appendix. The analysis does not account for dissipation of hydrogen between the surface of the grout and the top of the reactor due to advection. Accounting for this phenomenon would minimize the accumulation of hydrogen in this region.

The flux of hydrogen away from the surface is related to the superficial velocity,  $u_0$ . The superficial velocity may be expressed as:

$$u_0 = \beta^2 * [g * H_0 * (1 - (M_{\text{H}_2}/M_{\text{air}})) * X_{\text{LFL}}^3]^{1/2} \quad (4)$$

where  $\beta$  is a proportionality constant,  $g$  is the acceleration of gravity,  $H_0$  is the distance between the grout-air interface and the top of the reactor,  $M$  is the molecular weight of either hydrogen or air, and  $X$  is the volume % of hydrogen in air at the lower flammability limit (LFL). In the case of hydrogen the LFL is 4% by volume.

The incipient flammability condition occurs when the gas generation rate due to corrosion equals the flux of hydrogen through air. The boundary condition at the interface between the grout and air is that the hydrogen gas concentration is at the LFL. For safety class operations, with radioactive materials stored within a vessel, a criterion of 60% LFL is utilized for the evaluation [10]. The equation that describes this condition is:

$$Q * A_{\text{Al}} = u_0 * A_a \quad (5)$$

where  $A_{\text{Al}}$  is the surface area of aluminum in contact with grout and  $A_a$  is the void cross-sectional area of the reactor vessel. Equation 5 can be re-arranged to give the critical areal density ratio.

$$[A_{\text{Al}}/A_a]_c = u_0/Q \quad (6)$$

For the analysis, a plot of  $[A_{Al}/A_a]_c$  vs. H is prepared. Examples of this plot are shown in Figures 1 through 13. If the critical area density is greater than the actual areal density, there is a low probability of a flammable condition. On the other hand if it is less than the actual areal density, there is a possibility of a flammable condition developing.

### Thermal Analysis

Calorimetry experiments are being conducted to estimate the temperature rise that will occur in the grout during these operations [11]. Maximum temperatures observed during these tests for the different grout formulations may be used for final calculations. For this assessment, case studies will be performed for grout temperatures between 50 and 100 °C to understand the effect of temperature on the hydrogen generation rate for the various grout formulations.

### Determination of Areal Density Ratios

Actual areal density ratios are being calculated based on current facility process knowledge, surface observations, and drawings of the R- and P-reactor vessels [12]. The predominant aluminum components present in the reactor vessels are the universal sleeve housing (USH) and thimble tubes. It will be assumed that the inner and outer surfaces of these components will be exposed to the grout. The aluminum surface area,  $A_{Al}$ , as a function of the fill level, H, was calculated from the following relationship:

$$A_{Al}(h) = N_{USH} * \pi * (D_{USH_o} + D_{USH_i}) * H + N_T * \pi * (D_{T_o} + D_{T_i}) * H \quad (7)$$

where D is the diameter, subscript USH is for the USH tubes, subscript T is for the thimble tubes, subscript o represents the exterior surface, subscript i represents the interior surface, and N is the quantity of USH or thimble tubes. The calculation did not include the surface area of the ends of the tubes.

The cross-sectional area of the vessel,  $A_a$ , was calculated by subtracting the cross-sectional area of the USHs, thimble tubes, septifoils and spargers from the total tank cross-sectional area. This is represented by the following equation:

$$A_a = \pi * D_t^2/4 - N_{USH} * \pi * (D_{USH_o}^2 - D_{USH_i}^2)/4 - N_T * \pi * (D_{T_o}^2 - D_{T_i}^2)/4 - N_{ss} * \pi * D_{ss}^2/4 \quad (8)$$

where subscript a is for the cross-sectional area, subscript t is for the tank, and subscript ss is for the septifoils and the spargers. In P-reactor it is estimated that there are 432 USH tubes, 61 septifoils, and 66 thimble tubes and 6 spargers [13]. The USH tubes have outer and inner diameters, 4.25 inches and 4.00 inches, respectively. The outer and inner diameters for the thimble tubes are 1.5 inches and 1.0 inches, respectively. The septifoils and spargers were modeled as a cylinder with a diameter of 3.5 inches. Calculations of these areas are exhibited in the Appendix. In R-reactor, it was determined that there are no USH tubes present (i.e., only septifoils, thimbles and spargers are present). The lack of USH tubes means that  $A_{Al}$ , and hence the areal density ratio, for R-reactor is less than that of P-reactor by a factor of approximately 25 (see Figures 1-13).

### Determination of Volumetric Flow Rate of Hydrogen

The maximum volumetric flow rate of hydrogen generated during the grouting operations was also estimated. Knowledge of this value will assist in the evaluation of whether or not there is adequate ventilation to effectively disperse the hydrogen. The volumetric flow rate,  $Q_{TOT}$  is calculated from the following equation:

$$Q_{TOT} = Q * A_{AI} \quad (9)$$

A calculation of this flow rate is exhibited in the Appendix.

### Results

The case studies that were performed are summarized in Table 1 and the results are shown in Figures 1 through 13. Some of the key trends were:

- An increase in temperature resulted in a lower critical areal density and therefore greater risk of developing a flammable condition (e.g., compare Figures 1 and 2).
- An increase in pH resulted in a lower critical areal density and therefore a greater risk of developing a flammable condition (e.g., examine any figure).
- An increase in the fill rate resulted in a lower critical areal density, although the effect was not as great as temperature or pH (see Figure 11).
- The 60% LFL criterion provides a significant margin on the risk of developing a flammable condition (e.g., compare figures 2 and 13).
- An increase in the actual areal density ratio results in a greater risk of developing a flammable condition. Thus, as shown in the figures, there is a greater risk of developing a flammable condition in the P-reactor vessel than there is in the R-reactor vessel.

The results of the case studies for the P-reactor vessel demonstrate that two of the grout formulations, the ceramicrete and the silica fume, should not result in a flammable condition during reactor vessel grouting operations as long as they are within the parameters of the case studies. Even at 60% LFL the critical areal density ratio for the silica fume grout is at least 1 to 2 orders of magnitude greater than the actual areal density ratio, while the ratio for the ceramicrete is 3 to 4 orders of magnitude greater. At 100% LFL these margins increase further to 2 to 3 orders of magnitude for the silica fume grout and 4 to 5 orders of magnitude for the ceramicrete. The portland cement grout is not a viable option for the P-reactor vessel as it exceeds the 60% LFL criterion for each case that was examined.

The results of the case studies for the R-reactor vessel suggest that all three grout formulations may be viable. For example, at the Case 3 conditions (i.e., 70 °C, fill rate of 1 inch/min, 60% LFL, see Figure 3) the critical areal density ratio is a factor of 5.5 greater than the actual areal density ratio for the Portland cement, while the ratio for the

silica fume grout is 2 to 3 orders of magnitude greater and 4 to 5 orders of magnitude greater for the ceramicrete grout. Although not shown, similar margins would be obtained at a temperature of 80 °C with a fill rate of 0.5 inch/min.

The factor of 5.5 difference between the critical areal density ratio and the actual areal density was examined further to assess the risk associated with utilizing Portland cement grout for R-reactor. The surface area of the aluminum thimbles was approximately 96,400 square inches. A total aluminum surface area of approximately 530,300 square inches could be contained in the R-reactor vessel before the 60% LFL criterion would be exceeded (i.e., there would need to be an additional 433,900 square inches of aluminum in the reactor vessel). This surface area is roughly equivalent to 90 USH's. Thus, if the facility is confident in the information provided by current facility process knowledge and drawings, the risk of approaching the LFL is low.

Although these results are encouraging, due to the potential consequences, taking precautions that reduce the likelihood of a flammable condition are recommended. These measures include ensuring that the building has adequate ventilation during the grouting process, minimizing the grout temperature, and operating at a slower fill rate. In order to evaluate the ventilation needs, the volumetric flow rate of hydrogen was calculated for each case for the P and R-reactor vessels. The results are summarized in Tables 2 and 3.

For the P-reactor vessel, the hydrogen flow rates for the pH 8 and pH 10.4 grout are very small, less than 0.97 ft<sup>3</sup>/min (see Table 2). The flow rates for the pH 12.5 grout are higher than those for the lower pH grouts, ranging between 5.5 and 79 ft<sup>3</sup>/min, however, the rates could be manageable with proper ventilation. For the R-reactor vessel (see Table 3), the flow rates are a factor of approximately 25 less than the P-reactor vessel (i.e., proportional to the change in aluminum surface area).

**Table 1. Summary of Case Studies**

Case	Temperature (°C)	Fill Rate (inches/minute)	pH	LFL Level (%)
1	50	1	8, 10.4, and 12.5	60
2	100	1	8, 10.4, and 12.5	60
3	70	1	8, 10.4, and 12.5	60
4	80	1	8, 10.4, and 12.5	60
5	50	0.5	8, 10.4, and 12.5	60
6	60	0.5	8, 10.4, and 12.5	60
7	70	0.5	8, 10.4, and 12.5	60
8	50	2	8, 10.4, and 12.5	60
9	60	2	8, 10.4, and 12.5	60
10	70	2	8, 10.4, and 12.5	60
11	70	2, 8, and 16	10.4	60
12	100	2	8, 10.4, and 12.5	60
13	100	1	8, 10.4, and 12.5	100

**Table 2. Summary of Volumetric Flow Rates of Hydrogen for the P- Reactor Vessel Case Studies.**

Case	Temperature (°C)	Fill Rate (inches/min)	pH 10.4	pH 8	pH 12.5
			Qtot (cu.ft./min)	Qtot (cu.ft./min)	Qtot (cu.ft./min)
1	50	1	9.00E-02	5.90E-04	7.50E+00
2	100	1	8.25E-01	5.40E-03	6.72E+01
3	70	1	2.36E-01	1.50E-03	1.92E+01
4	80	1	3.66E-01	2.40E-03	2.98E+01
5	50	0.5	6.80E-02	4.40E-04	5.50E+00
6	60	0.5	1.11E-01	7.30E-04	9.03E+00
7	70	0.5	1.76E-01	1.16E-03	1.44E+01
8	50	2	1.05E-01	6.90E-04	8.58E+00
9	60	2	1.73E-01	1.10E-02	1.41E+01
10	70	2	2.76E-01	1.80E-03	2.25E+01
11	70	2	2.80E-01	NA	NA
11	70	8	3.10E-01	NA	NA
11	70	16	3.20E-01	NA	NA
12	100	2	9.66E-01	6.30E-03	7.87E+01
13	100	1	8.25E-01	5.40E-03	6.72E+01

**Table 3. Summary of Volumetric Flow Rates of Hydrogen for the R- Reactor Vessel Case Studies.**

Case	Temperature (°C)	Fill Rate (inches/min)	pH 10.4	pH 8	pH 12.5
			Qtot (cu.ft./min)	Qtot (cu.ft./min)	Qtot (cu.ft./min)
1	50	1	3.98E-03	2.61E-05	3.24E-01
2	100	1	3.60E-02	2.40E-04	2.97E+00
3	70	1	1.00E-02	6.83E-05	8.50E-01
4	80	1	1.62E-02	1.06E-04	1.32E+00
5	50	0.5	2.99E-03	1.95E-05	2.43E-01
6	60	0.5	4.90E-03	3.21E-05	4.00E-01
7	70	0.5	7.83E-03	5.12E-05	6.37E-01
8	50	2	4.66E-03	3.05E-05	3.80E-01
9	60	2	7.70E-03	5.02E-05	6.24E-01
10	70	2	1.22E-02	8.00E-05	9.95E-01
11	70	2	1.20E-02	NA	NA
11	70	8	1.40E-02	NA	NA
11	70	16	1.40E-02	NA	NA
12	100	2	4.30E-02	2.80E-04	3.48E+00
13	100	1	3.60E-02	2.40E-04	2.97E+00

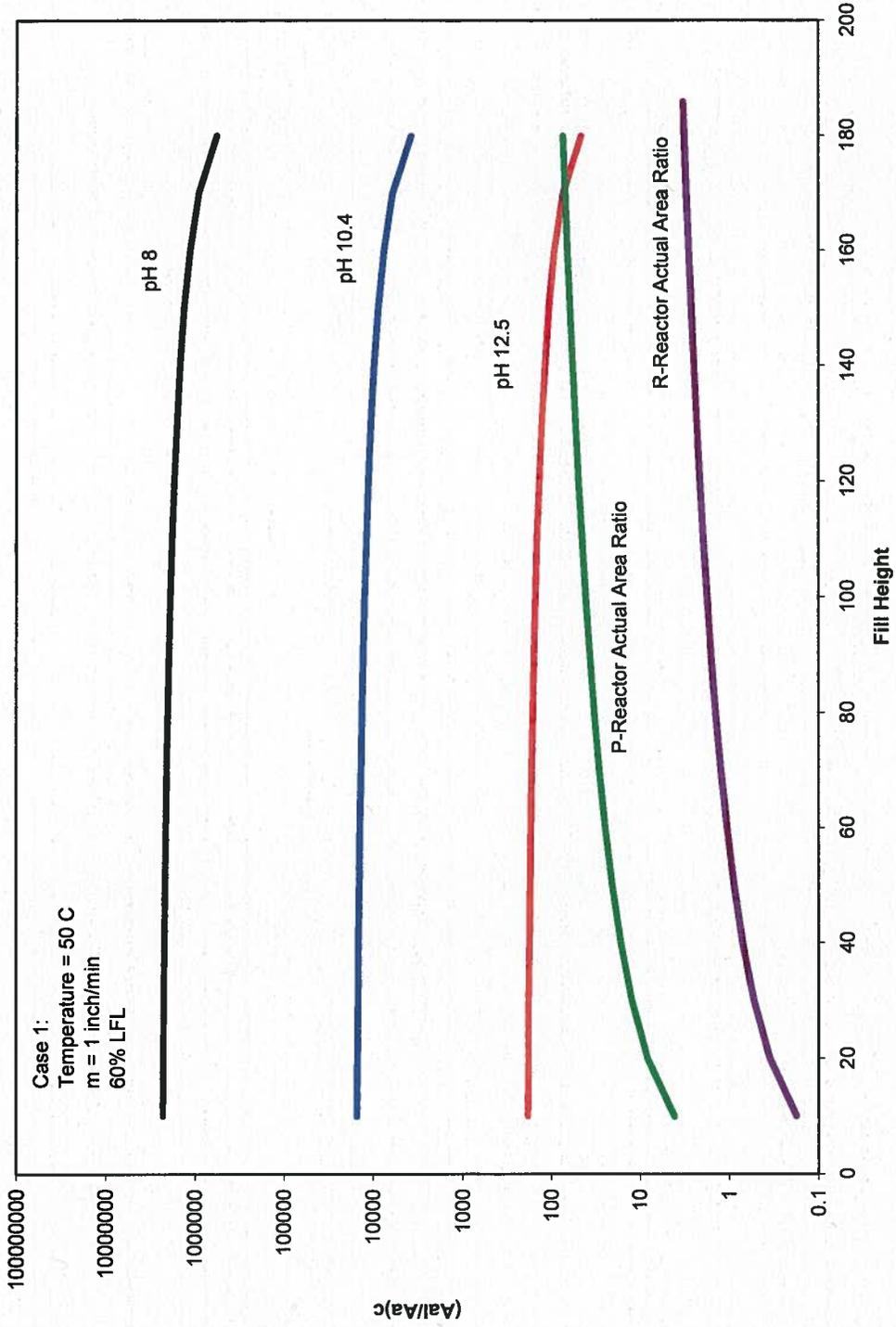


Figure 1. Critical areal density ratio for flammable condition in R& P Reactor Vessels for Case 1.

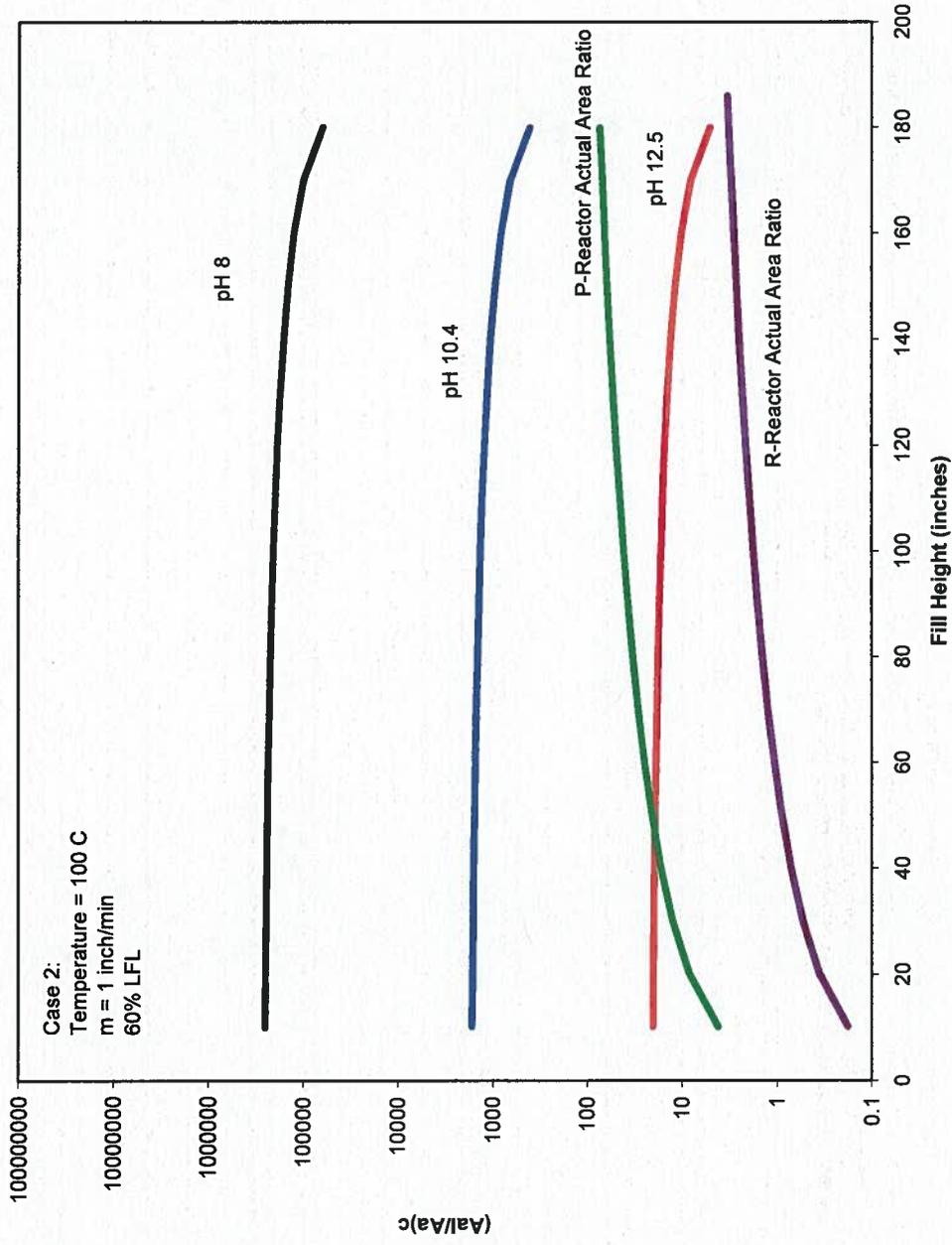


Figure 2. Critical areal density ratio for flammable condition in R& P Reactor Vessels for Case 2.

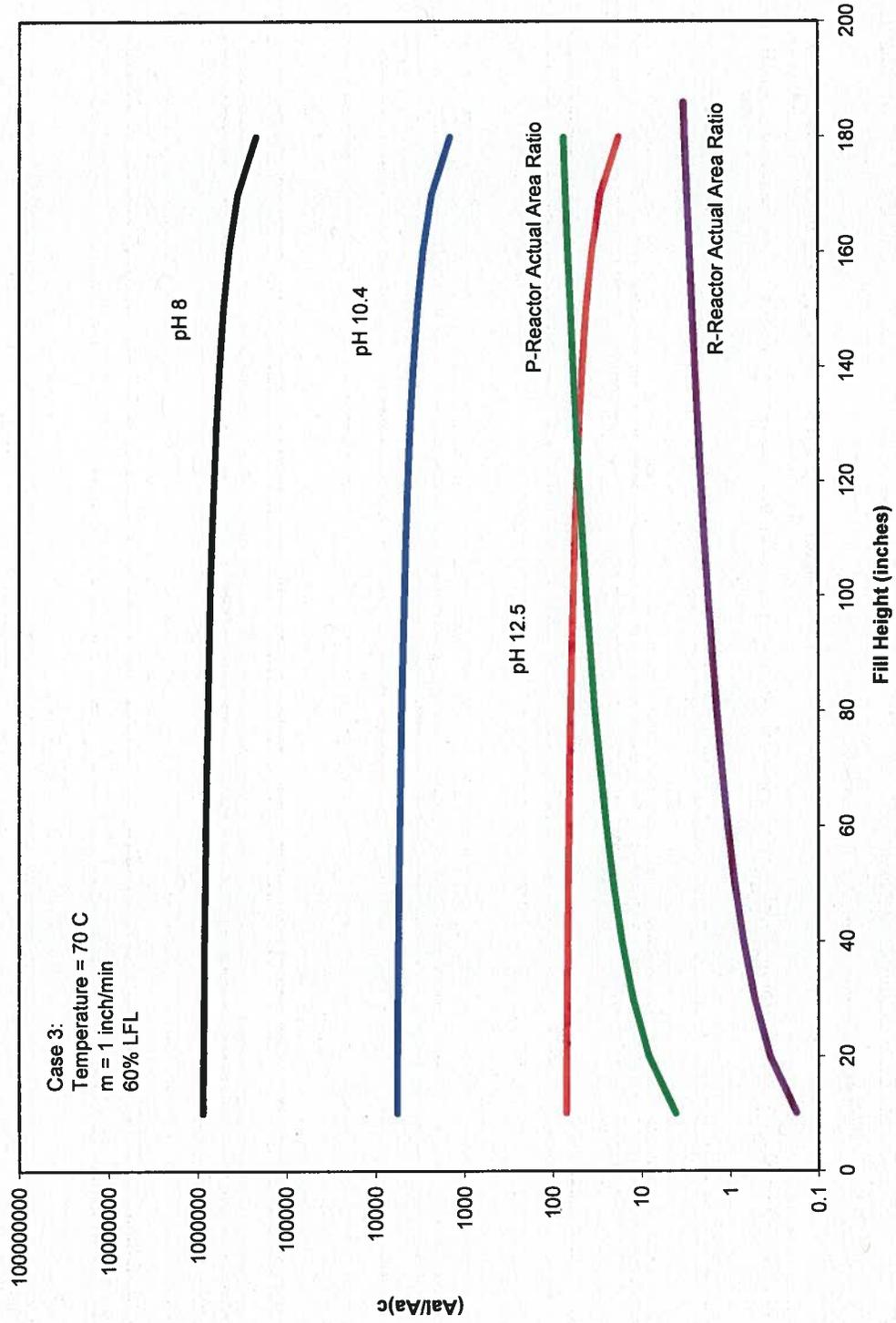


Figure 3. Critical areal density ratio for flammable condition in R & P Reactor Vessels for Case 3.

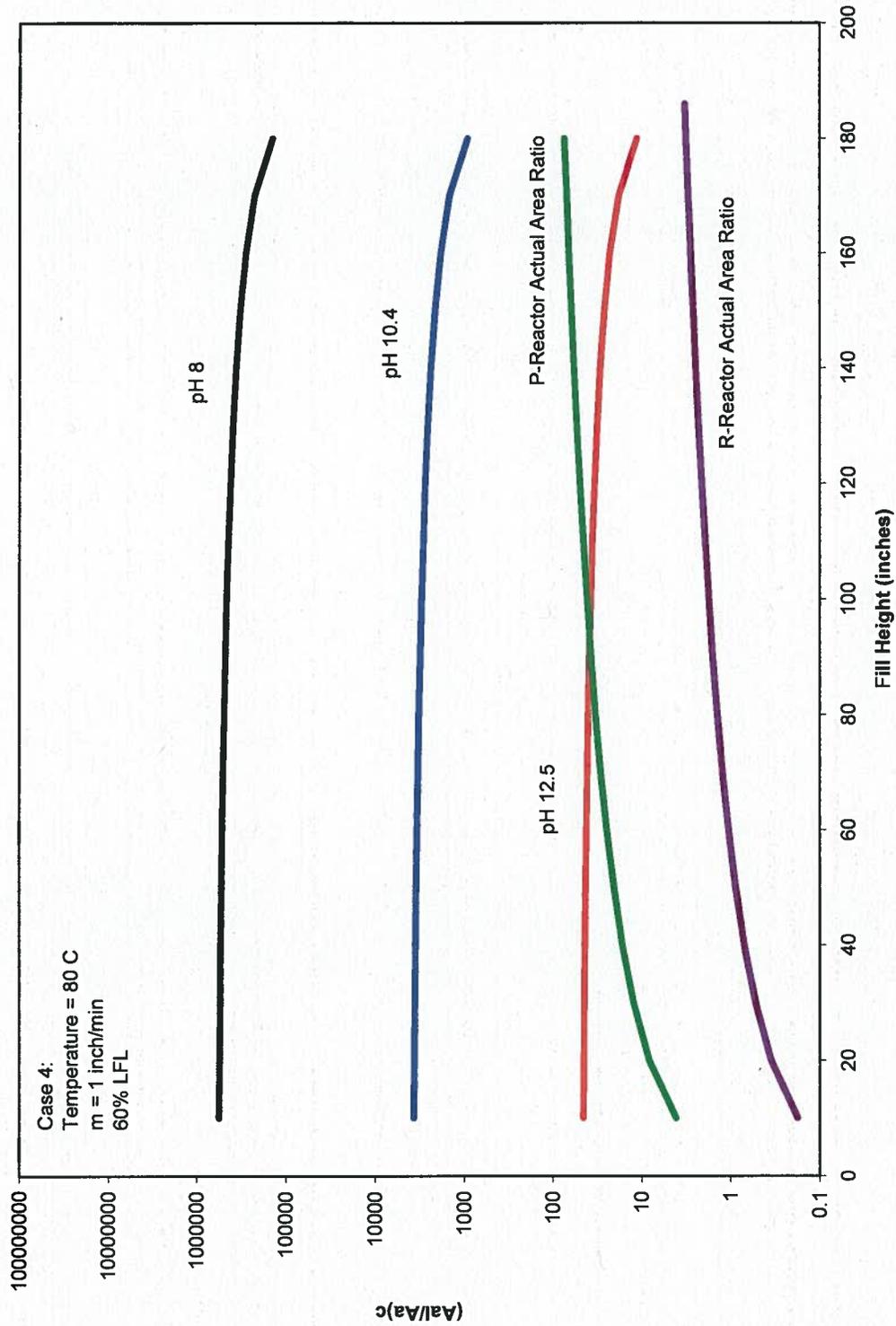


Figure 4. Critical area density ratio for flammable condition in R& P Reactor Vessels for Case 4.

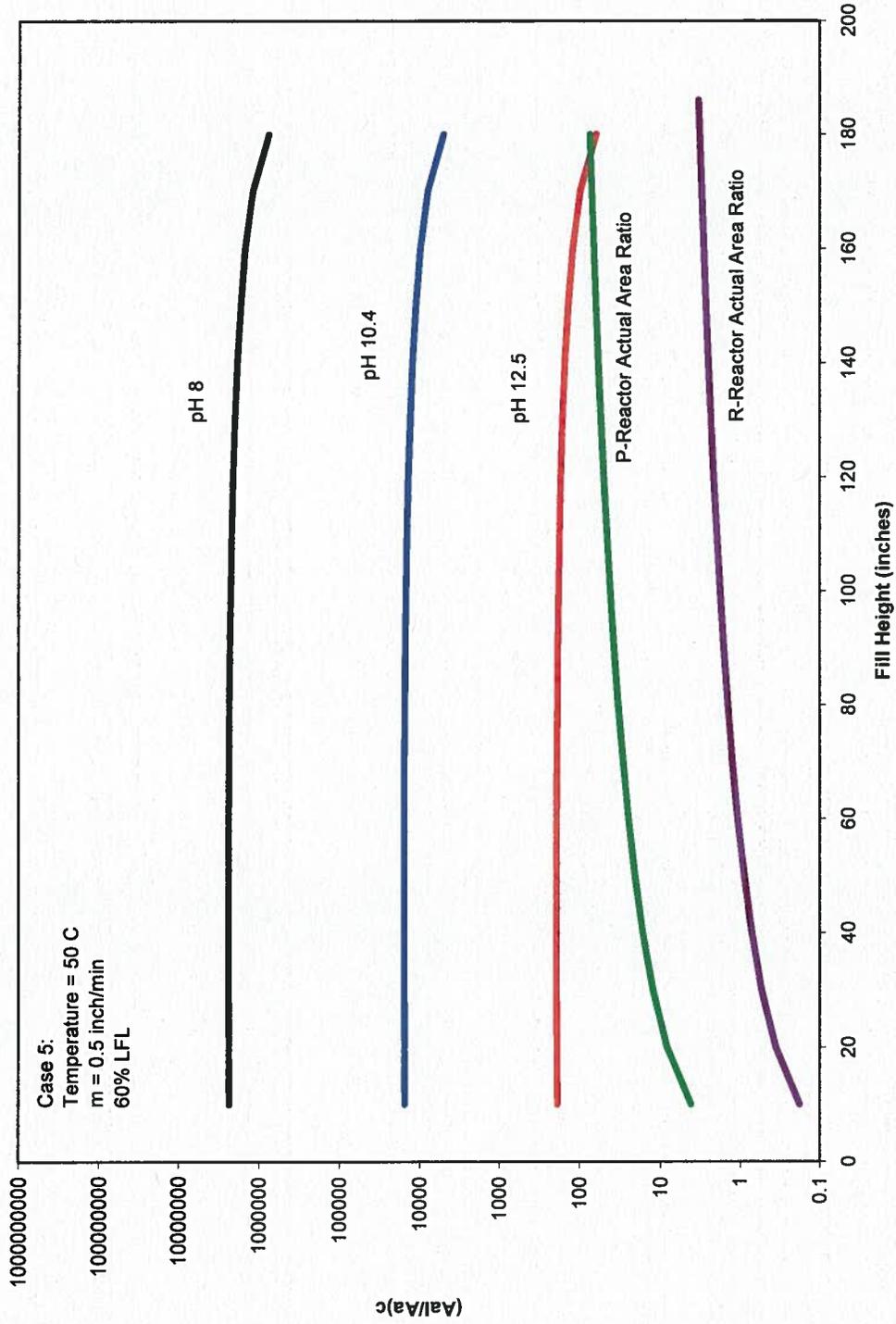


Figure 5. Critical areal density ratio for flammable condition in R& P Reactor Vessels for Case 5.

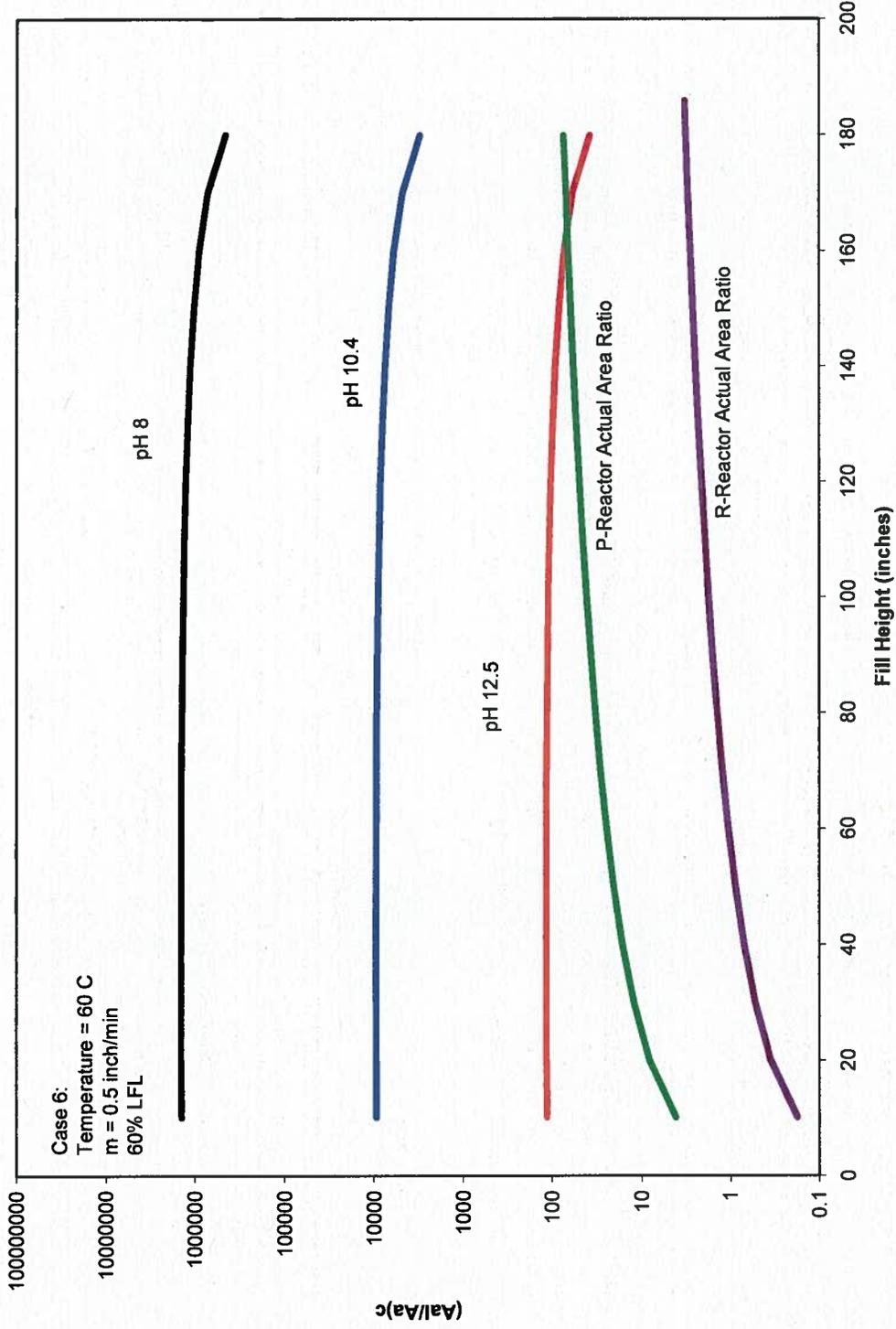


Figure 6. Critical area density ratio for flammable condition in R& P Reactor Vessels for Case 6.

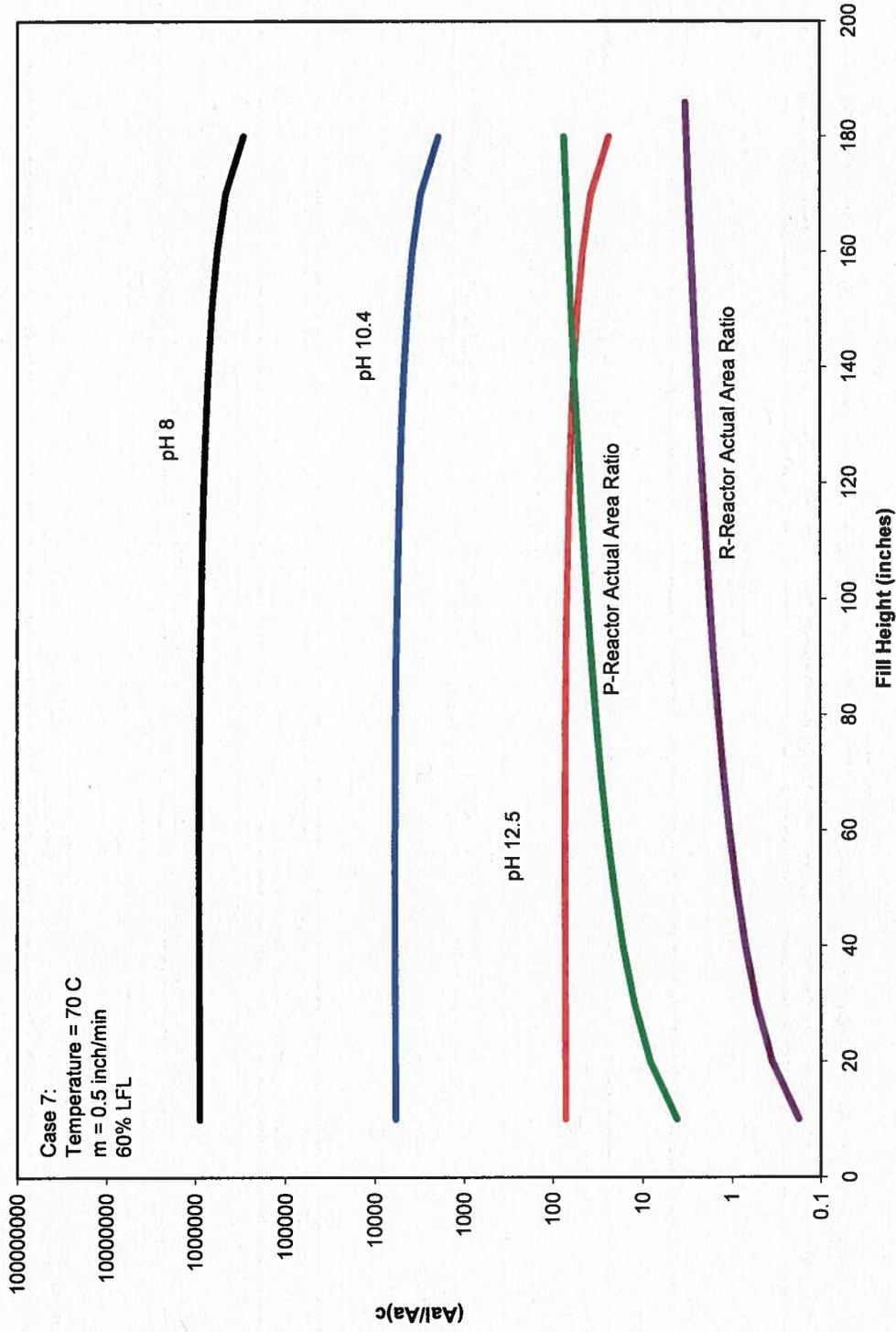


Figure 7. Critical area density ratio for flammable condition in R& P Reactor Vessels for Case 7.

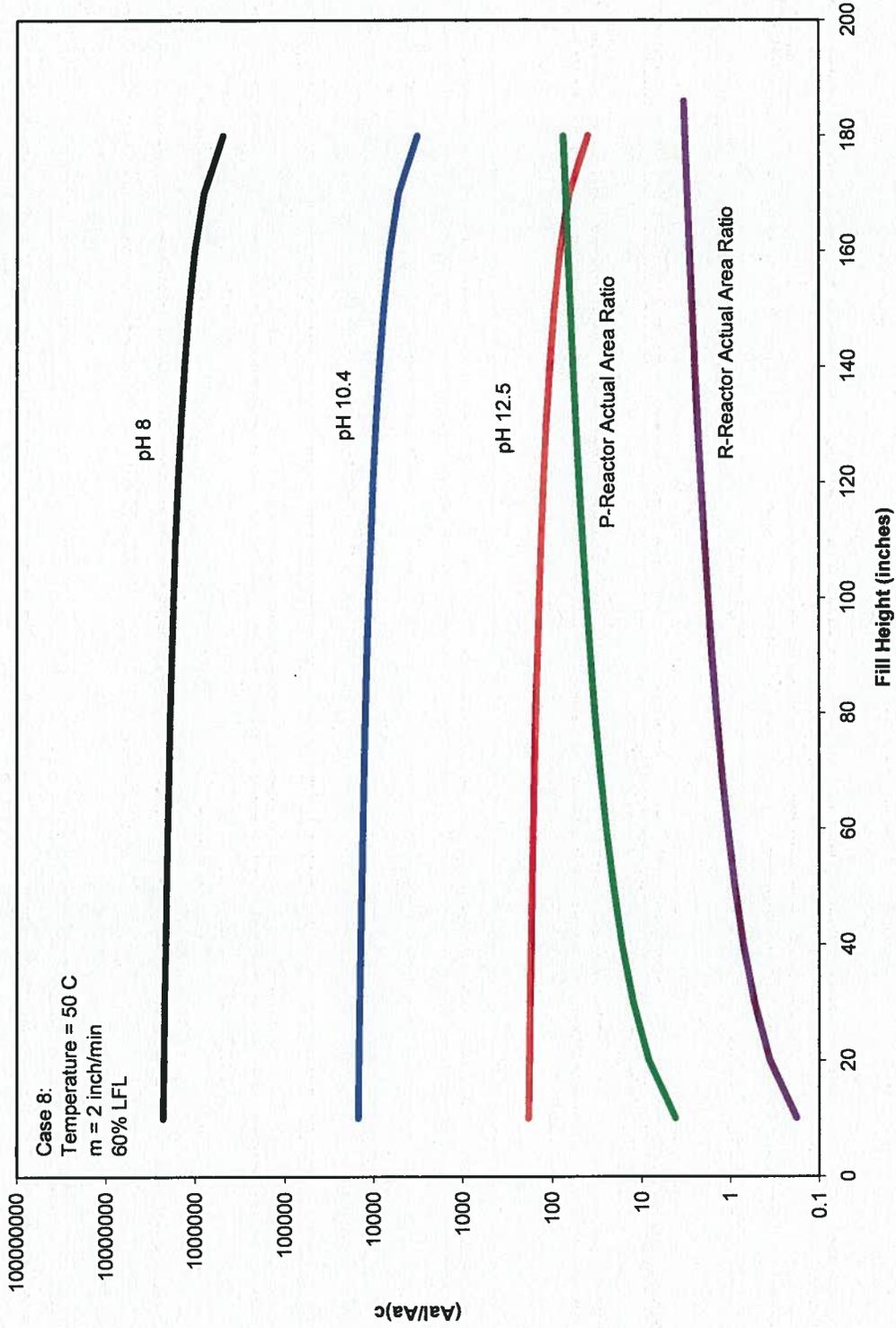


Figure 8. Critical area density ratio for flammable condition in R& P Reactor Vessels for Case 8.

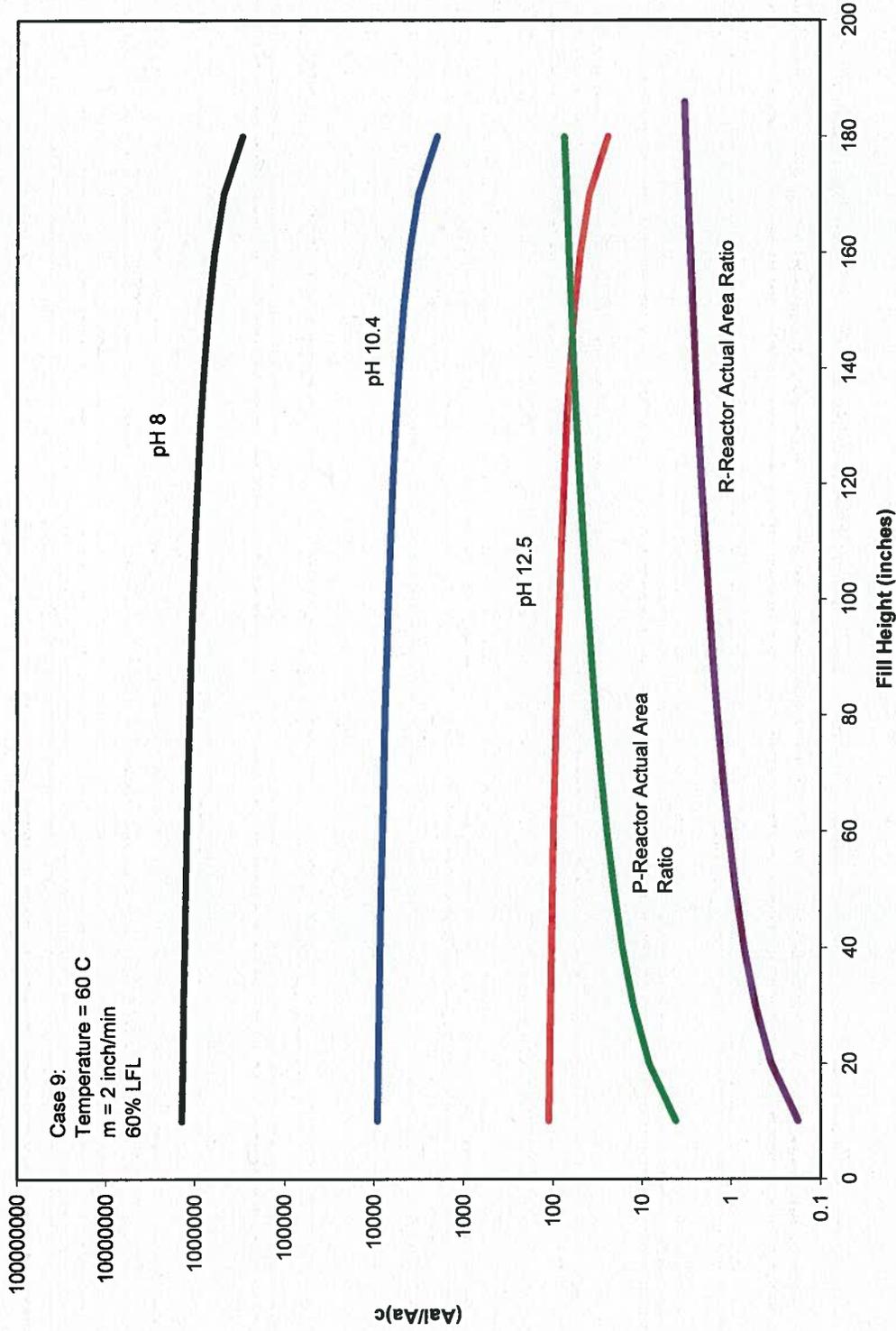


Figure 9. Critical area density ratio for flammable condition in R& P Reactor Vessels for Case 9.

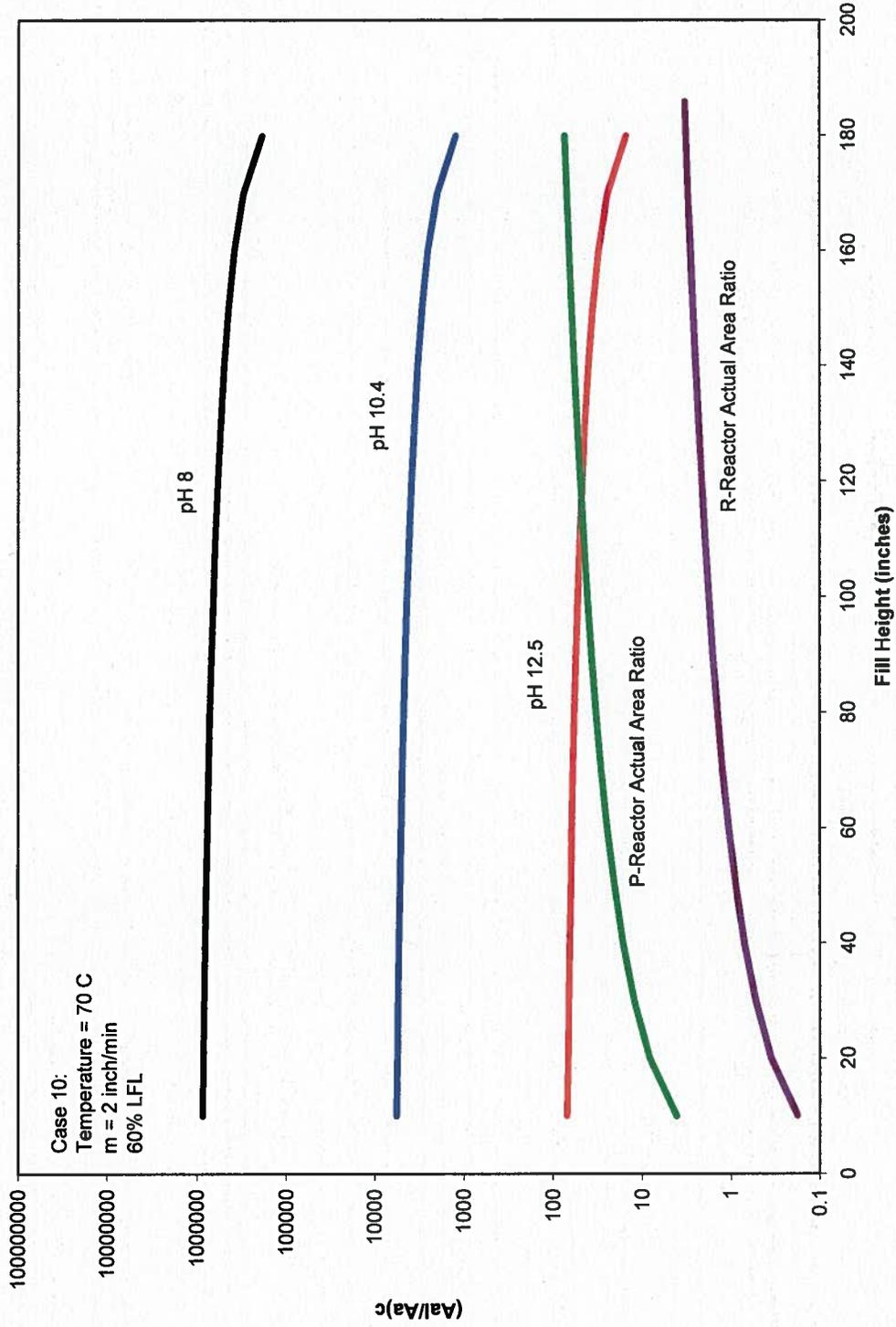


Figure 10. Critical areal density ratio for flammable condition in R & P Reactor Vessels for Case 10.

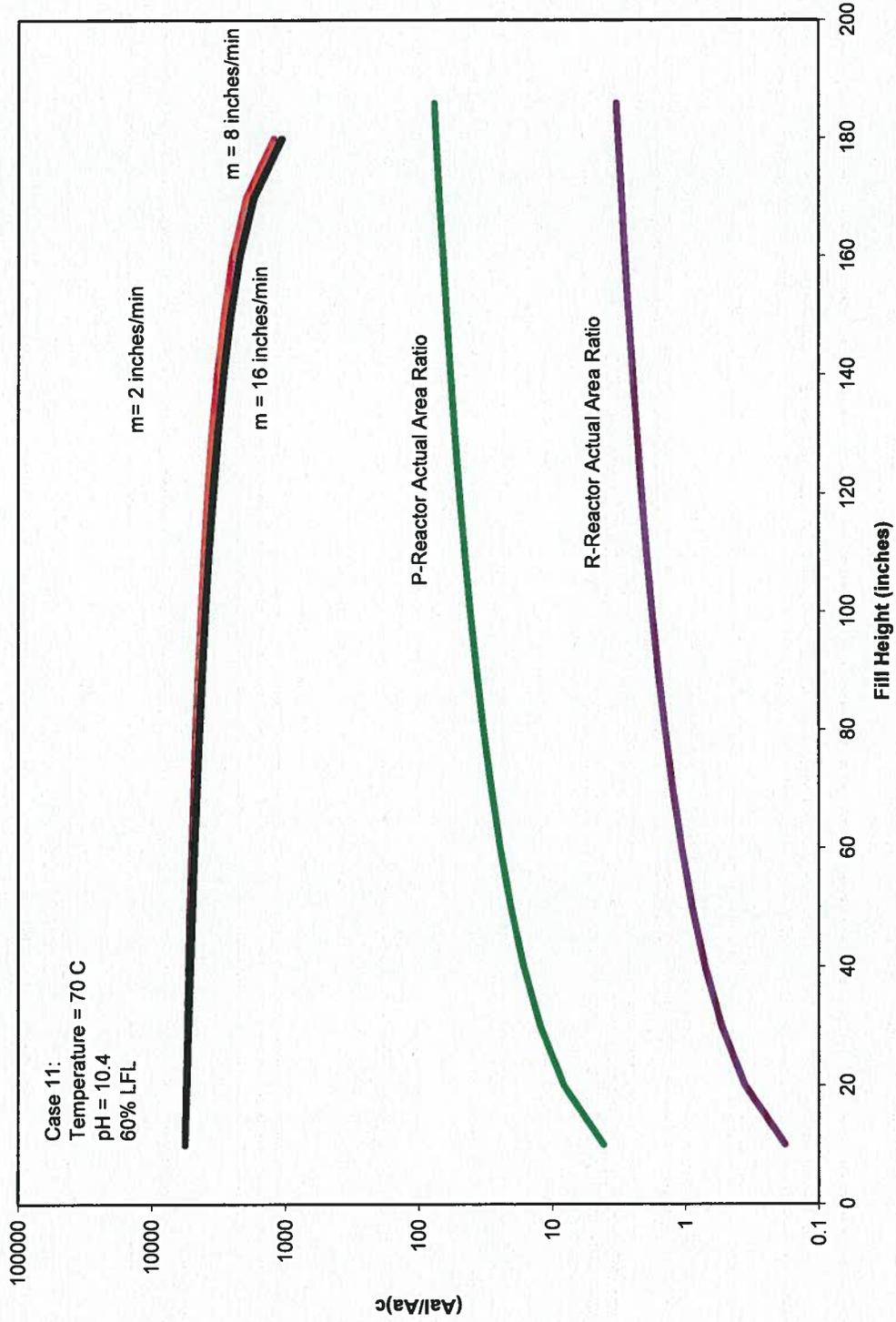


Figure 11. Critical areal density ratio for flammable condition in R& P Reactor Vessels for Case 11.

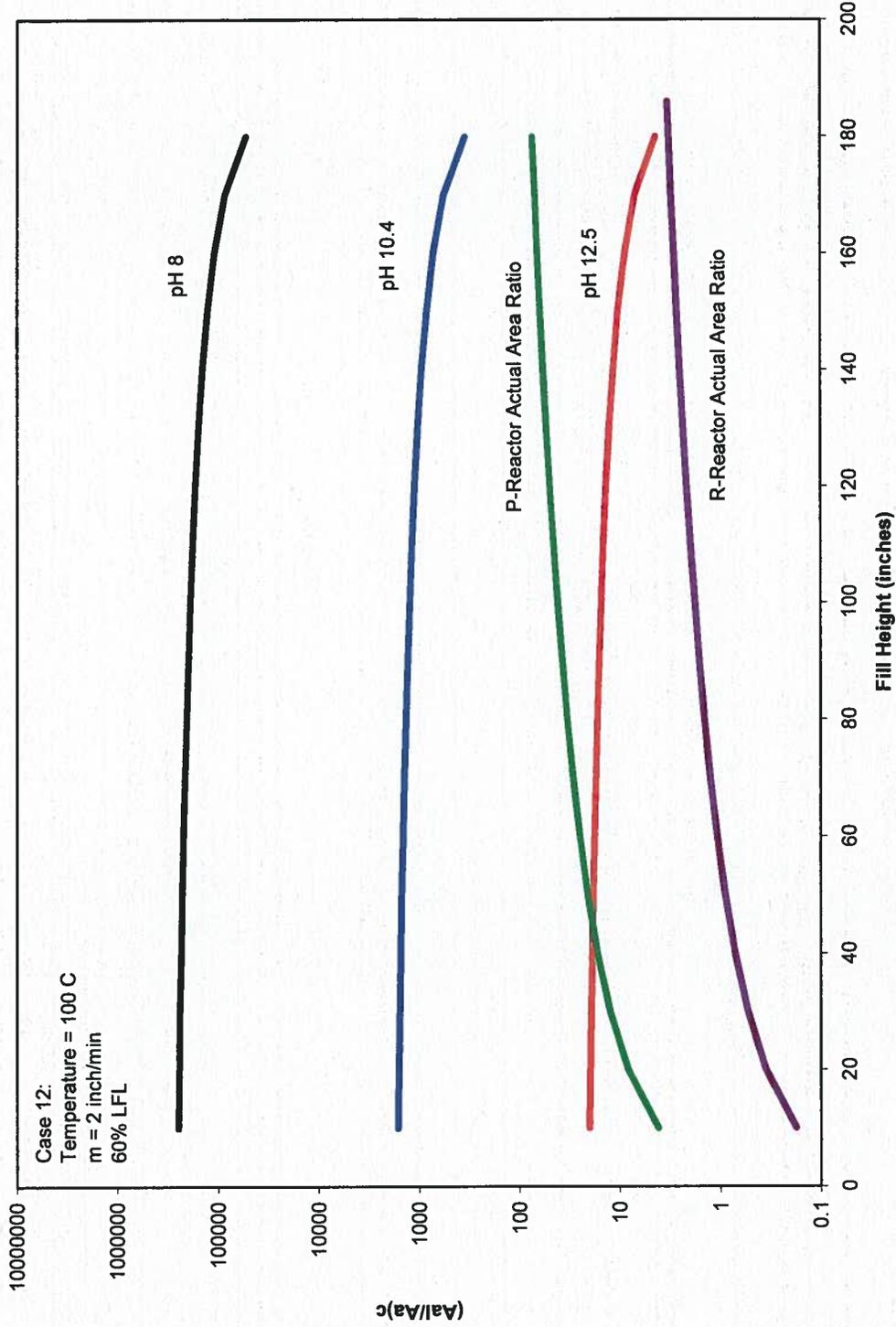


Figure 12. Critical area density ratio for flammable condition in R& P Reactor Vessels for Case 12.

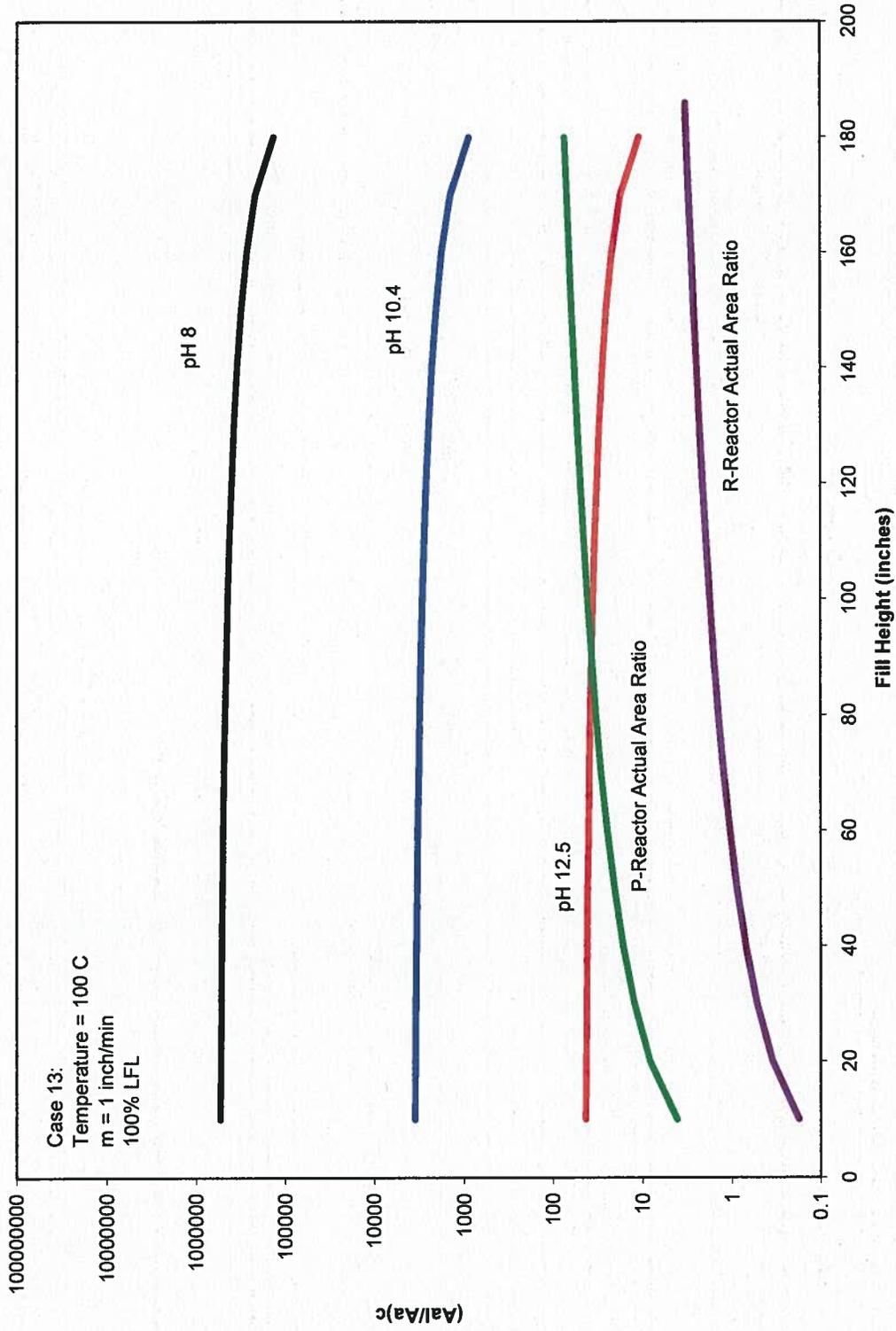


Figure 13. Critical area density ratio for flammable condition in R & P Reactor Vessels for Case 13.

## Conclusions and Recommendations

An assessment of the potential for hydrogen generation during grouting operations in the R- and P- Reactor vessels was performed. The assessment concluded that either ceramicrete or the silica fume grout may be used to safely grout the P-reactor vessel because neither grout will generate enough hydrogen to exceed 60% LFL. The risk of accumulation of a flammable mixture of hydrogen between the grout-air interface and the top of the reactor is very low. Portland cement grout, on the other hand, for the same range of process parameters does not provide a significant margin of safety against the accumulation of flammable gas in the reactor vessel during grouting operations in the P-reactor vessel. This accumulation of flammable gas exceeds 60% LFL. It is recommended that this grout not be utilized for this task.

Based on current facility process knowledge, drawings and surface observations, the R-reactor vessel contains significantly less aluminum than P-reactor. Thus a Portland cement grout may be considered as well. For example, if the grout fill rate is less than 1 inch/min and the grout temperature is maintained at 70 °C or less, the risk of hydrogen accumulation in the R-reactor vessel is low for the Portland cement. Alternatively, if the grout fill rate is less than 0.5 inch/min and the grout is maintained at a temperature of 80 °C, the risk is again low. In either case, accumulation of flammable gas does not exceed 60% LFL.

Although these calculations are conservative, there are some measures that may be taken to further minimize the potential for hydrogen evolution.

1. Minimize the temperature of the grout as much as practical. Lower temperatures will mean lower hydrogen generation rates. For P-reactor, grout temperatures less than 100 °C should provide an adequate safety margin for the pH 8 and pH 10.4 grout formulations. For R-reactor, grout temperatures less than 70 °C or 80 °C will provide an adequate safety margin for the Portland cement. The other grout formulations are also viable options for R-reactor.
2. Minimize the grout fill rate as much as practical. Lowering the fill rate takes advantage of passivation of the aluminum components and hence lower hydrogen generation rates. For P-reactor, fill rates that are less than 2 inches/min for the ceramicrete and the silica fume grouts will reduce the chance of significant hydrogen accumulation. For R-reactor, fill rates less than 1 inch/min will again minimize the risk of hydrogen accumulation.
3. Ventilate the building as much as practical (e.g., leave doors open) to further disperse hydrogen. The volumetric hydrogen generation rates in the P-reactor vessel, however, are low for the pH 8 and pH 10.4 grout, i.e., less than 0.97 ft<sup>3</sup>/min.

If further walk-down inspections of the reactor vessels suggest an increase in the actual areal density of aluminum, the calculations for the potential for hydrogen evolution should be re-visited.

**References**

1. B. J. Wiersma, "Reactive Metal (Al) Interactions During Grouting Operations of the R- and P-Reactor Vessels," SRNL-RP-2009-01198," Rev. 0, September 2009.
2. B. J. Wiersma, "Assessment of the Potential for Hydrogen Generation During Grouting Operations in R-Reactor Disassembly Basin", SRNL-STI-20090-00278, April, 2009.
3. S. M. Short and B. M. Parker, "Potential for Generation of Flammable Mixtures of Hydrogen from Aluminum-Grout Interaction During Basin Grouting", PNNL-15156, April 2005.
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6. Chatalov in *Atlas of Electrochemical Equilibria in Aqueous Solutions*, M. Pourbaix, NACE, Houston, TX, 1974.
7. A. B. McKee and R. H. Brown, "Resistance of Aluminum to Corrosion in Solutions Containing Various Anions and Cations", *Corrosion*, Vol. 3, December, 1947, p. 595.
8. T. Matsuo, et al., "LiNO<sub>3</sub> Effect on Corrosion Prevention of Aluminum with Complex Shapes", *J. Nuclear Science and Technology*, Vol. 34, No. 8, pp. 823-828, 1997.
9. T. Matsuo, et al., "Influence of Increased Temperature from Cement Hydration on Aluminum Corrosion Prevention when LiNO<sub>3</sub> is Added to the Cement", *Nuclear Technology*, Vol. 125, pp. 332-336, March 1999.
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12. N. Vrettos, "P&R Reactor Void Volume and Surface Area Derivation", SRNL-L1300-2009-00060, October 15, 2009.
13. Personal Communication from W. Epling to G. Rose, "Final As-Left Status of P Reactor Tank", October 9, 2006.

# APPENDIX

Title of Project R&amp;P Reactor Vessel Reactive Metal

Project No. \_\_\_\_\_

Subject Derivation of  $H_2$  Generation Rate

Works \_\_\_\_\_

Computer B.J. Wiersma

Date 9/30/09

Sheet No. 1

Problem: Determine the hydrogen generation rate due to aluminum corrosion in the R&P reactor vessels.

$Q =$  Hydrogen generation  $cm^3/min-cm^2$

$$Q = g(h, T, pH) = \dots$$

$h =$  height of grout in vessel Note: Height is a function of time  $t$

$T =$  temperature of grout

$pH =$  grout pH

$g(h)$  derivation

Inputs:

1) Due to passivation reactions [ref.1] the initial  $H_2$  generation rate decreases by 50% every 3 hours.

Half-life  
Equation

$$\frac{dg}{dt} = A g(t)$$

$A =$  constant

$$\frac{dg}{g} = A dt \rightarrow \ln g = At + B \rightarrow Q = B e^{At}$$

5/3/10

Note:

Constant A

was corrected

to  $-0.231$

$$@ t=0 \quad g = Q_0$$

$Q_0 =$  Initial  $H_2$  generation rate

$$g_0 = B \rightarrow g = Q_0 e^{At}$$

$$\frac{g}{g_0} = 0.5 = e^{3A} \rightarrow A = \frac{\ln 0.5}{3} = -0.231 \frac{1}{hr}$$

$$g = Q_0 e^{-0.231t}$$

Reference:

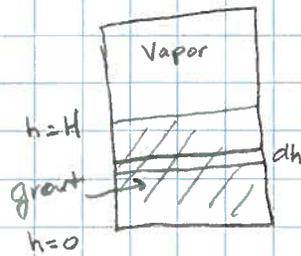
[1] S.M. Short and B.M. Parker, "Potential for Generation of Flammable Mixtures of Hydrogen from Aluminum-Grout Interaction in the K-Basin Grouting", PNNL-15156, April 2005.

Title of Project R & P Reactor Vessel Reactive Metal

Project No. \_\_\_\_\_

Subject Derivation of H<sub>2</sub> Generation Rate

Works \_\_\_\_\_

Computer B.J. WiersmaDate 9/30/09Sheet No. 2

@  $t = t_f$  2) Fill level increases as a linear function of time

$$h = mt \quad m = \text{fill rate in inches/min}$$

Perform a mass balance at  $t = t_f$  to determine the hydrogen generation rate from each volume slice  $A_c dh$ .  $A_c$  is the open cross-sectional area of the vessel.

$$g A_c H = \int_0^H Q_0 e^{-0.231t} A_c dh \quad t = \frac{h}{m}$$

$$g H = Q_0 \int_0^H e^{-0.231 \frac{h}{m}} dh$$

$$g = - \frac{Q_0 m}{H} \frac{1}{0.231 \times \frac{1 \text{ hr}}{60 \text{ min}}} e^{-0.231 \times \frac{h}{m}} \Big|_0^H$$

$$= - \frac{Q_0 m}{H} \frac{1}{0.00385} \left[ e^{-0.00385 \frac{H}{m}} - 1 \right]$$

$$g = \frac{Q_0 m}{0.00385 H} \left[ 1 - e^{-0.00385 \frac{H}{m}} \right]$$

5/3/10

Note: Constant A was corrected to -0.231

Title of Project R&P Reactor Vessel Reactive Metal

Project No. \_\_\_\_\_

Subject Derivation of H<sub>2</sub> Generation Rate

Works \_\_\_\_\_

Computer B.J. WiersmaDate 9/30/09Sheet No. 3

$$Q_0(pH, T) = S(T) U(pH)$$

$$U(pH)$$

Literature Values for corrosion rates of aluminum as a function of pH

Chatalov [ref. 2] Data @ 30°C

pH	Corrosion Rate (mg/dm <sup>2</sup> -hr)	Corrosion Rate (mg/dm <sup>2</sup> -day)
8	0.003	0.072
10	0.4	9.6
12	10	240

M<sup>e</sup>Kee and Brown [ref. 3] Data @ 30°C

pH	Corrosion Rate (mg/cm <sup>2</sup> -day)	Corrosion Rate (mg/dm <sup>2</sup> -day)
10	0.02	2
11	0.3	30
12	4	400
13	30	3000

Corrosion of Aluminum: Net reaction in caustic



∴ 1.5 moles of H<sub>2</sub> evolve for every 1mole of Al Corroded.

### References

- [2] Chatalov in Atlas of Electrochemical Equilibria in Aqueous Solutions, M. Pourbaix, NACE, Houston, TX, 1974.
- [3] A.B. McKee and R.H. Brown, "Resistance of Aluminum to Corrosion in Solutions Containing Various Anions and Cations", Corrosion, Vol. 3, Dec. 1947, p. 595.

Title of Project R&P Reactor Vessel Reactive Metal

Project No. \_\_\_\_\_

Subject Derivation of H<sub>2</sub> Generation Rate

Works \_\_\_\_\_

Computer B.J. WiersmaDate 9/30/09Sheet No. 4Equation for converting corrosion rate to H<sub>2</sub> generation rate

Ideal Gas Law  $V = \frac{nRT}{P}$

$$R' \equiv \text{Gas Constant} = 0.0821 \frac{\text{L-atm}}{\text{mole}\cdot\text{K}}$$

$$T = \text{Temperature} = 303 \text{ K}$$

$$P = \text{Pressure} = 1 \text{ atm}$$

$$n = \text{moles} = \frac{\text{mass}}{\text{MW}}$$

$$\text{MW} = \text{Molecular wt. of Al} = 27 \text{ g/mole} = 27,000 \frac{\text{mg}}{\text{mole}}$$

pH	Corrosion Rate ( $\frac{\text{moles Al}}{\text{cm}^2\cdot\text{day}}$ )	Corrosion Rate ( $\frac{\text{moles Al}}{\text{cm}^2\cdot\text{min}}$ )
8	$2.67 \times 10^{-6}$	$1.85 \times 10^{-11}$
10	$3.55 \times 10^{-4}$	$2.47 \times 10^{-9}$
10	$7.41 \times 10^{-5}$	$5.15 \times 10^{-10}$
11	$1.11 \times 10^{-3}$	$7.71 \times 10^{-9}$
12	$8.88 \times 10^{-3}$	$6.17 \times 10^{-8}$
12	$1.48 \times 10^{-2}$	$1.03 \times 10^{-7}$
13	$1.11 \times 10^{-1}$	$7.71 \times 10^{-7}$

pH H<sub>2</sub> generation  $U(\text{pH}) = \frac{\text{Corr. Rate} \times \left(1.5 \frac{\text{moles H}_2}{\text{mole Al}}\right) RT}{P}$

$$U(\text{pH}) = \frac{1000 \text{ cm}^3}{12} \frac{\text{Corr. Rate} \times 1.5 \left(0.0821 \frac{\text{L-atm}}{\text{mole}\cdot\text{K}}\right) (303 \text{ K})}{1 \text{ atm}}$$

$$= 3.73 \times 10^4 \times \text{Corr. rate}$$

Title of Project R & P Reactor Vessel Reactive Metal

Project No. \_\_\_\_\_

Subject Derivation of H<sub>2</sub> Generation Rate

Works \_\_\_\_\_

Computer B.J. WiersmaDate 9/30/09Sheet No. 5

<u>pH</u>	<u>U ( <math>\frac{\text{cm}^3}{\text{cm}^2 \cdot \text{min}}</math> )</u>
8	$6.93 \times 10^{-7}$
10	$9.22 \times 10^{-5}$
10	$1.92 \times 10^{-5}$
11	$2.88 \times 10^{-4}$
12	$2.31 \times 10^{-3}$
12	$3.84 \times 10^{-3}$
13	$2.88 \times 10^{-2}$

PNNL report [ref. 1]:  $U = 0.3 \text{ cm}^3/\text{min}$  on a  $48.3 \text{ cm}^2$  sample @ pH 12.5 @ 27°C

$$U = 6.21 \times 10^{-3} \text{ cm}^3/\text{cm}^2 \cdot \text{min}$$

Note: H<sub>2</sub> generation rate in grant agrees w/ literature

See plot of pH vs. U on sheet No. 6

$$U(\text{pH}) = 3 \times 10^{-4} e^{2.0952 \cdot \text{pH}} \quad \frac{\text{cm}^3}{\text{cm}^2 \cdot \text{min}} \quad @ T \approx 30^\circ\text{C}$$

Curve was fitted using EXCEL regression fit

S(T) derivation

• Hydrogen generation rate can be described by the Arrhenius eqn.

• H<sub>2</sub> generation in Cd(OH)<sub>2</sub> solutions increased by a factor of 5 as the solution temperature increased from 23°C + 52°C [ref. 1]

$$Q'_{\text{H}_2}(23^\circ\text{C}) = Q'_0 \exp\left(\frac{-T_{\text{act}}}{296}\right)$$

$$Q'_{\text{H}_2}(52^\circ\text{C}) = Q'_0 \exp\left(\frac{-T_{\text{act}}}{325}\right)$$

$$Q'_{\text{H}_2}(52^\circ\text{C}) = 5Q'_0(23^\circ\text{C})$$

(Go to sheet 7)

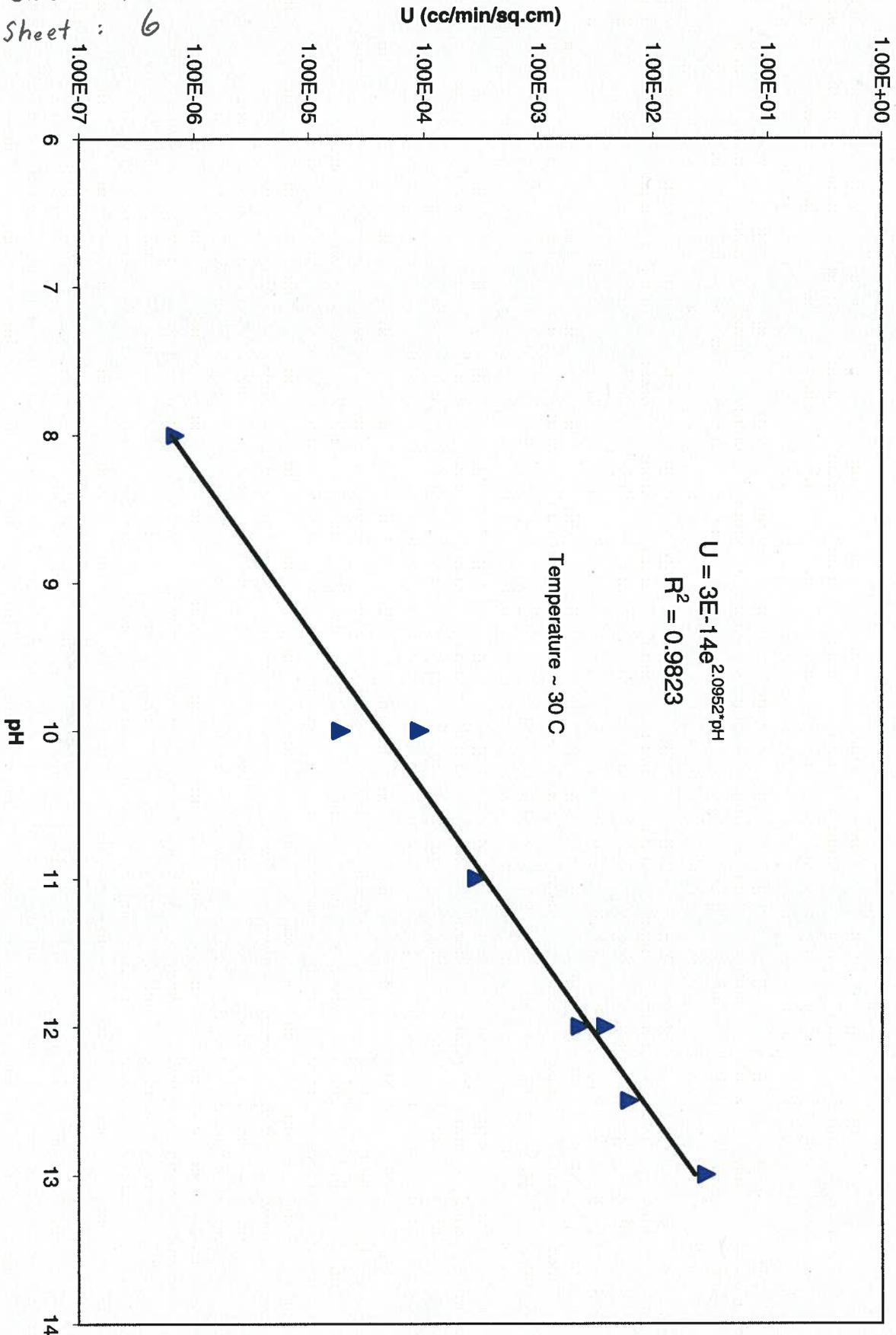
Project : R&P Reactor Vessel Reactive Metal

Subject : Derivation of H<sub>2</sub> generation Rate

Computer : B.J. Wiersma

Date : 9/30/09

Sheet : 6



Title of Project R#P Reactor Vessel Reactive Metal

Project No. \_\_\_\_\_

Subject Derivation of H<sub>2</sub> generation Rate

Works \_\_\_\_\_

Computer B.J. WiersmaDate 10/3/09Sheet No. 7

$$5 Q_0' \exp\left(\frac{-T_{act}}{296}\right) = Q_0' \exp\left(\frac{-T_{act}}{325}\right)$$

$$5 = \exp\left(\frac{T_{act}}{296} - \frac{T_{act}}{325}\right)$$

$$\ln 5 = T_{act} \left(\frac{1}{296} - \frac{1}{325}\right)$$

$$T_{act} = 5339 \text{ K}$$

$$S(T) = Q_0' \exp\left(\frac{-5339}{T}\right)$$

$$Q_0(P, T) = 3 \times 10^{-14} e^{2.0952 P^H} \exp\left(-5339\left(\frac{1}{T} - \frac{1}{300}\right)\right) \frac{\text{cm}^3}{\text{cm}^2 \cdot \text{min}}$$

$$Q = \frac{Q_0 \cdot m}{0.00385 H} \left[ 1 - \exp\left(-\frac{0.00385 H}{m}\right) \right] \frac{\text{cm}^3}{\text{cm}^2 \cdot \text{min}}$$

Vertical Turbulent Diffusion [ref. 1]

 $u_0$  = Superficial Velocity @ ground level H

$$u_0 = \beta^2 \left[ g H_0 \left(1 - \frac{M_{H_2}}{M_A}\right) X_{LFL}^3 \right]^{1/2}$$

 $X_{LFL} = 0.024$  volume % H<sub>2</sub> @ 60% of the lower flammability limit $H_0$  = distance from ground level to top of reactor

$$H_0 = (186 - H)$$

186" = height of Reactor H = level of ground

$$g = 9.8 \text{ m/s}^2$$

 $\beta$  = proportionality constant = 0.164 $M_{H_2}$  = Molecular wt of H<sub>2</sub> = 2g/mole $M_A$  = Molecular wt of Air = 29g/mole

$$u_0 = (0.164)^2 \left[ 9.8 \frac{\text{m}}{\text{s}^2} \left(\frac{100 \text{ cm}}{1 \text{ m}}\right) (186 - H) \times (2.539) \left[ 1 - \frac{2}{29} \right] \left[ 0.024 \right]^3 \times \frac{3600 \text{ s}}{\text{min}} \right]^{1/2}$$

$$u_0 = (0.164)^2 \left[ 115 \cdot (186 - H) \right]^{1/2} \frac{\text{cm}^3}{\text{cm}^2 \cdot \text{min}}$$

Title of Project R &amp; P Reactor Vessel Reactive Metal

Project No. \_\_\_\_\_

Subject Derivation of Critical Areal Density Ratio

Works \_\_\_\_\_

Computer B.J. Wiersma

Date 10/7/09

The incipient flammability condition occurs when the gas generation rate due to corrosion equals the turbulent diffusion rate of hydrogen through air. The boundary condition is that the  $H_2$  concentration at the interface between the grout and the vapor space is at 60% LFL. The 60% LFL criterion provides a safety margin against the possibility of developing a flammable mixture. This safety margin is used for the flammability calculations for the radioactive waste tanks at Savannah River Site [ref. 4]. The equation is:

$$Q A_{Al} = u_0 A_a$$

$$\frac{A_{Al}}{A_a} = \frac{u_0}{Q}$$

where  $A_{Al}$  is the aluminum surface area in contact w/ grout and  $A_a$  is the void cross-sectional area of the reactor vessel

A plot of  $\frac{A_{Al}}{A_a}$  vs.  $H$  (the grout fill level) is prepared. The ratio is a function of temperature, pH, and fill rate. An example plot is shown on sheet 9. Also included on the plot is the actual ratio of  $A_{Al}/A_a$  as a function of  $H$  (see sheet 10 for derivation). If the calculated values for  $A_{Al}/A_a$  are less than the actual the margin on the LFL condition has been reduced. Safe operating conditions exist when the calculated values are greater than the actual values.

Calculations were performed on an EXCEL spreadsheet.

Reference 4: B.C. Landeene, "CSTF Flammability Control Program", WSRC-TR-2003-00087, rev. 13, January 31, 2008.

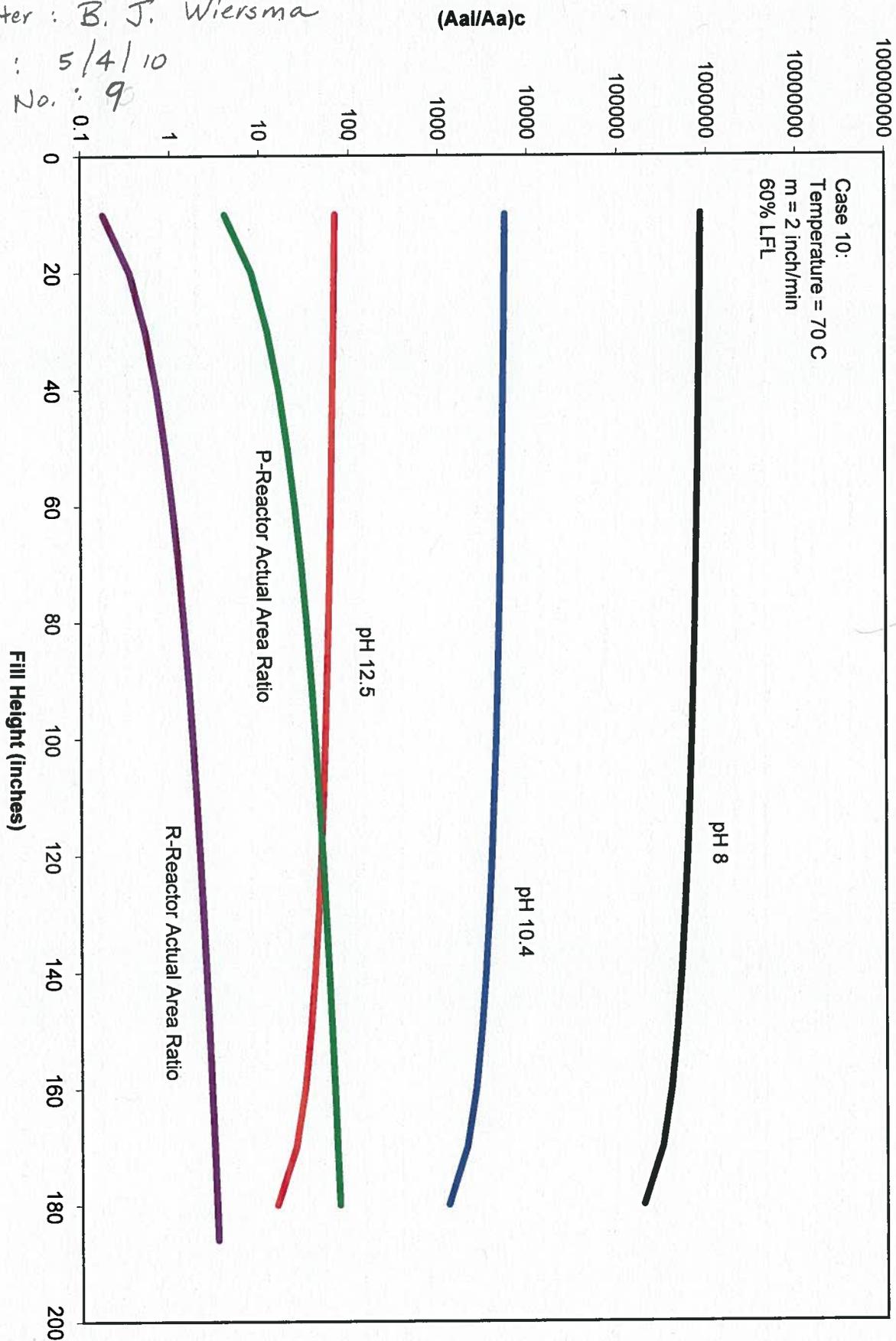
Project: R & P Reactor Vessel Reactive Metal

Subject: Derivation of Critical Areal Density Ratio

Computer: B. J. Wiersma

Date: 5/4/10

Sheet No.: 9



Title of Project R & P Reactor Vessel Reactive Metal

Project No. \_\_\_\_\_

Subject Calculation of Actual Areal Density Ratio

Works \_\_\_\_\_

Computer B.J. WiersmaDate 10/22/09

Calculate surface area of aluminum exposed to graft. Use equation 7.

$$A_{Al} = N_{USH} * \pi * (D_{USH-o} + D_{USH-i}) * H + N_T * \pi * (D_{T-o} + D_{T-i}) * H$$

@ H = 10 inches

$$A_{Al} = 432 * \pi * (4.25 + 4.0) * 10 + 66 * \pi * (1.5 + 1.0) * 10$$

$$= 117,150 \text{ in}^2$$

Cross-Sectional Area of Reactor vessel. Use Equation 8.

$$A_a = \pi * D_t^2 / 4 - N_{USH} * \pi * (D_{USH-o}^2 - D_{USH-i}^2) / 4$$

$$- N_T * \pi * (D_{T-o}^2 - D_{T-i}^2) / 4 - N_{SS} * \pi * D_s^2 / 4$$

$$A_a = \pi / 4 * (194.75)^2 - 432 * \frac{\pi}{4} * (4.25^2 - 4^2) - 66 * \frac{\pi}{4} * (1.5^2 - 1.0^2)$$

$$- 67 * \frac{\pi}{4} * 3.5^2$$

$$= 28,379 \text{ in}^2$$

@ H = 10

$$\frac{A_{Al}}{A_a} = \frac{117,150 \text{ in}^2}{28,379 \text{ in}^2} = 4.13$$

Agrees w/ EXCEL spreadsheet

Title of Project R & P Reactor Vessel Reactive Metal

Project No. \_\_\_\_\_

Subject Derivation of Maximum Flow Rate of H<sub>2</sub>

Works \_\_\_\_\_

Computer B.J. WiersmaDate 10/16/09Sheet No. 11

Problem: Determine the maximum volumetric flow rate of H<sub>2</sub>.

Approach: Use the equation for the generation of H<sub>2</sub> from corrosion (Eqn. 2) and the equation for the surface area of aluminum (Eqn. 1) to determine the volumetric flow rate of aluminum.

$$Q_{TOT} = Q \times A_{Al}$$

Determine maximum by taking derivative of  $Q_{TOT}$  with respect to  $H$ . Set this equal to zero and solve for  $H$ . The maximum could also be at the boundary condition. Check these as well for  $H_{max}$ . Determine  $Q_{TOT}$  at  $H_{max}$  and at the boundary condition. It is assumed that  $T$ ,  $pH$ , and fill rate are constant. Calculate the maximum  $Q_{TOT}$  for each case study.

$$Q_{TOT} = Q \times A_{Al}$$

$$= \frac{Q_0 \times M}{0.00385 H} \left[ 1 - \exp(-0.00385 \times H/m) \right] \times H \times \pi + [N_{USH} (D_{USH,0} + D_{USH,i}) + N_T (D_{T,0} + D_{T,i})]$$

$$= \frac{Q_0 \times M \times \pi}{0.00385} \left[ N_{USH} (D_{USH,0} + D_{USH,i}) + N_T (D_{T,0} + D_{T,i}) \right] \left[ 1 - \exp\left(-\frac{0.00385 H}{m}\right) \right]$$

$$= B \left[ 1 - \exp\left(-\frac{0.00385 H}{m}\right) \right]$$

$$\frac{dQ_{TOT}}{dH} = 0 = B \left[ 0 - \left(-\frac{0.00385}{m}\right) \exp\left(\frac{-0.00385 H}{m}\right) \right]$$

Maximum  $Q_{TOT}$  is at upper boundary. Assume height of reactor 186 inches

$Q_{TOT}$  is calculated in spreadsheet

Title of Project R & P Reactor Vessel Reactive Metal Project No. \_\_\_\_\_Subject Derivation & Calculation of Maximum Flow Rate of H<sub>2</sub> Works \_\_\_\_\_Computer B.J. WiersmaDate 10/16/09Sheet No. 12

@ 186 inches  $T = 100^\circ\text{C}$   $m = 2 \text{ inches/min}$   $\text{pH} = 12.5$   
 $N_{\text{USH}} = 432$   $N_T = 66$   $D_{\text{usH}_2\text{O}} = 4.25''$   $D_{\text{usH}_2} = 4.0''$

$D_{\text{Co}} = 1.5''$   $D_{\text{Ti}} = 1.0''$

$$Q_0 = 3 \times 10^{-14} \exp(2.0952 * \text{pH}) * \exp[-5339 * (\frac{1}{33} - \frac{1}{303})]$$

$$= 0.194 \text{ cm}^3/\text{cm}^2/\text{min}$$

$$Q_{\text{TOT}} = \frac{(0.194 \text{ cm}^3/\text{cm}^2/\text{min}) \times 2 \frac{\text{inches}}{\text{min}} \times 6.446 \frac{\text{cm}^2}{\text{in}^2} \times [432(4.25 \text{ in} + 4.0 \text{ in}) + 66(1.5 \text{ in} + 1.0 \text{ in})]}{0.00385 \frac{1}{\text{min}}} \times [1 - \exp(-\frac{0.00385 \frac{\text{in}}{\text{min}}}{2 \frac{\text{inches}}{\text{min}}} \times 186 \text{ in})]$$

$$= 739,827 \frac{\text{cm}^3}{\text{min}} = 0.740 \frac{\text{m}^3}{\text{min}} \text{ H}_2$$

$$= 80.9 \text{ ft}^3/\text{min} \text{ H}_2$$

Conservative because it neglects diffusion of H<sub>2</sub> through the grout.