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Potential for Generation of Flammable Mixtures of Hydrogen from Aluminum-Grout Interaction in the K Basins During Basin Grouting

S. M. Short
B. M. Parker

April 2005

Prepared for
Fluor Hanford, Inc.
PNNL Project Number 46980

Work supported by
the U.S. Department of Energy
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Pacific Northwest National Laboratory
Richland, Washington 99352



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Executive Summary

During the course of deactivation and decommissioning (D&D) of the K Basins, the basins will be partially filled with grout so as to immobilize residual equipment and debris. Some of this residual debris, principally empty fuel canisters, identification tags, and long-handled tools, contain aluminum metal. The aluminum metal will corrode when contacted with the high pH grout, resulting in the generation of hydrogen. Pacific Northwest National Laboratory (PNNL) evaluated existing experimental and analytical studies of this issue to 1) determine whether sufficient hydrogen will be generated and collected during the K Basins grouting activity to potentially create the conditions for hydrogen deflagration/explosion and 2) identify process constraints that will provide assurance that the conditions for hydrogen deflagration/explosion will not exist.

Based on the review of available experimental and analytical studies, it was concluded that the likelihood of generating a flammable mixture of hydrogen from interaction of residual aluminum metal with grout is low but not zero. However, a flammable mixture of hydrogen will not be generated anywhere in the basin facility during grouting of the KE Basin as long as the following conditions are met:

- The residual aluminum metal inventory in the basin, especially the fuel canisters, is not stacked on top of one another. This will prevent over-concentrating the aluminum metal inventory over a small surface area of the basin floor.
- The temperature of the grout is maintained below 90°C (194°F) during pouring and at least three hours after the aluminum metal has been covered (lower grout temperatures result in lower hydrogen generation rates). After about three hours immersed in the grout, an oxide or corrosion layer has formed on the aluminum metal significantly reducing the corrosion/hydrogen generation rates assumed in this analysis.
- The basin water temperature is less than 60°C (140°F) for at least three hours after interruption of the grout pour if the aluminum metal in the basin has not been completely covered [so as to minimize reaction of the uncovered aluminum metal with Ca(OH)₂]. This can effectively be done by ensuring that the basin water temperature is less than 21°C (70°F) prior to initiating grouting of the basin and ensuring that the basin water level is at least 10 feet above the surface of the grout.
- The basin water is not removed at the same time as grout is being poured (to avoid removing the hydrogen to another potential collection point). This condition is not necessary if the water removal system is appropriately vented to prevent accumulation of hydrogen in the system or after the aluminum metal has been covered with grout for at least three hours.

These conclusions are supported as long as the amount and physical configuration of the residual aluminum inventory in the KE Basin is consistent with the assumptions described in Appendix A.

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1.0 Background

During the course of deactivation and decommissioning (D&D) of the K Basins, the basins will be partially filled with grout so as to immobilize residual equipment and debris. Some of this residual debris, principally empty fuel canisters, identification tags, and long-handled tools, contain aluminum metal. The aluminum metal will corrode when contacted with the high pH grout, resulting in the generation of hydrogen. Pacific Northwest National Laboratory (PNNL) evaluated existing experimental and analytical studies of this issue to 1) determine whether sufficient hydrogen will be generated and collected during the K Basins grouting activity to potentially create the conditions for hydrogen deflagration/explosion and 2) identify process constraints that will provide assurance that the conditions for hydrogen deflagration/explosion will not exist.

2.0 Assumptions

The hydrogen bubbles generated from corrosion of aluminum metal during grouting of the K Basins will bubble to the surface of the basin water surface and, upon breaking the water surface, will diffuse upward. Flammable mixtures of hydrogen will only be generated if conditions exist in the basin facility to collect the hydrogen. Underlying assumptions made in this analysis about the condition of the basin facility at the time of grouting are as follows:

- The aluminum metal sources are situated on the bottom of the basin pool and are not covered by or contained within structures where hydrogen could accumulate.
- Long-handled tools made of aluminum metal are laying down on the basin floor.
- The basin facility is ventilated, preventing accumulation of hydrogen within the basin superstructure.

Based on these assumptions, this analysis and previous analyses conclude that the only place that hydrogen could potentially accumulate during grouting of the basin is 1) in the area between the basin water surface and the basin grating and 2) in the water collection system used to remove the water displaced by the grout.

3.0 Hydrogen Generation Rate Experimental and Analytical Analyses

Fluor Hanford, Inc. (FH) commissioned PNNL in 2003/2004 to 1) experimentally measure the hydrogen generation rate from the reaction of aluminum metal and grout and 2) determine if there were safety implications from this interaction for the KE Basin D&D Project (report provided in Appendix A). Experimental tests were performed to measure the hydrogen generation rate of non-corroded aluminum metal coupons immersed both in grout and in a saturated $\text{Ca}(\text{OH})_2$ solution. $\text{Ca}(\text{OH})_2$ is formed when water is added to Portland cement during the grout production process. The experimental results are provided in Figure 3-2 of Appendix A, which shows hydrogen generation rate (cm^3/min) as a function of the total time (min) the aluminum metal coupon was immersed in the hydroxide solution/cement mixture for five different tests. These results suggest the following:

- The initial hydrogen generation rate of non-corroded aluminum metal in grout (Test #5, $0.30 \text{ cm}^3/\text{min}$) is about one-third the rate of aluminum metal in $\text{Ca}(\text{OH})_2$ (Test #1, $1.1 \text{ cm}^3/\text{min}$) at the same grout/hydroxide solution temperature (about 25°C or 77°F).
- The initial hydrogen generation rate of non-corroded aluminum metal in $\text{Ca}(\text{OH})_2$ increases by a factor of 5 (Test #2, #3, and #4, $5.4 \text{ cm}^3/\text{min}$) if the temperature of the grout/hydroxide solution is doubled (about 50°C or 122°F).
- The hydrogen generation rate of non-corroded aluminum metal in $\text{Ca}(\text{OH})_2$ drops significantly (about a factor of 4 at 25°C and about a factor of 30 at 50°C) after about 2 to 3 hours to about the same as that in grout (see Test #1 through #4 in Figure 3-2 of Appendix A). The rate in grout decreases by about one-half over the same time period (Test #5). The decrease in corrosion rate is principally due to the formation of a corrosion product (principally tricalcium aluminum hydroxide and hydrocalumite) layer on the surface of the aluminum metal.

These experimental results were then used in the PNNL report to estimate the amount of aluminum metal that can be tolerated in the basin during grouting and not result in flammable mixtures of hydrogen occurring at the surface of the basin water or, in other words, collecting between the basin water surface and the grating above the basin. This analysis conservatively assumed that upon breaching the basin water surface, the hydrogen would slowly dissipate upward solely due to molecular diffusion (ignoring dissipation via Fickian diffusion, advection, etc.). Upon reaching the grating, the hydrogen is assumed to be removed rapidly due to advection.

Because both the rate of hydrogen generation and subsequent rate of diffusion above the basin water surface are dependent upon the amount of exposed aluminum metal surface area and not total residual aluminum metal inventory, the PNNL results are cast in terms of allowable reactive surface area of the aluminum per unit surface area of the basin floor. These results are then compared with estimates of the actual amount of residual aluminum metal to determine if there is potential for the formation of a flammable mixture of hydrogen between the basin water surface and the grating. These results are summarized as the lower line in Figure 1, which shows the allowable aluminum metal surface area ratio as a function of grout temperature at the lower flammability limit (LFL) for hydrogen of 4% in air (extrapolation from experimentally measured data points was assumed to be exponential). These results

assume the initial reaction rate for aluminum metal in grout (Test #5). The line would be lower for aluminum metal in $\text{Ca}(\text{OH})_2$ due to the higher corrosion rate of aluminum metal in $\text{Ca}(\text{OH})_2$ than in grout.

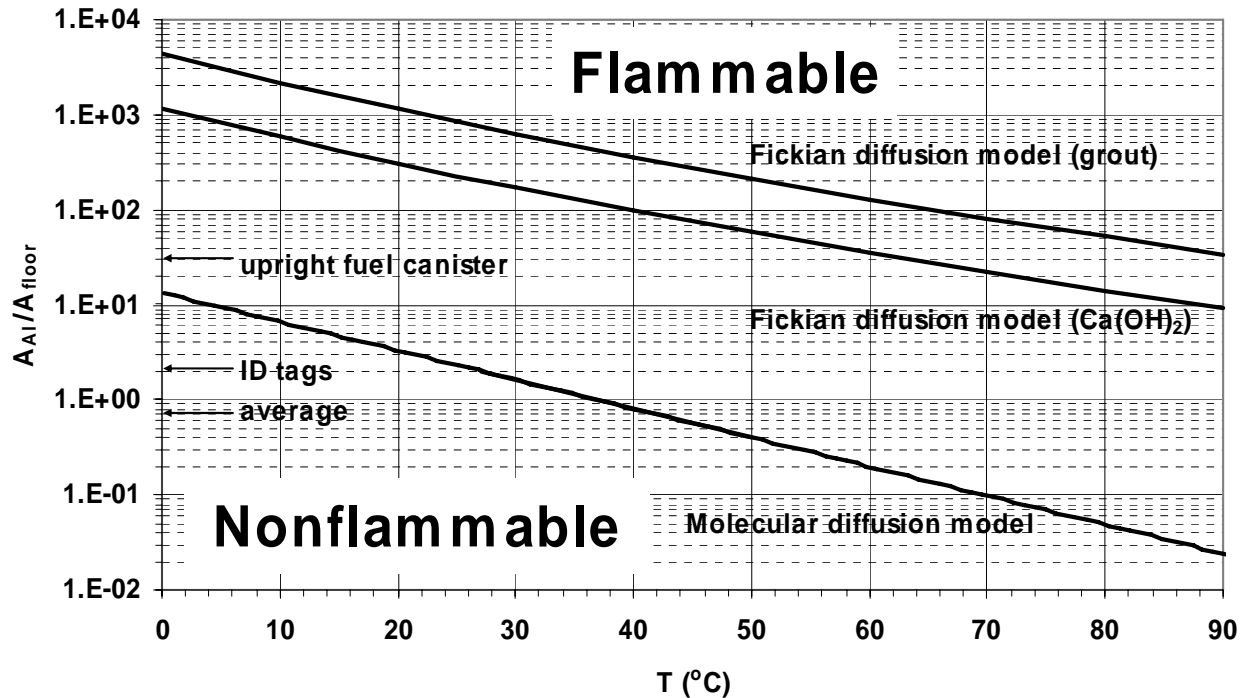


Figure 1. Aluminum Metal Surface Area Ratio for Flammable Condition

If the ratio of the reactive aluminum metal surface area to the surface area of the basin floor is above the line, then there is the potential for formation of a flammable mixture of hydrogen; below the line, there is no potential. The figure shows that if the total reactive surface area of the residual aluminum metal inventory in the basin were spread evenly over the entire basin (which is not practical), and the temperature of the grout was below about 40°C, then there is no potential for formation of a flammable mixture of hydrogen. Figure 1 also shows that the grout temperature must be below about 27°C (81°F) to avoid the potential for formation of a flammable mixture of hydrogen from corrosion of a single identification tag (assumes identification tags are not stacked on top of one another). Finally, Figure 1 shows that there is the potential for a flammable mixture of hydrogen if fuel canisters are set upright in the basin under any grout temperature condition. Assumptions about the total amount of residual aluminum metal, and corresponding reactive surface area, in the basin are provided in Table 1-1 of Appendix A.

Subsequent to this analysis, FH commissioned Fauske & Associates, LLC to remove some of the conservatism in the PNNL analysis by accounting for dissipation of hydrogen above the basin water surface via Fickian diffusion (report provided in Appendix B). This result is presented as the upper line in Figure 1 (for the LFL for hydrogen), which is the same line as shown in Figure 1 of Appendix B. This analysis shows that there is no potential for formation of a flammable mixture of hydrogen above the basin water surface for even a single upright fuel canister for grout temperatures less than 90°C (194°F). Again, these results assume the initial reaction rate for aluminum metal in grout (Test #5). The line would be lower for aluminum metal in $\text{Ca}(\text{OH})_2$ due to the higher corrosion rate of aluminum metal in $\text{Ca}(\text{OH})_2$ than in grout.

During grouting of the aluminum metal in the basins, the concentration of Ca(OH)_2 in the basin water will increase as the Ca(OH)_2 in the grout dissolves in the water, forming a concentration gradient in the water layers above the grout. The middle line in Figure 1 (for the LFL for hydrogen) shows the results for the Fauske model (Fickian diffusion) in which the aluminum metal is immersed in Ca(OH)_2 solution (pH of 12.8). This shows that there is a potential for formation of a flammable mixture of hydrogen above the basin water surface, for a single upright fuel canister, if the temperature of the Ca(OH)_2 solution is greater than about 60°C (140°F). This is conservative since under basin grouting conditions 1) only a fraction of the surface area of the aluminum fuel canister would actually be immersed in Ca(OH)_2 solution and 2) the Ca(OH)_2 solution is actually a solution of water and Ca(OH)_2 at varying concentrations.

The aluminum metal in the basin can potentially be exposed to Ca(OH)_2 for an extended period of time if grouting of the basin is halted for operational or other reasons. As previously discussed, the time period of interest is the first three hours after interrupt of the grout pour, after which the hydrogen generation rate drops significantly as a result of the formation of a protective aluminum oxide layer on the aluminum metal. A conservative heat transfer analysis was performed to determine the potential rise of the basin water temperature after grouting is halted (see Appendix C). The results of this analysis are provided in Figure 2, which shows the temperature of the basin water for different water thicknesses above the grout surface for different initial basin water temperatures at the start of the grouting operation. These results show that as long as the initial basin water temperature is less than 21°C (70°F) and the water thickness above the grout surface is greater than 3 meters (10 feet), the temperature of the Ca(OH)_2 solution will never be greater than 60°C (140°F). In other words, for these conditions, there is no potential for formation of a flammable mixture of hydrogen above the basin water surface for even a single upright fuel canister for grout temperatures less than 90°C (194°F).

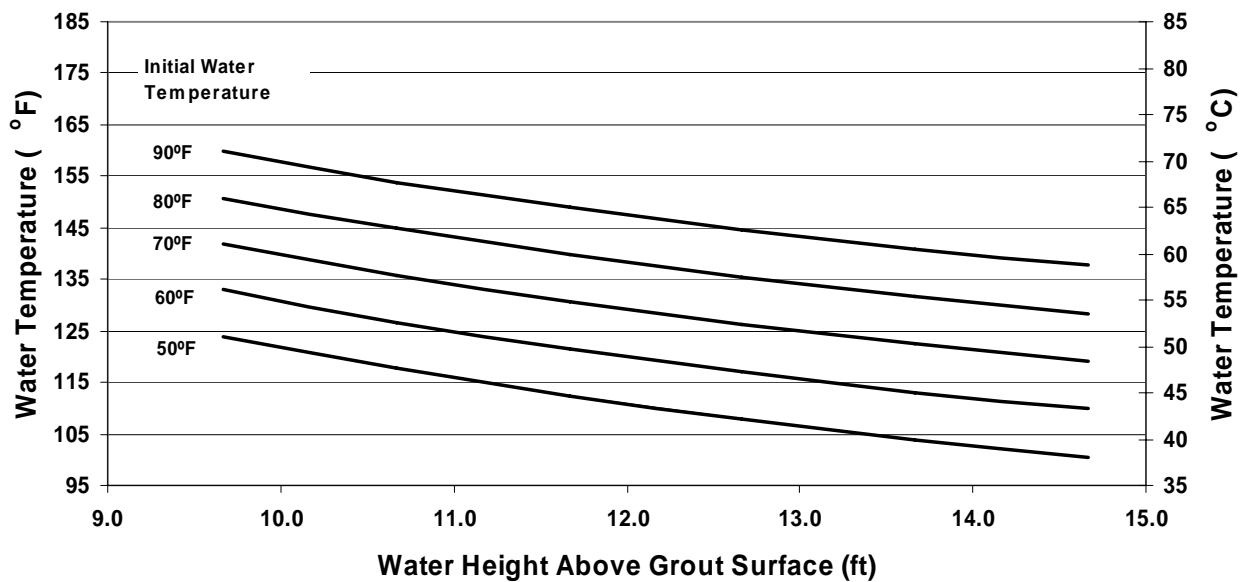


Figure 2. Basin Water Temperature After Interrupt in Grouting Operation

Finally, as shown in Figure 1, the identification tags pose no potential for generating a flammable mixture of hydrogen above the basin water surface for the Fickian diffusion model. Also, while Figure 1 does not show the surface area ratio for long-handled tools (these tools have a variety of designs and

configurations), as long as the tools are laying down in the basin when grouted their surface area ratio will be closer to that of the identification tags than that of an upright fuel canister. Under these conditions, the long-handled tools will pose no potential for generating a flammable mixture of hydrogen above the basin water surface for the Fickian diffusion model.

4.0 Conservatism and Uncertainties

The original PNNL (Appendix A), Fauske (Appendix B), and thermal (Appendix C) analyses include the following conservatisms in their analyses:

- The experimentally measured hydrogen generation rate used in these analyses was for clean or non-corroded aluminum metal. The surface of aluminum metal canisters in the basins is visibly corroded. The aluminum metal in the basins has been there for many years and the surface is protected by either 1) a thin hydroxide film that would have naturally formed over the exposed surface area after immersion of the aluminum canisters in the basin water or 2) by corrosion products that would have formed over those surfaces exposed to corrosion attack by the basin water. In either case, the rate of hydrogen generation from corrosion would be lower than that measured for the non-corroded aluminum metal coupons used in the laboratory tests thereby increasing the allowable ratio of aluminum surface area to basin floor surface area for flammable condition.
- The aluminum metal identification tags are made of anodized aluminum. The anodic coating over the aluminum metal is a very thin layer of aluminum oxide that provides resistance to corrosion. The hydrogen generation rate for anodized aluminum would therefore be less than that for aluminum metal thereby increasing the allowable ratio of aluminum surface area to basin floor surface area for flammable condition assumed in the PNNL and Fauske analyses.
- Neither analyses account for dissipation of hydrogen between the basin water surface and the grating via advection. Accounting for this phenomenon would accelerate the rate of hydrogen dissipation once it breaks the basin water surface and thereby increase the allowable ratio of aluminum surface area to basin floor surface area for flammable condition.
- Both analyses assume that the lateral expanse of the hydrogen bubble plume generated from corrosion of the aluminum metal is the same as the basin floor surface area occupied by the aluminum metal source. In reality, local concentrated sources of aluminum metal (i.e., an upright fuel canister or stacked canisters) will produce a bubble plume, which spreads laterally as it rises through the basin pool. Accounting for this phenomenon would decrease the surface area ratio for an upright fuel canister.
- The thermal analysis assumed the grout and basin water were a closed system and there was no thermal losses to the basin structure (floor and walls) or to the air above the basin. Furthermore, only heat conduction from the grout to the basin water was assumed, ignoring heat loss via natural convection.
- The quantity of heat generated from the formation of hydrates (heat of hydration) used for the thermal analysis was for a cumulative period over seven days. This is very conservative since the time period of interest is the first three hours after exposure to $\text{Ca}(\text{OH})_2$. Also, this analysis did not evaluate the use of a temperature retardant in the grout to delay the formation of hydrates and therefore the heat of hydration generation rate.

The PNNL and Fauske analyses include the following uncertainties in their analyses:

- The hydrogen generation rate utilized in these analyses was based on only one relevant gas generation test (Test #5) for aluminum metal immersed in grout. On the other hand, four tests were conducted measuring the hydrogen generation rate from corrosion of aluminum metal immersed in a $\text{Ca}(\text{OH})_2$ solution, the results of which were in good agreement with one another. While more test results for grout would provide increased confidence in the PNNL and Fauske results, the hydrogen generation rate result for grout is consistent with those measured in the $\text{Ca}(\text{OH})_2$ solution based on chemistry fundamentals [i.e., mass transfer conditions in grout are poorer than those in $\text{Ca}(\text{OH})_2$]. Furthermore, the uncertainty in the hydrogen generation rate in grout is likely not significant relative to the significant conservatisms in the analyses.
- The one relevant gas generation test (Test #5) for aluminum metal immersed in grout was performed at a grout temperature of 27°C (81°F). Extrapolation of this result to other grout temperatures was made using the test results on hydrogen generation from aluminum metal immersed in a $\text{Ca}(\text{OH})_2$ solution (i.e., increasing temperature of $\text{Ca}(\text{OH})_2$ solution from ambient temperature ($\sim 20^\circ\text{C}$) to $\sim 50^\circ\text{C}$ increases hydrogen generation rate by about a factor of 5). Again, while more test results for grout at higher temperatures, and especially at the grout temperatures expected to be used during grouting of the basins, would provide increased confidence in the PNNL and Fauske results, the hydrogen generation rate result for grout is consistent with those measured in the $\text{Ca}(\text{OH})_2$ solution based on chemistry fundamentals. Also, as with the previous bullet, the uncertainty in the hydrogen generation rate in grout is likely not significant relative to the significant conservatisms in the analyses.

5.0 Conclusions

Based on the review of available experimental and analytical studies, it was concluded that the likelihood of generating a flammable mixture of hydrogen from interaction of residual aluminum metal with grout is low but not zero. However, a flammable mixture of hydrogen will not be generated anywhere in the basin facility during grouting of the KE Basin as long as the following conditions are met:

- The residual aluminum metal inventory in the basin, especially the fuel canisters, is not stacked on top of one another. This will prevent over-concentrating the aluminum metal inventory over a small surface area of the basin floor.
- The temperature of the grout is maintained below 90°C (194°F) during pouring and at least three hours after the aluminum metal has been covered (lower grout temperatures result in lower hydrogen generation rates). After about three hours immersed in the grout, an oxide or corrosion layer has formed on the aluminum metal significantly reducing the corrosion/hydrogen generation rates assumed in this analysis.
- The basin water temperature is less than 60°C (140°F) for at least three hours after interruption of the grout pour if the aluminum metal in the basin has not been completely covered [so as to minimize reaction of the uncovered aluminum metal with $\text{Ca}(\text{OH})_2$]. This can effectively be done by ensuring that the basin water temperature is less than 21°C (70°F) prior to initiating grouting of the basin and ensuring that the basin water level is at least 10 feet above the surface of the grout.
- The basin water is not removed at the same time as grout is being poured (to avoid removing the hydrogen to another potential collection point). This condition is not necessary if the water removal system is appropriately vented to prevent accumulation of hydrogen in the system or after the aluminum metal has been covered with grout for at least three hours.

These conclusions are supported as long as the amount and physical configuration of the residual aluminum inventory in the KE Basin is consistent with the assumptions described in Appendix A.

Appendix A

Experimental and Calculational Evaluation of Hydrogen Generation During Grouting of Aluminum-Containing Hardware in the K Basins

Experimental and Calculational Evaluation of Hydrogen Generation During Grouting of Aluminum-Containing Hardware in the K-Basins

Greg A. Whyatt
Chris M. Fischer
Wooyong Um
R. Jeff Serne
Steve Schlahta

Introduction

This evaluation was performed to assess the potential impact of imbedding equipment and debris within a layer of grout in K-basins during D&D activities in order to provide shielding and to fix contamination. The presence of aluminum in the form of empty canisters, identification tags or other hardware will lead to the generation of hydrogen as high pH grout contacts and reacts with the aluminum metals. The hydrogen will bubble up through the basin water and be released into the space between the basin water surface and the grating. If the rate of hydrogen dissipation from this region is insufficient, flammable mixtures of hydrogen could collect and create a hazard.

This main section of this letter report begins with a brief overview and discussion of the work performed. Then recommendations and suggestions for mitigation approaches and further investigation are provided. Additional detail and supporting information is then provided in 3 attachments which include:

Attachment 1, pg 8:

Calculation of Hydrogen Dissipation by Diffusion During Grouting of Basins Containing Aluminum Components
This attachment calculates the extent of hydrogen dissipation that can be expected relying on diffusion alone. This rate of dissipation is then compared to the estimated surface area of aluminum in the basins and the estimated gas generation rate based on experimental measurements.

Attachment 2, pg 14:

Literature Review on Hydrogen Generation from Corrosion of Aluminum Components
Available literature on aluminum metal corrosion with hydrogen generation is reviewed.

Attachment 3, pg 17:

Experimental Measurement of Hydrogen Generation From Corroding Aluminum Alloy 5086 Coupons in Ca(OH)₂ Solution and Portland Cement Paste

Experimental measurements of hydrogen generation are made using (a) calcium hydroxide solutions, the main soluble constituent in cement pore water, and (b) Portland cement paste. Characterization results for the protective precipitate layer that was observed to form on the aluminum surface during corrosion are also reported.

Overview and Discussion

Hydrogen generation from grouted aluminum occurs due to reaction of the aluminum with elevated hydroxide levels present in the pore water of the grout. Portland cement contains 60 to 67% CaO by weight. When added to water the CaO hydrates to form Ca(OH)₂. As a result, a saturated Ca(OH)₂ solution approximates the high hydroxide environment within the grout. In addition, since mass transport in a stirred slurry is more rapid than in a grout, a Ca(OH)₂ slurry should provide conservatively high values. Measurements of the gas generation rate for coupons of aluminum alloy 5086 in saturated calcium hydroxide solutions yielded relatively high rates initially. Maximum generation rates of ~5 cm³/min were observed at ~50°C for a coupon measuring 1 x 3 x 0.185 inches. At ambient temperature the rate was about a factor of 5 lower. However, regardless of temperature, the rate of gas generation was observed to drop to extremely low levels within 2 to 3 hours of contact between the aluminum coupon and solution. While some of this drop in reaction rate is attributed to changes in the solution composition, the dominant factor appears to be the formation of a precipitate on the aluminum coupon surface which significantly slows the corrosion of the aluminum. XRD analysis of the precipitates show that tricalcium aluminum hydroxide

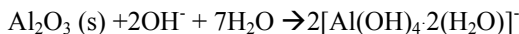
(Ca₃Al₂(OH)₁₂) and hydrocalumite (Ca₂Al(OH)₇·2H₂O) are present and does not suggest much amorphous material is present. Acid digestion of the precipitate followed by ICP-OES indicates the molar ratio of Ca to Al in the precipitate is 1.57:1. From this it can be inferred that the molar distribution between the two precipitate phases is approximately 23.7 % Ca₂Al(OH)₇·2H₂O and 76.3% of the Ca₃Al₂(OH)₁₂.

The chemistry of the aluminum corrosion reactions in the Ca(OH)₂ solution is believed to be as follows:

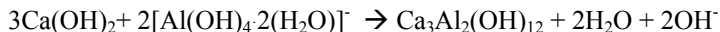
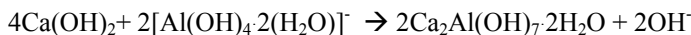
At the aluminum metal surface, the metal reacts with oxygen in the thin oxide layer covering the metal surface, which creates an oxygen vacancy in the oxide layer. The vacancy is then eliminated by reaction with water at the interface of the oxide layer and the solution resulting in the following overall reaction:



The oxide layer is simultaneously being dissolved at the surface through the reaction:



The dissolved aluminate may then either remain in solution or it may precipitate at the surface of the aluminum coupon, possibly through the following reactions:



The formation of the precipitate hinders the access of hydroxide to the oxide layer covering the metallic aluminum surface resulting in a reduction in the rate of hydrogen production.

The gas generation rate observed when an aluminum coupon was placed directly in a wet Portland cement paste was about 1/3 of the rate observed when aluminum coupons were placed in the calcium hydroxide solution. This is believed to be related to the poor mass transfer conditions in the Portland cement paste relative the stirred calcium hydroxide slurry (a solution with some excess solid Ca(OH)₂ to ensure saturation). Pretreatment of a coupon with Ca(OH)₂ slurry dramatically reduced the hydrogen generation observed when the coupon was later placed into a wet Portland cement paste.

The total inventory of aluminum surface area is estimated to be about 6417 ft². The sources of aluminum surface area are estimated to be 59% canisters, 29% ID tags, and 12% tools. This aluminum exists in the East basin which consists of 3 bays, each measuring ~70 ft x 40 ft for a total floor area of 8400 ft². If the aluminum were distributed uniformly across the floor of the three bays, there would be 0.764 ft² of aluminum surface area per ft² of basin floor area.

Average Sources

Calculations were performed to estimate how much hydrogen could diffuse from the water surface to the grating level without reaching flammable mixtures at the water surface. These results can then be combined with the estimated hydrogen generation rates under various conditions to determine the amount of aluminum surface area that can be tolerated under those conditions before a flammable mixture of hydrogen may occur at the surface of the basin water. These values are summarized in Table 1. Footnotes are provided to explain the conditions under which the tolerable aluminum surface areas are calculated. The information is expressed differently in Figure 1.

If the aluminum is uniformly distributed and instantly covered by grout at ambient temperature, the data suggests that the existing aluminum area could be tolerated if uniformly distributed (compare 2.0 to 0.76 area ratio in Table 1). However, if Ca(OH)₂ concentrations in the basin water increase prior to covering by grout this could result in higher hydrogen generation rates. Also, if the grout is heated to ~50°C due to mixing, pumping and hydration reactions, the hydrogen generation will increase substantially. While data was not available to evaluate exposure to Portland cement paste at 50°C an extrapolation based on temperature sensitivity in Ca(OH)₂ indicates this to be the most conservative case examined. Under these conditions, it is estimated that 0.4 ft² of aluminum per ft² of basin floor can be tolerated before flammable mixtures occur at the water surface. This is roughly half of the amount of

aluminum surface area currently estimated to exist in the basins. If under the same conditions, it is desired to maintain the hydrogen concentration at the water surface below 25% of the LFL (1% H₂) then only 1/8th of the aluminum can remain in the basin during grouting.

Table 1. Tolerable Average Aluminum Surface Area Relative to Basin Floor Area for Various Conditions. The maximum tolerable level is taken as the LFL for hydrogen (4% H₂) at water surface, except where noted otherwise.

Value Description	Ratio of Aluminum Surface Area to Basin Floor Area, [ft² aluminum surface area/ ft² basin floor area]
Existing Area Ratio For Comparison (a)	0.76
Portland Cement – 27.1°C (b)	2.0
Portland Cement ~50°C <i>Extrapolated</i> (c)	0.4
Portland Cement ~50°C <i>Extrapolated</i> , Tolerable level = 25%LFL limit or 1% H ₂ (d)	0.1
Ca(OH) ₂ in Basin Water – 22.8°C (e)	0.54

- (a) Estimated total aluminum surface area distributed evenly over floor area of three 70 ft x 40 ft basins.
- (b) Tolerable area ratio assuming aluminum is encapsulated in Portland cement paste. This is the most representative value for aluminum after it is completely covered by grout. Source value is test#5 in attachment 3, which involved an aluminum coupon in a Portland cement paste at 27.1°C. The dissipation value is based on dissipation calculated using diffusion in air at 10°C.
- (c) Tolerable area ratio assuming the grout mixture achieves temperatures in the ~50°C range early in curing. The source is assumed to increase 5X similar to what is observed in Ca(OH)₂ solution. No data is available in this temperature range for cement paste. Heating could occur due to mixing and pumping energy inputs and hydration reactions. If temperatures in this range are expected, data on the actual source value in cement paste is recommended.
- (d) Identical to the preceding row of the table except that the maximum allowable hydrogen concentration is taken as 25% of the LFL or 1% hydrogen. The lower threshold value is selected in order to provide a margin of safety between the operating conditions and the LFL of hydrogen which is 4% hydrogen in air.
- (e) Tolerable area ratio based on basin water becoming saturated in Ca(OH)₂ at 22.8°C ahead of aluminum being covered by grout. The actual rate of Ca(OH)₂ dissolution into basin water is unknown. Hydrogen source is based on data in test #1 in attachment 3. Dissipation is based on air at 10°C. If basin water is cooler than 22.8°C the hydrogen generation rate would be lower although no data at lower temperatures is available.

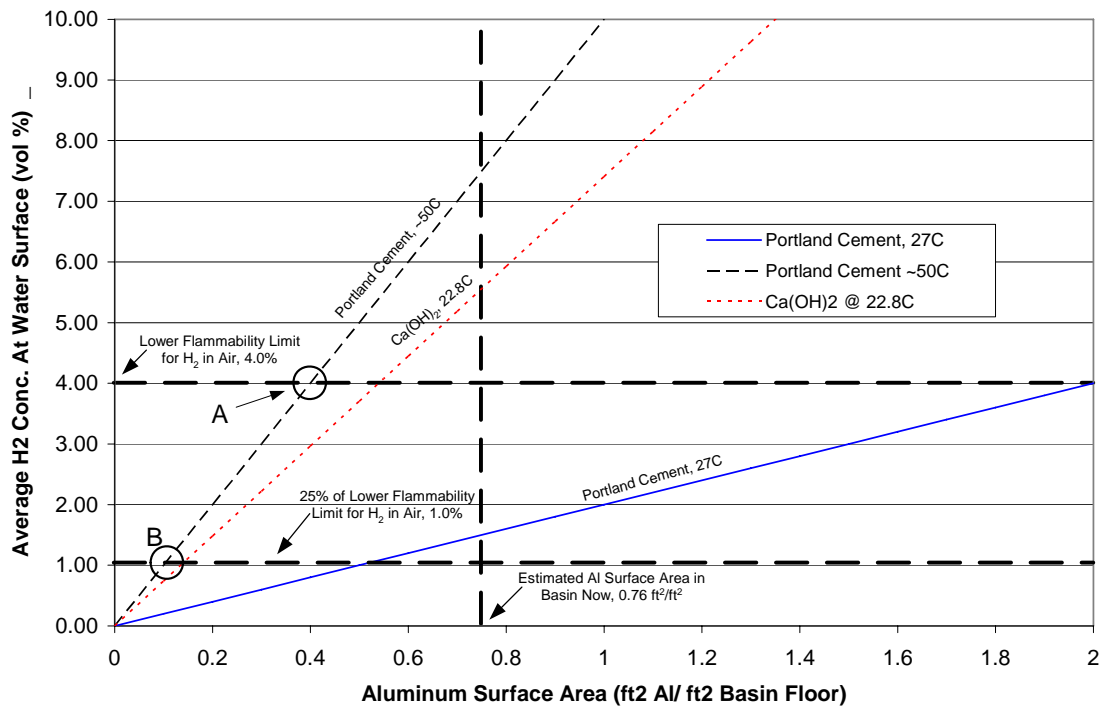


Figure 1. Average Hydrogen Concentration at Water Surface as a Function of Aluminum Surface Area. A uniform distribution of aluminum surface area is assumed. The hydrogen concentration averaged over the entire air space between the surface of the water and the grating will be one half of the concentration at the water surface. The line for *Portland Cement, ~50°C* is based on a case where the grout temperature is elevated. Based on this line about half of the aluminum would need to be removed to remain below 4% H₂ (point A on graph). The *Ca(OH)₂, 22.8°C* case assumes Ca(OH)₂ dissolves into basin water and contacts aluminum ahead of the grout covering the surface. The *Portland Cement 27°C* line assumes aluminum is quickly covered in grout at 27°C. In the most conservative treatment, if it is assumed that the Portland cement heats to 50°C and the requirement is that hydrogen cannot exceed 25% of the LFL (in order to provide a margin of safety) then only 0.1 ft² Al per ft² of floor area can be tolerated (point B on graph). This would imply 87% of the aluminum surface area would need to be removed prior to grouting.

Concentrated Sources

Table 1 and Figure 1 discuss the *average* concentration of aluminum across the basin floor and is based on dissipation by diffusion in 1 dimension from a uniform concentration at the water surface to a zero concentration at the grating where advection is assumed to dilute the hydrogen to very low levels. Certainly, as bubbles of hydrogen break the surface of the water there will be a localized region roughly the size of the bubble where flammable mixtures will occur before the hydrogen is diluted by diffusion into the air. On a larger scale, the geometric configuration of the aluminum hardware will create local concentrations of aluminum surface area greater than the average value. In this case there may be regions where bubbling is more intense resulting in areas of higher concentration roughly the same scale as the hardware in question. ID tags lying flat on the floor will provide a ratio of ~2 ft²/ft² over the floor area they are covering. More significantly, one 8" diameter tube from a canister orientated vertically covers 50 in² of floor area and has 1500 in² area for a ratio of 30 ft²/ft². This value is substantially greater than the average surface area tolerable values in Table 1. The value for a canister tube may be

reduced somewhat by cutting the tube in half along its length and laying the halves flat on the floor which results in a ratio of 3.4 ft² Al/ft² basin floor.

Concentrated sources may disperse to a greater area as they pass through the grout and water layers and once reaching the surface would dissipate into the air by diffusing laterally to lower concentration areas as well as vertically toward the grating. This would increase the rate of dissipation from a concentrated source. However, this report has not considered these effects for concentrated sources.

The safety implications of small concentrated sources of hydrogen being in the flammable range are much less than the implications for average concentrations across the surface of the water being in the flammable range. If ignited, a localized source will burn a small amount of hydrogen and extinguish without spreading if concentrations in adjacent regions are outside the flammable range. While this report does not attempt to make a judgment on the size of a localized high concentration region that may be tolerated within the basins during grouting the impact of ignition of such a pocket is clearly less severe than if high concentrations exist over a broader area.

Suggestions and recommendations are summarized in the next section with additional details provided in the three attachments.

Recommendations/Suggestions

Removing half of the surface area of aluminum currently in the basin will allow the generated hydrogen to dissipate without reaching an *average* hydrogen concentration at the water surface in the flammable range. This is based on assuming the grout heats to 50°C or less in the first few hours of curing and/or that Ca(OH)₂ dissolves into the basin water and reacts with aluminum prior to covering with grout. The aluminum surface area must be distributed evenly across the area of the basin in order to avoid regions with high aluminum surface area concentrations. If the criteria selected is to maintain H₂ concentrations <25% of the LFL then ~87% (~7/8ths) of the aluminum surface area must be removed from the basin prior to grouting.

The acceptability of small localized regions of air above the basin water reaching flammable mixtures, corresponding to individual pieces of hardware, needs to be evaluated. The potential for a localized concentration point is greatest above a vertically orientated canister. If desired, the extent of concentration can be reduced by cutting the tubes in half along the length and placing the two halves on the basin floor with inner surfaces facing upward.

If elevated grout temperatures *and* Ca(OH)₂ concentrations existing in the basin water prior to grout encapsulation can both be ruled out as possible phenomenon then the currently existing quantity of aluminum may be tolerated without average concentrations reaching flammable levels. If this approach is taken, care should be taken to assure that grouting in one bay of the basin does not cause an unacceptable increase in the Ca(OH)₂ concentration in adjacent bays.

The current evaluation, based on one-dimensional diffusion only, is considered very conservative. The following activities could remove some of the conservatism in the current analysis:

- The current calculations neglect the effect of advection. An analysis of the effects of natural convection due to density differences may increase the amount of hydrogen that can dissipate from the region below the grating without reaching a flammable concentration.
- The current calculations assume that the anodized aluminum fuel ID tags, which make up ~29% of the aluminum surface area in the K basin, will release as much hydrogen per unit area as the alloy 5086 canisters. However, we speculate the presence of the thick oxide layer initially on the metal surface may reduce the quantity of hydrogen generated prior to the establishment of the protective precipitate coating on the metal. Testing of anodized aluminum specimens matching the ID tags may be able to reduce the estimated rate of hydrogen generation from this source.

- Experimental gas generation rates were measured using aluminum coupons which are not visibly corroded. The surface of aluminum canisters within the basins is visibly corroded. The presence of a thicker layer of corrosion products on the metal surface may reduce the peak rate of H₂ generation when grout contacts the aluminum. Measurements using coupons with a corroded surface representative of the non-anodized basin aluminum surfaces could reduce the estimated H₂ generation from this source.

Possible mitigation approaches that could be investigated for the hydrogen generation and accumulation above the basin water include:

- Use of fans during grouting and for a few hours after grouting to dissipate H₂.
- Minimize temperatures in the grout and basin water to slow reactions.

Additional details on these possible approaches as well as other options considered but rejected are provided below.

In all cases, bench-scale confirmatory tests should be performed using the actual grout formulation over the anticipated temperature range and for all aluminum alloys identified as present in the basin.

Use of Fans to Dissipate Hydrogen

If a source of forced convection is provided in the air space below the grating for a few hours during and after grouting this would greatly enhance the rate at which the hydrogen would disperse. This could take the form of a number of small portable fans laid face down on the grating and operated for a few hours after each section of the basin is grouted. The number of fans needed could be limited by grouting the basin in sections. Alternatively, one or two larger fans could be used to create an air jet that would sweep air over the 70 ft length of the basin. Since the current rate of hydrogen generation is on the same order as what will dissipate by pure diffusion, it is likely that forced convection in the region could readily disperse the hydrogen to well below the flammable limit. A check on the ability of the building ventilation to adequately vent the hydrogen removed from below the grating should be made but this is unlikely to be a limitation.

Minimize Temperature in the Grout and Basin Water

Data on hydrogen generation in Ca(OH)₂ and Portland cement at temperatures below ambient were not collected as part of this scoping study. However, assuming Arrhenius behavior for the reaction kinetics¹, the extent of reaction rate reduction for aluminum exposed to Ca(OH)₂ solution can be estimated based on data at 22.8°C and 51.9°C. Extrapolating to lower temperatures the relationship predicts a 70% reduction in hydrogen generation rate as the temperature is reduced from 22.8°C to 4.0°C. A similar effect would be expected to occur in the grout as well. If this approach is to be considered, data on reaction rates at the temperatures of interest should be obtained to verify the extrapolation.

Alternate Approach Rejected - Pretreatment of Aluminum Surfaces Using Basin Water Chemistry Prior to Grouting

It is possible to reduce hydrogen generation using a controlled exposure of aluminum surfaces to Ca(OH)₂ in the basin water. Corrosion of the aluminum in the presence of a high pH Ca(OH)₂ solution forms a protective precipitate that reduces hydrogen generation rates to very low levels within a few hours. By introducing calcium hydroxide to the basin water prior to grouting, a protective precipitate layer could be deposited on aluminum surfaces resulting in very low rates of hydrogen generation during grouting. While the initial rate of generation observed in saturated Ca(OH)₂ solution is greater than for Portland cement paste, it is hypothesized that the rate of hydrogen generation resulting from Ca(OH)₂ addition to basin water can be controlled by controlling the rate of addition. It is anticipated that formation of the protective precipitate may be accomplished over a couple days time frame. Once the protective layer is established on the aluminum surfaces, the grouting can be performed with very little additional hydrogen generation. Addition of Ca(OH)₂ to the basin water will cause the basin water to absorb carbon dioxide from the air. However, due to the relatively rapid formation of the protective precipitate layer, the amount of hydroxide consumed is likely manageable. This approach was rejected due to a need to keep the ion exchange modules on-line prior to the grouting operation. Addition of soluble calcium to the

¹ An Arrhenius rate expression is of the form (Rxn Rate)=A*Exp[-E/(R*T)] where T is the absolute temperature, R is the gas constant, and E is an activation energy.

basin water would rapidly saturate the current ion exchange resin. Thus, changes to the ion exchange approach such as using cesium-selective ion exchange resins to selectively remove ^{137}Cs would be needed prior to adding $\text{Ca}(\text{OH})_2$ to the basin water. While a similar concern will exist during grouting as the $\text{Ca}(\text{OH})_2$ from the grout dissolves into the basin water, the quantity of calcium in the water will be less and the duration shorter during grouting than it would be if aluminum hardware were corroded using $\text{Ca}(\text{OH})_2$ addition.

If it is decided to pursue this approach additional data would be needed. In order to properly control the rate of $\text{Ca}(\text{OH})_2$ addition to limit hydrogen generation, laboratory data on the relationship between $\text{Ca}(\text{OH})_2$ concentration and hydrogen generation rate for the alloys involved will be needed.

Alternate Approach Rejected – Alternate Method for Formation of Protective Coating

Literature indicates that under neutral pH conditions the presence of a lanthanide salt such as $\text{Ce}(\text{NO}_3)_3$ can protect aluminum surfaces from corrosion through a similar mechanism (in this case the hydroxide generated in aluminum corrosion results in precipitation of the cerium at the corrosion location). If used directly as an additive to grout, the cerium may precipitate nearly completely leaving very little in solution to react at the aluminum surface. However, the use of $\text{Ce}(\text{NO}_3)_3$ under neutral pH conditions could be investigated as an alternate method of forming a protective layer on the aluminum prior to grouting. This would require laboratory investigation.

Alternate Approach Rejected – Sodium Hydroxide Addition

Another alternate approach considered but rejected was the addition a sodium hydroxide to the basin water with the objective of fully corroding the entire aluminum mass prior to grouting. It is postulated that corrosion with sodium hydroxide would not form the protective precipitate layer on the surface of the aluminum which would allow complete corrosion of the aluminum. The major drawback to this approach is that the total quantity of hydrogen generated would be much greater than either direct grouting or $\text{Ca}(\text{OH})_2$ addition. In corrosion by Portland cement paste or $\text{Ca}(\text{OH})_2$ slurry the aluminum quickly forms a protective layer so that only a small fraction of the aluminum mass actually reacts to form hydrogen. As a comparison, a corrosion coupon inserted into Portland cement paste generated 30.9 cm^3 of gas (test#5 in attachment 3). The estimated gas generated for complete corrosion of the coupon with sodium hydroxide is 33100 cm^3 . The actual disparity will vary with the surface area to volume ratio of the aluminum being corroded but in any case is very significant.

If this option were selected, the rate of hydrogen generation could be controlled by controlling the rate of sodium hydroxide addition to the basin water. The operation may be performed either with fans to help remove generated hydrogen, or it could be performed using an extended period of slow corrosion relying on diffusion to disperse the hydrogen. The only advantage of this approach is that once the aluminum is fully corroded, the potential for hydrogen generation from reactions between aluminum metal and hydroxide are eliminated. The sodium hydroxide concentrations would likely need to be in the range of 0.01 and 0.1 M depending on the time frame desired for the corrosion. Carbon dioxide from the atmosphere would be absorbed by the basin water which would neutralize the hydroxide and increase the amount of sodium hydroxide addition required. If corrosion is extended over long time frames this could be a significant factor. As is the case with other options with additives to the basin water, this could significantly affect the ion exchange system if it is being operated during the addition.

Data on hydrogen generation rates as a function of sodium hydroxide concentration would be needed in order to provide estimates of the concentrations and times that would be suitable.

Alternate Approach Rejected - Pouring Grout in Lifts

The pour rate of the grout is projected to be $100 \text{ yd}^3/\text{hr}$. This will place about 1 ft per hour in a 70 x 40 ft basin. Since the gas generation tends to drop to very low levels within 2 to 3 hours, the grout could be placed in lifts, with pauses between the pours. The objective here would be to divide the hydrogen source into multiple segments such as tools and ID tags in the first lift, the bottom half of canisters in the second lift and the top half of canisters in the third lift. The major difficulty with this approach is that it is expected that pouring of grout in the bottom of the basin will result in dissolution of $\text{Ca}(\text{OH})_2$ into the basin water. Hydrogen generation rates observed for coupons exposed to $\text{Ca}(\text{OH})_2$ solutions were about 3 times greater than those exposed directly to Portland cement paste. Hence pouring in lifts may actually increase the hydrogen generation rates by allowing greater time for $\text{Ca}(\text{OH})_2$ to dissolve into the basin water above the grout layer and react with exposed aluminum.

Attachment 1:

Calculation of Hydrogen Dissipation by Diffusion During Grouting of Basins Containing Aluminum Components

Greg A. Whyatt

Introduction

This evaluation was performed to assess the potential impact of imbedding equipment and debris within a layer of grout in K-basins during D&D activities in order to provide shielding and to fix contamination into a non-dispersible form. The presence of aluminum in the form of empty canisters, identification tags or other hardware will lead to the generation of hydrogen in the grout layer. This attachment describes a scoping calculation which estimates the rate at which hydrogen may dissipate by diffusion from the area between the water surface and the grating level in the basin during grouting. The scoping calculation is intended to determine whether it is possible to accumulate a flammable mixture of hydrogen in the space between the surface of the basin water and the bottom of the grating.

The conceptual layout of the calculation is summarized in Figure 1-1.

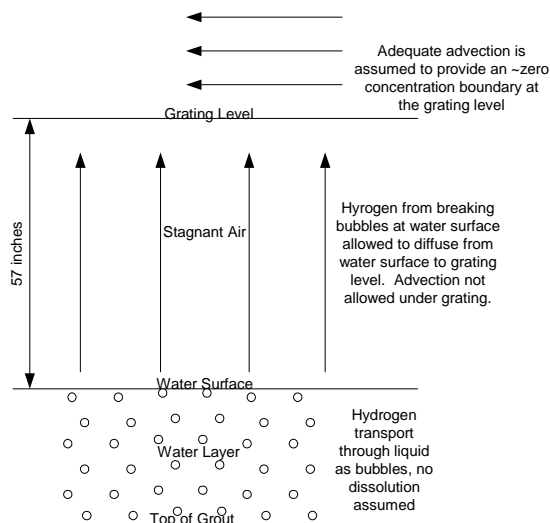


Figure 1-1. Conceptual Layout of Calculation. Hydrogen introduced to the air layer via breaking bubbles diffuses from the water surface to the grating level.

A one-dimensional, steady-state diffusion calculation is performed to determine the rate of diffusive flux that can be achieved between the water surface and grating level. A flux rate is calculated for the condition where the layer of air along the water surface is at 4 volume percent H_2 which is the approximate lower flammable limit for the hydrogen-air mixture². It should be noted that as individual bubbles break and mix into the air layer at the water surface there will be very localized high hydrogen concentrations as each bubble disperses into the air layer. However, for this study, it is assumed that these very small, discontinuous concentrations do not constitute a hazard. Only if sufficient hydrogen is being released that a larger zone of gas reaches a flammable concentration would there be a potential hazard.

Advection is being neglected in this calculation. Advection would tend to increase the rate at which hydrogen could be dissipated from the air layer below the grating (leading to lower H_2 concentrations). The low molecular weight

² CRC Handbook of Chemistry and Physics, 69th edition, pg D-124

of the hydrogen (and lower density of hydrogen/air mixtures) would tend to favor advection of hydrogen up and out of the air layer below the grating. For this scoping analysis, neglecting advection is very conservative.

Input Data:

Typical air temperatures range between 50°F and 80°F (10.0°C – 26.6°C).

Correlations are available for estimating diffusivity of hydrogen in air³. The estimated diffusivity of hydrogen in air at one atmosphere pressure and various temperatures of interest are:

0°C	0.647 cm ² /s
10°C	0.688 cm ² /s
26.6°C	0.757 cm ² /s

The value at 0°C is in good agreement with the value of 0.634 cm²/s found in the CRC Handbook of Chemistry and Physics for this condition⁴.

Diffusion Calculation:

The diffusion in this case is considered to be uni-component (H₂) in nature. Because the concentrations of hydrogen are small relative to the air, no corrections for phase drift are applied. This is conservative. Similarly, potential phase drift effects due to water vapor diffusion either to or from the surface of the basin pool surface are neglected. The steady-state diffusion problem can be reduced to provide the following expression for the hydrogen flux as a function of diffusion distance, diffusivity and limiting hydrogen concentration:

$$\text{Flux, mol H}_2/(\text{s cm}^2) = D * (C_0/H)$$

where D = diffusivity of hydrogen in air at temperature of interest, cm²/s (listed above for both temperatures of interest)

C₀=limiting hydrogen concentration in mol/cm³ (use the ideal gas law n/V = P/RT with P = 1 atm to determine total gas molar concentration and multiply by 0.04 for 4% flammability limit).

H = distance from water surface to grating, cm (equals 144.8 cm in K basin)

The concentration term C₀ may be used directly (rather than a concentration difference) due to the assumption that the concentration at grating level is held at zero due to advection above the grating.

Diffusion Calculation Result

The limiting hydrogen concentrations for the two temperatures of interest as determined by the ideal gas law for 1 atm pressure and 0.04 fractional volume are 1.72 x 10⁻⁶ mol/cm³ and 1.63 x 10⁻⁶ mol/cm³ at 10°C and 26.6°C, respectively. Using these values for C₀, cited diffusivities, and distance that the H₂ must diffuse to reach the open air at 10°C and 26.6°C, in the above equation, the calculated fluxes that produce a 4% hydrogen mixture at the water surface at steady state for 1 atm pressure are:

$$10^\circ\text{C flux} = 8.19 \times 10^{-9} \text{ mol H}_2/(\text{s cm}^2)$$

$$26.6^\circ\text{C flux} = 8.51 \times 10^{-9} \text{ mol H}_2/(\text{s cm}^2).$$

Effect of Pressure:

All calculations are performed for 1 atm pressure. The diffusivity value is inversely proportional to absolute pressure such that decreasing pressure will lead to an increase in diffusivity. Since local atmospheric pressure is typically less than 1 atm the diffusivity value used should be conservative. Atmospheric pressure at the Hanford weather station averages 0.9766 atm and ranges between a maximum of 1.0103 atm and minimum of 0.9408 atm (Hanford weather station data 1955-2002). Small deviations from ambient pressure may also occur due to the building ventilation system. In addition to the effect on diffusivity, the molar concentration to achieve 4% will decrease with decreasing pressure which would tend to offset the pressure effect. In addition, some adjustment in the hydrogen flammability limit (represented as 4 vol% in the calculation) may be possible to provide a more precise adjustment of the calculation for pressure changes.

³ Correlations used are from Chemical Engineer's Handbook, 5th Edition, pgs 3-231 to 234, eqns. 3-29, 3-29(a), (b), (c) and (d) with data from tables 3-306, 307 and 308.

⁴ CRC Handbook of Chemistry and Physics, 69th edition, pg F-48

Aluminum Surface Area in the Basin

Aluminum surface area is expected to come from:

- 182 aluminum canisters fabricated in aluminum alloy 5086
- 3000 identification tags fabricated in aluminum alloy 5005, anodized⁵
- 150 long-handled tools, 1” diameter x 20 ft long⁶

Canisters are described as consisting of 2, 8-inch diameter, 28” long cylinders with solid bottoms and open tops. Wall thickness is 0.090-inch. The diameter was not specified as inside or outside so both internal and external surface area is calculated based on a diameter of 8 inches. Area associated with the cross member joining the two cylinders is neglected. The calculated surface area of each 2-cylinder canister is 3000 in².

Identification tags have a diameter of 7.5 inches and thickness of 0.125 inches. The surface area per tag is calculated as 88.4 in², neglecting the edge area.

The long-handled tools have different radii and wall thicknesses. It is not clear whether grout would be able to penetrate to the interior of the tool to cause reaction on interior surfaces. As a result the area on tools is calculated on the external surface area only providing an area of 754 in² per tool.

The breakdown of area overall is then as shown in Table 1-1.

Table 1-1. Estimated Aluminum Surface Area Currently in Basin

Object	Number	Area per Object, in ²	Total area, in ²	Percent of Area
Canisters	182 ^(a)	3000	5.46 x 10 ⁵	59.1%
ID Tags	3000	88.4	2.65 x 10 ⁵	28.7%
Tools	150	754	1.13 x 10 ⁵	12.3%
Total			9.24 x 10 ⁵	

(a) each canister consists of a pair of cylinders

Concentration of Aluminum Surface Area on a Per Unit Basin Floor Area Basis

There are 3 basins each measuring ~ 70 x 40 ft for a total surface area of 8400 ft². If evenly distributed the aluminum would provide an areal aluminum surface area concentration of $(9.24 \times 10^5 \text{ in}^2 \text{ Al}) / (8400 \text{ ft}^2 \times 144 \text{ in}^2/\text{ft}^2) = 0.764 \text{ in}^2 \text{ Al} / \text{in}^2 \text{ basin floor (or water surface)}$.

Comparison to Experimental Value of Hydrogen Production

The most representative measurement is test#5 in attachment 2. This test involved a fresh coupon immersed in Portland cement paste. The maximum gas generation rate from a 48.3 cm² coupon in the early stages was 0.30 cm³/min at 27°C and ~1 atm. At these conditions this is equivalent to a gas generation from the coupon of $4.14 \times 10^{-9} \text{ [mol/(s} \cdot \text{cm}^2 \text{ Al)]}$. Based on a ratio of aluminum area to water area of 0.764 the extent of hydrogen removal to achieve steady state at this gas rate would be

$$[0.764 \text{ (cm}^2 \text{ Al/cm}^2 \text{ water surface)}] \times 4.14 \times 10^{-9} \text{ [mol H}_2\text{/(s} \cdot \text{cm}^2 \text{ Al)]} = 3.16 \times 10^{-9} \text{ mols H}_2\text{/(s cm}^2 \text{ water surface)}.$$

⁵ The information was provided to PNNL by the Fluor Client with the following reference: “Refer to drawing H-1-34910, Identification Plate Fuel Storage Canister. The drawing identifies the material as ASTM B-209 alloy 5005-H34 AL, anodized both sides, 0.063 inches thick.”

⁶ IWTS drawings (HNF-FMP-03-16080-R0B) provided the following tool information on composition: 1 in. dia., sch. 40, ASTM 6061/6063 AL, 1/2 in. dia., sch. 40, ASTM 6061-T6, as well as some stainless alloy tools. Breakdown on total surface area by alloy was not available.

By comparison, the diffusive dissipation values were 8.19×10^{-9} at 10°C and 8.51×10^{-9} at 26.6°C . Hence the maximum gas generation rate in the Portland cement paste is observed to be 37% to 39% of what can be dispersed by diffusion alone. The initial rate of gas generation in grout is expected to increase with increasing temperature. Observations of behavior in saturated $\text{Ca}(\text{OH})_2$ indicate the initial gas generation increases by a factor of 5 between 22.8°C and 59.1°C . Extrapolating this behavior to the grout would result in a hydrogen source of:

$$3.16 \times 10^{-9} \times 5 = 1.58 \times 10^{-8} \text{ mols H}_2/(\text{s cm}^2 \text{ water surface})$$

This value is 1.9 times greater than the maximum dissipation rate for which flammable mixtures are avoided (calculated assuming an air temperature of 10°C).

Also, when pouring the grout in the basin the aluminum above the grout surface will be exposed to some concentration of calcium hydroxide occurring due to contact with the fluid grout. If it is assumed that the basin water rapidly becomes saturated with $\text{Ca}(\text{OH})_2$ early in the grouting operation, then the rate of hydrogen generation from aluminum not yet covered by grout will dominate the hydrogen source. Based on hydrogen generation rates for aluminum in saturated $\text{Ca}(\text{OH})_2$ solution at ambient temperature (22.8°C , test #1 in attachment 3), the rate of hydrogen generation would be $1.517 \times 10^{-8} \text{ mol}/(\text{s cm}^2 \text{ Al})$. This leads to a requirement to dissipate:

$$[0.764 (\text{cm}^2 \text{ Al}/\text{cm}^2 \text{ water surface})] \times 1.517 \times 10^{-8} [\text{mol H}_2/(\text{s} \cdot \text{cm}^2 \text{ Al})] = 1.16 \times 10^{-8} \text{ mols H}_2/(\text{s cm}^2 \text{ water surface}).$$

This is 1.4 times greater than the dissipation rate calculated to avoid flammable mixtures for an air temperature of 10°C ($8.19 \times 10^{-9} \text{ mol}/\text{s cm}^2$). Basin water is typically cooler than the test temperature of 22.8°C . The rate of hydrogen generation would be less at lower basin water temperatures although experimental data at temperatures below ambient are not available. In any case, the extent to which the basin water increases in $\text{Ca}(\text{OH})_2$ concentration prior to aluminum surfaces becoming covered with grout may be an important factor in determining the amount of aluminum that can be tolerated in the basin during grouting without resulting in unacceptable hydrogen accumulation.

The result is expressed in different terms in Table 1-2 below.

Table 1-2. Allowable Quantities of Aluminum Area for Various Assumptions

Value Description	Ratio of Aluminum Surface Area to Basin Floor Area, [ft ² aluminum surface area/ ft ² basin floor area]
<u>Existing Ratio</u> Estimated total aluminum surface area distributed evenly over floor area of three 70 ft x 40 ft basins.	0.76
<u>Portland Cement – 27.1°C</u> Tolerable area ratio assuming aluminum is encapsulated in Portland cement paste. This is the most representative value for aluminum after it is completely covered by grout. Source value is test#5 in attachment 3, which involved an aluminum coupon in a Portland cement paste at 27.1°C. The dissipation value is based on dissipation calculated using diffusion in air at 10°C.	2.0
<u>Portland Cement ~50°C Extrapolated</u> Tolerable area ratio assuming the grout mixture achieves temperatures in the ~50°C range early in curing. The source is assumed to increase 5X similar to what is observed in Ca(OH) ₂ solution. No data is available in this temperature range for cement paste. Heating could occur due to mixing and pumping energy inputs and hydration reactions. If temperatures in this range are expected, data on the actual source value in cement paste is recommended.	0.4
<u>Portland Cement ~50°C Extrapolated - Using 1% H₂ Limit</u> Identical to the previous table entry except that the tolerable hydrogen concentration is drawn at 1% rather than at the LFL of 4%. The tolerable area is then simply 1/4 th of the previous entry.	0.1
<u>Ca(OH)₂ in Basin Water – 22.8°C</u> Tolerable area ratio based on basin water becoming saturated in Ca(OH) ₂ at 22.8°C ahead of aluminum being covered by grout. The actual rate of Ca(OH) ₂ dissolution into basin water is unknown. Source data is based on test #1 in attachment #3. Dissipation is based on air at 10°C. If basin water is cooler than 22.8°C the hydrogen generation rate would be lower although no data at lower temperatures is available.	0.54

Looking at Table 1-2 above, the tolerable aluminum surface area once the aluminum is covered by grout is 2 ft²/ft², which is greater than the aluminum surface area content if evenly distributed across the basins (0.76 ft²/ft²). However, if the basin water Ca(OH)₂ concentration is increased due to grouting operations prior to covering of the aluminum area by grout, the current aluminum content of 0.76 ft²/ft² would exceed the tolerable quantity of 0.54 ft²/ft². Also, if the grout temperature is elevated due to mixing and pumping energy inputs or curing reactions then this will reduce the tolerable surface area to 0.4 ft²/ft² indicating only about half the aluminum can remain in the basin while staying below 4% hydrogen at the water surface. At these conditions, if the target is selected to maintain the hydrogen concentration above the water below 25% of the LFL (1% H₂) then only about 1/8th of the aluminum can remain in the basin during grouting. Due to the formation of the protective precipitate layer on the surface of the aluminum, increases in grout temperature which occur after the first couple hours will not affect the maximum hydrogen rate. A comparison point for hot basin water was not calculated since no mechanism for rapid heating of the basin water could be identified.

The information in Table 1-2 is presented in a different form in Figure 1-2 below. The diffusion rate for dissipation is linearly related to the concentration at the water surface. The amount of hydrogen generated is a linearly related to the amount of aluminum surface area present. As a result, the average hydrogen concentration at the surface of the water is linearly related to the amount of aluminum surface area present. Figure 1-2 allows estimation of the average hydrogen content occurring at the water surface for a given aluminum surface area concentration. Alternatively, the maximum surface area can be determined by selecting the maximum desired hydrogen concentration and reading off the surface area allowed.

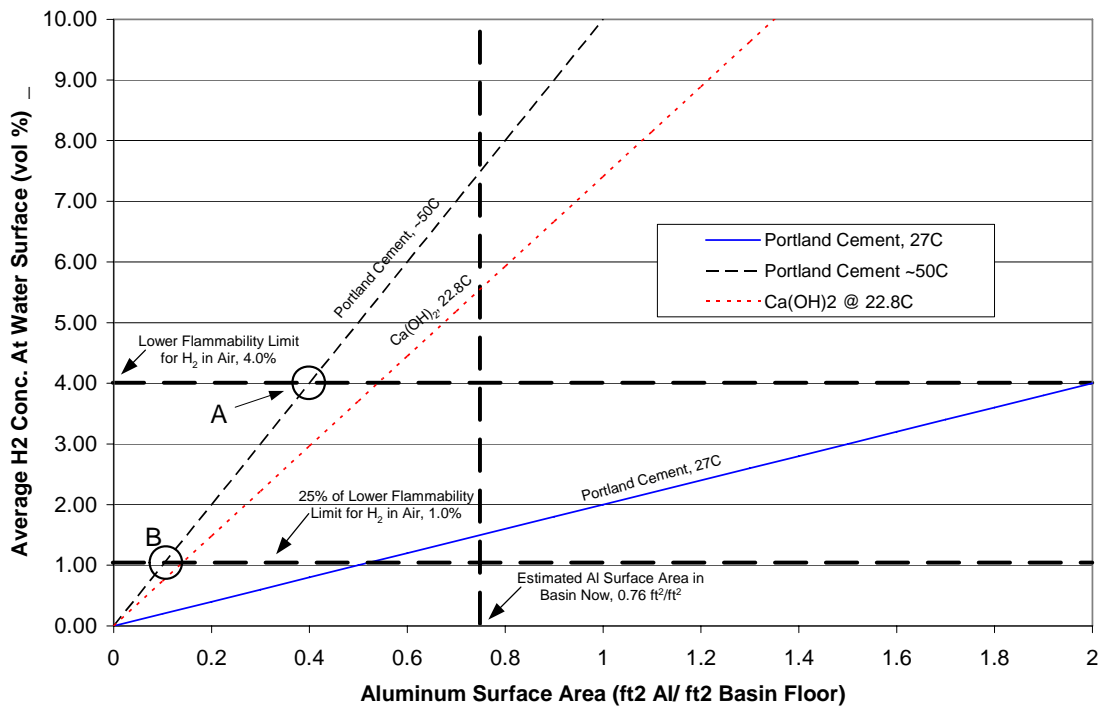


Figure 1-2. Average Hydrogen Concentration at Water Surface as a Function of Aluminum Surface Area.

Each line represents a different experimental basis for the hydrogen generation that can be expected. A uniform distribution of aluminum surface area is assumed. The hydrogen concentration corresponds to the water surface. The hydrogen concentration averaged over the entire air space between the surface of the water and the grating will be one half of the concentration at the water surface. The line for *Portland Cement, ~50°C* is based on a case where the grout temperature is elevated. In this case about half of the aluminum would need to be removed to remain below 4% hydrogen (point A). The *Ca(OH)₂, 22.8°C* case assumes *Ca(OH)₂* dissolves into basin water and contacts aluminum ahead of the grout covering the surface. The *Portland Cement 27°C* line assumes aluminum is quickly covered in grout at 27°C. In the most conservative treatment, if it is assumed that the Portland cement heats to 50°C and the requirement is that hydrogen cannot exceed 25% of the LFL (in order to provide a margin of safety) then only 0.1 ft² Al per ft² of floor area can be tolerated (point B on graph). This would imply 87% of the aluminum surface area would need to be removed prior to grouting.

Attachment 2: Literature Review on Hydrogen Generation from Corrosion of Aluminum Components

Wooyong Um

This evaluation was performed to assess the potential impact of imbedding equipment and debris within a layer of grout in K-basins during D&D activities in order to provide shielding and to fix contamination. To support the evaluation, a literature review was conducted for information on H₂ gas generation resulting from Al alloy corrosion under alkaline conditions. Because the D&D approach being evaluated will result in contact between aluminum hardware in the basin and the high pH of the grout pore water, it is necessary to estimate the amount of H₂ that may be generated. Unfortunately there were not many literature resources that have focused on the specific Al corrosion and H₂ generation issue. This literature review summarizes some basic corrosion studies and typical techniques used to suppress H₂ generation.

Al corrosion controlling factors

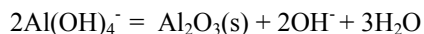
The corrosion of Al in various aqueous environments occurs through an oxide film via ionic migration through the oxide film followed by dissolution at the oxide/electrolyte interface [1]. When the oxidation reaction of the aluminum is with oxygen atoms originating from water molecule electrolysis, hydrogen is generated. In alkaline solutions, the Al dissolution process readily occurs, suggesting high corrosion rates for Al and subsequent generation of H₂. The H₂ evolution rate or at least total amount generated has been found to increase with increasing pH [2,3]. Al corrosion rates also increase with increasing temperature. Different Al alloys, composed of Al with various trace compounds, corrode with different rates under various conditions. The Al alloy of our interest to the K Basin is AA 5086 consisting of Mn(0.45 wt. %), Mg (4.0 wt. %), Cr (0.15 wt. %), and Al (95.4 wt. %) [4]. One article describes a potential problem at least for Al corrosion under acidic conditions. When halides are present in acidic (1 M HCl) solutions, they encourage pitting attack of the aluminum and may increase hydrogen generation rates. Enhanced rates of H₂ evolution result from local breakdown of the oxide film, because the exposed metal surface at the bottom of micro-pits formed during prior cathodic polarization serves as a preferential site for Cl⁻ ion attack during the following anodic polarization [5]. We could not find any literature that addresses whether the presence of halides in alkaline solutions, such as grout porewater, causes similar pitting and enhanced hydrogen gas generation. But we recommend that halide salts not be used as additives to the dry blend materials.

H₂ generation from Al corrosion

The corrosion of Al during cathodic polarization is promoted by increased pH and this cathodic corrosion of Al in aqueous solutions proceeds via a chemical dissolution reaction of aluminum by hydroxide ions and water following reaction at very high pH:



If enough Al dissolves such that the pH is reduced the dissolved aluminate ion will precipitate solid aluminum oxide, and form water and more hydroxide to promote further dissolution via the following reaction



Eventually if the Al metal dominates the system, the net reaction will become as all the caustic is consumed



Every oxidizing reaction taking Al metal to Al³⁺ species in solid or solution phases is going to require to release of 1.5 moles of H₂ gas per mole of Al. One reference was found that directly measured the rate of hydrogen generation from an Al metal coupon in a large volume of caustic solution that was assumed to remain at 0.5 M NaOH. The rate of H₂ generation for this solution over short time frames (up to 30 minutes) at room temperature (20 to 23 °C) was found to be 0.04 ml/cm²/min and the rate remained fairly constant for the 30 minute duration of the experiment [2].

Corrosion control and suppression of H₂ generation

Although there are several methods developed to protect Al metal corrosion such as Cr and surfactant coating, lanthanide salts are considered as environmentally friendly corrosion inhibitors of aluminum alloys and stainless steel [6-8]. The inhibitor behavior of CeCl₃ has been studied for AA 5083 alloy (Mn(0.7%), Mg(4.4%), Cr(0.15%)) in aerated NaCl solutions [6]. A process of local corrosion prevails in the area immediately surrounding the intermetallic compound of the aluminum-magnesium alloy. The lanthanide salts are cathodic with respect to the metallic matrix and they act as sites for the reaction (reduction) of O₂. Since the predominant cathodic reaction, where oxygen is reduced (or H₂ generated), is the rate controlling stage of the process of corrosion, it is advisable to use a cathodic inhibitor for corrosion protection. The positive effect of cerium has been attributed to inhibition of cathodic reactions. The corrosion of AA 5083 was inhibited by the precipitation of cerium compounds on the Al-(Mn,Fe,Cr) intermetallic surface that acts as permanent cathode [6]. A high concentration of OH⁻ ions was generated on these intermetallic compounds in the first stage of the corrosion process. These hydroxyl ions reacted with the Ce³⁺ cations giving rise to an insoluble oxide/hydroxide that precipitates on the intermetallic compounds, inhibiting the cathodic reaction by blocking the cathodic areas where H₂ generation occurred.

This is the same mechanism as we found in our lab experiments (reduced H₂ generation due to the hydrocalumite and tricalcium aluminum hydroxide precipitates covering the Al coupon surface see Attachment 3). Essentially the Ca ions in the saturated lime solution are forming insoluble Ca and Al oxyhydroxide coatings within a few hours of testing. Since Ce is found to impede corrosion of Al alloy and because of the high pH condition in grout solution, the addition of Ce(NO₃)₃ before grouting or during grouting will lead to Ce(OH)₃ precipitates that enhance the suppression of H₂ generation. Because the presence of NO₃⁻ can also suppress hydrogen gas generation [9], it is recommended that Ce(NO₃)₃ rather than CeCl₃ be used in controlling the corrosion rate. If used directly as an additive to grout, the cerium may precipitate as the hydroxide to such low levels that there would be very little in solution to react at the aluminum surface. This could result in having very little beneficial effect when added directly to a grout mixture. However, the use of Ce(NO₃)₃ in a grout mixture or use separately under neutral pH conditions could be investigated as an alternate method of forming a protective layer on the aluminum prior to grouting.

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Attachment 3:

Experimental Measurement of Hydrogen Generation From Corroding Aluminum Alloy 5086 Coupons in Ca(OH)₂ Solution and Portland Cement Paste

Christopher M. Fischer
Greg A. Whyatt
Wooyong Um

Introduction

This evaluation was performed to assess the potential impact of imbedding equipment and debris within a layer of grout in K-basins during D&D activities in order to provide shielding and to fix contamination. The presence of aluminum in the form of empty canisters, identification tags or other hardware will lead to the generation of hydrogen as high pH grout contacts and reacts with the aluminum metals. The hydrogen will bubble up through the basin water and be released into the space between the basin water surface and the grating. If the rate of hydrogen dissipation from this region is insufficient, flammable mixtures of hydrogen could collect and create a hazard.

While the grout formulation is not yet specified, it is assumed to be a cementitious grout containing some quantity of Portland cement. The pore water of the grout is therefore expected to exhibit a pH of ~12.4 at ambient temperatures due to the pore water being in equilibrium with solid calcium hydroxide. Under high pH conditions the protective oxide layer on the aluminum will thin due to dissolution allowing the aluminum to corrode and generate hydrogen. There is concern that if the rate of hydrogen gas generation is too high, flammable mixtures of hydrogen gas could create a hazard above the surface of the water in the basins during grouting. The testing described here is intended as a scoping study of magnitude and duration of this hydrogen generation. As described in Attachment 2, only one article was found that measured H₂ from one Al metal in contact with caustic solution, 0.5 M NaOH. The measured hydrogen gas generation rate was 0.04 ml H₂/cm² of Al surface area/min. At 1 atm pressure and 25°C this is equivalent to 1.63 x 10⁻⁶ mol H₂/cm²/min, a rate that would lead to a flammable air space above the basin water surface if diffusion is the only process dispersing the gas mixture. Testing is performed with Ca(OH)₂ rather than NaOH because Ca(OH)₂ is more representative of the grout pore water environment. The corrosion tests were performed as follows.

Equipment/Procedures

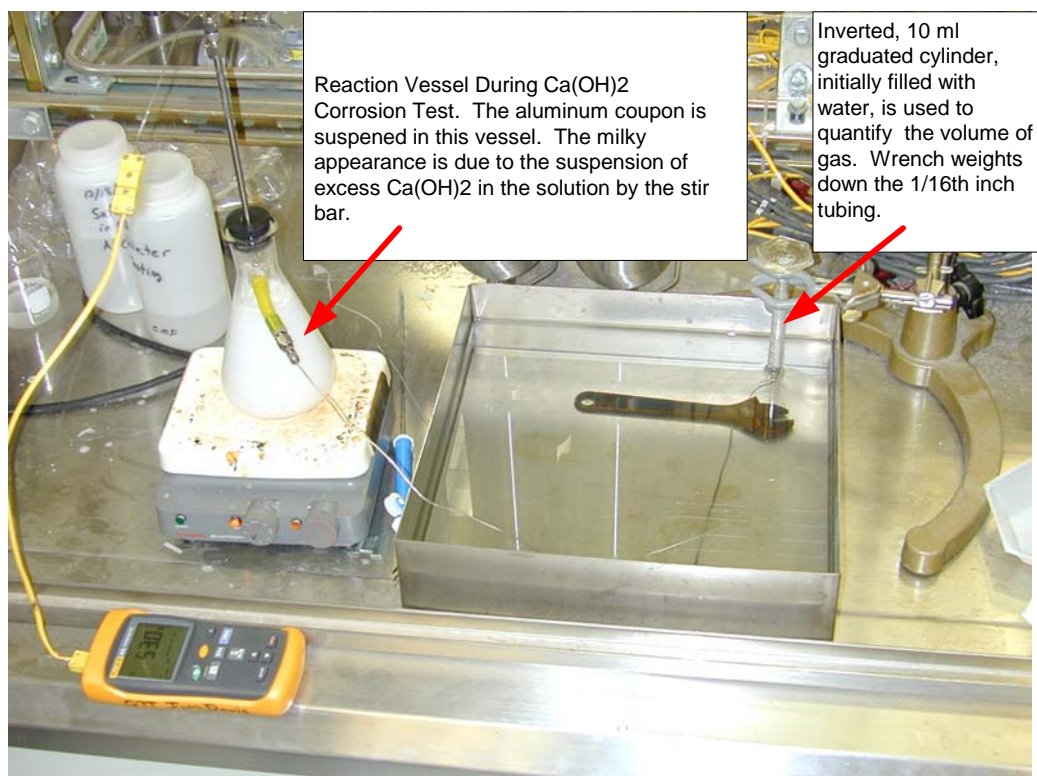
Figure 3-1 below shows the test stand used to conduct the aluminum coupon corrosion study.

A 500 mL vacuum flask sealed with a rubber stopper was used as the reaction vessel. Temperatures were monitored by inserting a length of 1/4" stainless tubing through the rubber stopper to serve as a port. A type-K thermocouple was then inserted into the tubing and secured with a Swagelok nut and Altech graphite ferrule. The test coupons were suspended from a hook imbedded in the underside of the rubber stopper using a plastic tie. A 1/16" stainless steel line plumbed from the vacuum port to an inverted 10 cm³ graduated cylinder was used to collect the hydrogen generated. A hotplate equipped with a magnetic stirrer was used to mix and heat the solutions.

Aluminum Coupon Preparation

The aluminum alloy chosen for the test matches that used to construct the aluminum canisters in the K-Basin. A sample of the aluminum was provided to PNNL and identified as alloy 5086. The composition of alloy 5086 is provided in Table 3-1.

The aluminum sample received was sheared into coupons measuring 3" x 1" x 0.185". A hole was placed at one end of each coupon to allow it to be suspended in the solution and each sample was stamped with an identification number. Each coupon was cleaned with methanol before recording initial weights. After completing a test, each coupon was rinsed with DI water and patted dry with a towel.



Reaction Vessel During Ca(OH)₂ Corrosion Test. The aluminum coupon is suspended in this vessel. The milky appearance is due to the suspension of excess Ca(OH)₂ in the solution by the stir bar.

Inverted, 10 ml graduated cylinder, initially filled with water, is used to quantify the volume of gas. Wrench weights down the 1/16th inch tubing.

Figure 3-1: Test setup for measuring hydrogen generation. Generated gas passes through the 1/16th inch tube and is collected in the 10 ml graduated cylinder. Gas displaces water in the inverted graduated cylinder.

Table 3-1: Composition of aluminum alloy 5086.

Component	wt%
Aluminum	Balance
Chromium	0.05 - 0.25
Copper	0.1 max
Iron	0.5 max
Magnesium	3.5 - 4.5
Manganese	0.2 - 0.7
Silicon	0.4 max
Titanium	0.15 max
Zinc	0.25 max

Calcium Hydroxide Solutions

The solutions were prepared by adding either 2.5 or 5.0 g of Ca(OH)₂ to 500 mL of DI water in the vacuum flask and mixing with a magnetic stirrer. The flask was sealed with the rubber stopper to prevent reactions with CO₂ in the air. Before inserting the coupon, the solution was either allowed to cool to room temperature or heated to ~50°C depending on test condition. Hydrogen was bubbled into the flask for ~10 minutes to saturate the calcium hydroxide solution with hydrogen gas and the pH was measured prior to inserting the aluminum coupon.

Portland Cement Mixtures

Portland cement (Quickrete Brand, without aggregate) was measured into a 500 mL beaker and mixed with DI water for a water/cement ratio of 0.534 g-water/g-cement. The water was slowly added to the cement and stirred with a metal rod for ~20 minutes. The mixture was poured into the vacuum flask (wrapped with Kaowool) and the aluminum coupon was immediately inserted. The grout-Al coupon mixture was not stirred during hydrogen gas generation testing.

Results/Discussion

Table 3-2 and Figures 3-2 and 3-3 below summarize the tests conducted for the corrosion study.

Table 3-2: Summary of corrosion testing with AA 5086 alloy coupons

Test#	Solution	pH ⁽¹⁾		Avg temp (°C)	Total Time ⁽²⁾ (min)	Total H ₂ collected ⁽³⁾ (cm ³)	Initial H ₂ Rate (cm ³ /min)	AA 5086 Coupon Weights ⁽⁴⁾			
		Initial	Final					Initial wt (g)	Final wt (g)	Meas. Δ (g)	Calc Δ ⁽⁸⁾ (g)
1	5 g/l Ca(OH) ₂	-	12.78	22.8	211	98.8	1.1	24.0050	23.8943	0.1107	0.0736
2	5 g/l Ca(OH) ₂	-	12.81	51.9	130	132.2	5.45	24.0556	24.0426	0.0130	0.0985
3	10 g/l Ca(OH) ₂	12.80	12.81	51.9	151	216.7	5.02	24.0330	23.9013	0.1317	0.1615
4	10 g/l Ca(OH) ₂ ⁽⁵⁾	12.81	12.80	51.9	59	89.7	5.42	-	-	-	0.0669
5	0.547 g H ₂ O/g cement	-	-	27.1	155	30.9	0.30	24.1306	-	-	0.0230
6	0.533 g H ₂ O/g cement	-	-	25.9-51.8 ⁽⁶⁾	205	4.6	0	24.2140 ⁽⁷⁾	-	-	0.0034

- (1) All pH measurements at room temperature. Only had pH 7 and 10 buffers available for calibration (may explain pH reading greater than 12.4 to 12.6 reported in literature as the equilibrium pH for saturated lime solutions).
- (2) total time aluminum coupon was in the hydroxide solution/cement mixture (min).
- (3) Total volume of hydrogen gas collected during each test (cm³).
- (4) Coupons were cleaned with methanol before testing. An initial weight was not taken for test #4. Coupons 1 and 2 had all traces of white material removed through rinsing and brushing before taking the final weight.
- (5) Used solution from test #3.
- (6) Water bath used to heat flask (details given in text).
- (7) This used the coupon from test #4. White oxide layer left on coupon.
- (8) Hydrogen volume at 21°C, 1 ATM. Assumed 1 mol Al consumed for each 1.5 mol of H₂ generated.

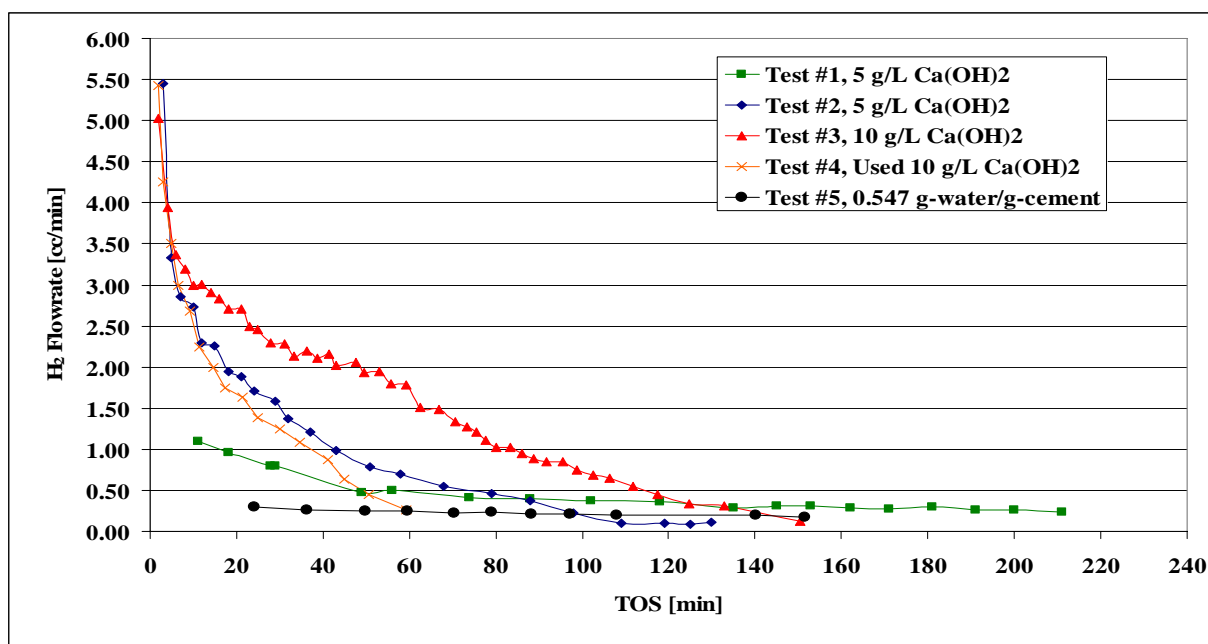


Figure 3-2: Measured hydrogen flowrate versus time for tests 1–5.

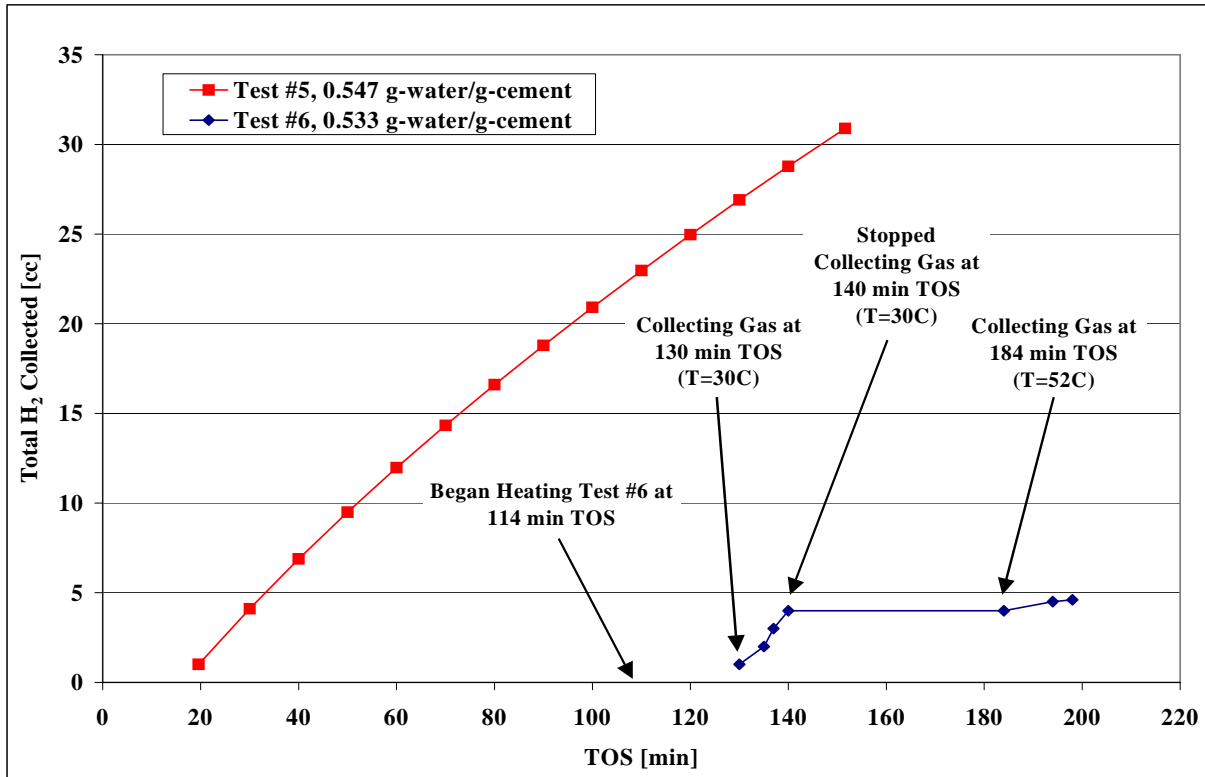


Figure 3-3: Total hydrogen gas collected versus time for tests 5–6. Test 5 provided an initial rate of 0.30 cm³/min which dropped over time to 0.17 cc/min at 152 minutes after which gas generation halted. In test 6 the precipitate coated coupon placed in Portland cement paste did not generate gas until the sample was heated.

The hydrogen flowrate was measured by recording the time required to displace a given volume of water in the graduated cylinder. The first flowrate measured was not included because approximately 1–3 cm³ of air would flow out of the flask when the stopper was initially inserted. Sufficient mixing was achieved by setting the magnetic stirrer to “Slow.” Uniform solution temperature was confirmed by measuring the temperature with a thermocouple in one-inch intervals from the bottom of the flask to the surface of the solution.

The following observations were made from the data in Table 3-2 and Figure 3-2 for tests 1–4:

1. The initial rate of hydrogen production increased by a factor of 5 when increasing the solution temperature from 23°C to 52°C.
2. Changes in the solution affected the extent of corrosion observed but had little effect on the initial corrosion rate observed. A greater excess of Ca(OH)₂ added initially to the solution increased the total hydrogen generated. Test 3, with twice as much Ca(OH)₂ addition as test 2, produced 64% more hydrogen. Reuse of the test 3 solution in test 4 with a fresh coupon produced less hydrogen than either test 2 or 3. However, the initial rates of tests 2, 3 and 4 were all comparable. Possible explanations include consumption of calcium and hydroxide ions due to reaction and possibly the addition of soluble compounds to the solution due to reaction with the aluminum. However, no changes in pH before and after testing could be detected.
3. In all cases, the rate of gas generation decreases to a value below the detection capability of the current experiment within a few hours. This is believed to be the result of formation of a calcium/aluminum oxide or hydroxide precipitate layer on the coupon surface. The precipitate layer covers the coupon and limits the access of hydroxide to the oxide layer of the coupon. Figure 3-4 compares the appearance of a corroded coupon with the white oxide/hydroxide precipitate layer to that of a new coupon.



Figure 3-4: Corroded coupon appearance (left) with white oxide layer compared to new coupon (right).

4. The amount of coupon material lost during the tests is small and difficult to quantify. Aluminum lost to the solution is confounded with precipitate deposited on the sample. While the precipitate could be removed, the use of aggressive cleaning methods was avoided since this could remove more aluminum than was dissolved or reacted during the experiment.

After completing tests 1–4, two additional tests were conducted using a mixture of water and Portland Cement as the corrosion medium. The initial rate of hydrogen generation as well as the total hydrogen generated in these tests was less than observed with the $\text{Ca}(\text{OH})_2$ solutions (i.e. test#1 in $\text{Ca}(\text{OH})_2$ provided $1.1 \text{ cm}^3/\text{min}$ and 98.8 cm^3 total while test #5 yielded $0.30 \text{ cm}^3/\text{min}$ initial and 30.9 cm^3 total). The most probable explanation is the mass transfer resistance associated with the unstirred paste compared to the stirred solution. The rate of hydrogen generation in the Portland cement paste decreased by about a third over 2.5 hours and then dropped off rapidly to a level below detection limits of the apparatus. It is expected that the decrease in gas generation over time is related to the formation of the calcium-aluminum precipitate on the surface of the coupon.

The precipitate-covered corrosion coupon from test 4 was used for the final test to determine the extent to which the precipitate layer formed during exposure to the calcium hydroxide solution might reduce the hydrogen generation during subsequent exposure to Portland cement paste. The results from tests 5 and 6 are compared in Figure 3-3. At room temperature, no hydrogen was collected in the graduated cylinder in test 6. Occasionally, a small bubble could be seen in the water layer above the cement mixture (Figure 3-5). However, the volume was too small to quantify.

In test #6, heat was applied after observing no gas generation for approximately 2 hours. As the mixture reached 30°C , 4.0 cm^3 of gas was collected over 9 minutes. Initially, the flask was heated directly using the hot plate. However, there was a concern over the potential for uneven heating and when the temperature was at $\sim 35^\circ\text{C}$ the flask was placed in a hot water bath as shown in Figure 3-6 to provide uniform heat to all sides of the flask. After the mix reached 52°C , an additional 0.6 cm^3 of gas was collected over a period of 14 minutes. After that, no more gas was collected in the graduated cylinder.



Figure 3-5: Separated Water Layer above the Portland Cement Paste. Some bubbles were observed here in test 6 at near ambient temperature but the quantity was too small to quantify



Figure 3-6: Water bath configuration used to heat vacuum flask filled with Portland Cement mixture.

Characterization of White Corrosion Products

After the aluminum alloy coupon reacted with $\text{Ca}(\text{OH})_2$ solution (Test # 3), the white corrosion product on the aluminum coupon surface was gently removed by scraping/scrubbing with a spatula. The mineralogy of the precipitate was identified by x-ray diffraction (XRD) on a Philips PW3040/00 X'pert MPD system and JADE software for peak matching complex spectra to a combination of known minerals in the database. With knowledge of possible chemical elements, the software can be quite good at delineating what minerals are present in the precipitates. The precipitate was then oven dried for 24 hours, acid digested using 8M nitric acid and then analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES)⁷.

The XRD scan showed that two crystalline compounds were present in the observed pattern (Figure 3-7). Tricalcium aluminum hydroxide ($\text{Ca}_3\text{Al}_2(\text{OH})_{12}$) and hydrocalumite ($\text{Ca}_2\text{Al}(\text{OH})_7 \cdot 2\text{H}_2\text{O}$) were identified as being present. The XRD pattern does not suggest much amorphous material is present. The ICP analysis of the digested precipitate indicates a Ca:Al ratio of 1.5673. Assuming that the two identified phases are the only materials present, the overall Ca:Al ratio can be used to determine the ratio of the two phases present. On a molar basis, it is estimated that the mole fractions in the precipitate layer are:

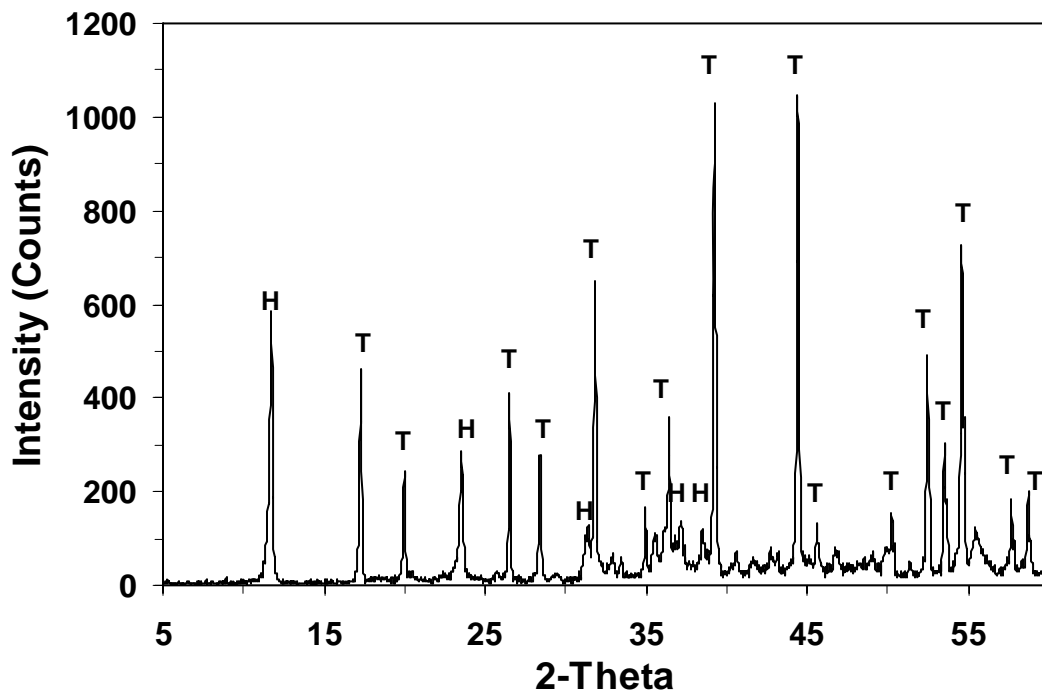
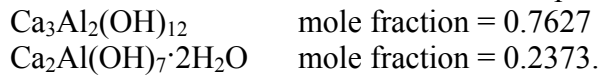


Figure 3-7. XRD pattern for white corrosion products (H: hydrocalumite, T: tricalcium aluminum hydroxide).

⁷ ICP-AES is an alternate acronym for the same technique.

Appendix B

Potential for Flammable Atmosphere Above the K Basin Pool During Grouting



Fauske & Associates, LLC

DATE: September 30, 2004
TO: James P. Slougher, Hanford K Basins Closure Project
FROM: Michael Epstein and Martin Plys
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 H₂ 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 H₂/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 H₂ 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 (H₂) through a heavier miscible fluid medium (air).

Since the rate of generation of H₂ 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 AI area ratio; see Whyatt et al., 2004). The analysis presented here demonstrates that the residual AI area ratios that can be tolerated without creating a flammability hazard above the basin pool are much higher than the AI area ratio based on the actual aluminum inventory in the basin.

3.0 TURBULENT NATURAL CONVECTION DIFFUSION COEFFICIENT

The upward transport of light H₂ 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 H₂/air mixture, because vertical diffusion of the light H₂ 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

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

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 AI 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

$$\ell = \beta H \quad , \quad \beta = 0.164 \quad (2)$$

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:

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

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

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

where

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

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

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

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

$$X_L = 0 \quad \text{at} \quad z = H \quad (7)$$

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

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

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

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

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

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

5.0 PROPOSED ARRHENIUS RATE LAW FOR H₂ GENERATION

Measurements of H₂ 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 H₂ generation was 0.3 cm³ 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 cm². Thus the H₂ volumetric gas generation rate per unit area of Al was

$$\dot{Q}_{H_2}'' = 1.04 \times 10^{-6} \text{ m}^3 \text{ H}_2 \text{ m}^{-2} \text{ s}^{-1} \quad \text{at } T = 27.1^\circ\text{C} \quad (11)$$

The data on H₂ 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

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

where the activation temperature $T_{\text{act}} = 5339\text{K}$. 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 H₂ gas-chemical-generation rate becomes equal to the upward H₂ turbulent diffusion rate through air when the H₂ concentration at the pool surface is equal to its LFL value:

$$\dot{Q}_{H_2}'' A_{\text{Al}} = u_0 A_{\text{floor}} \quad (13)$$

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

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

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 H₂ 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 H₂ 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

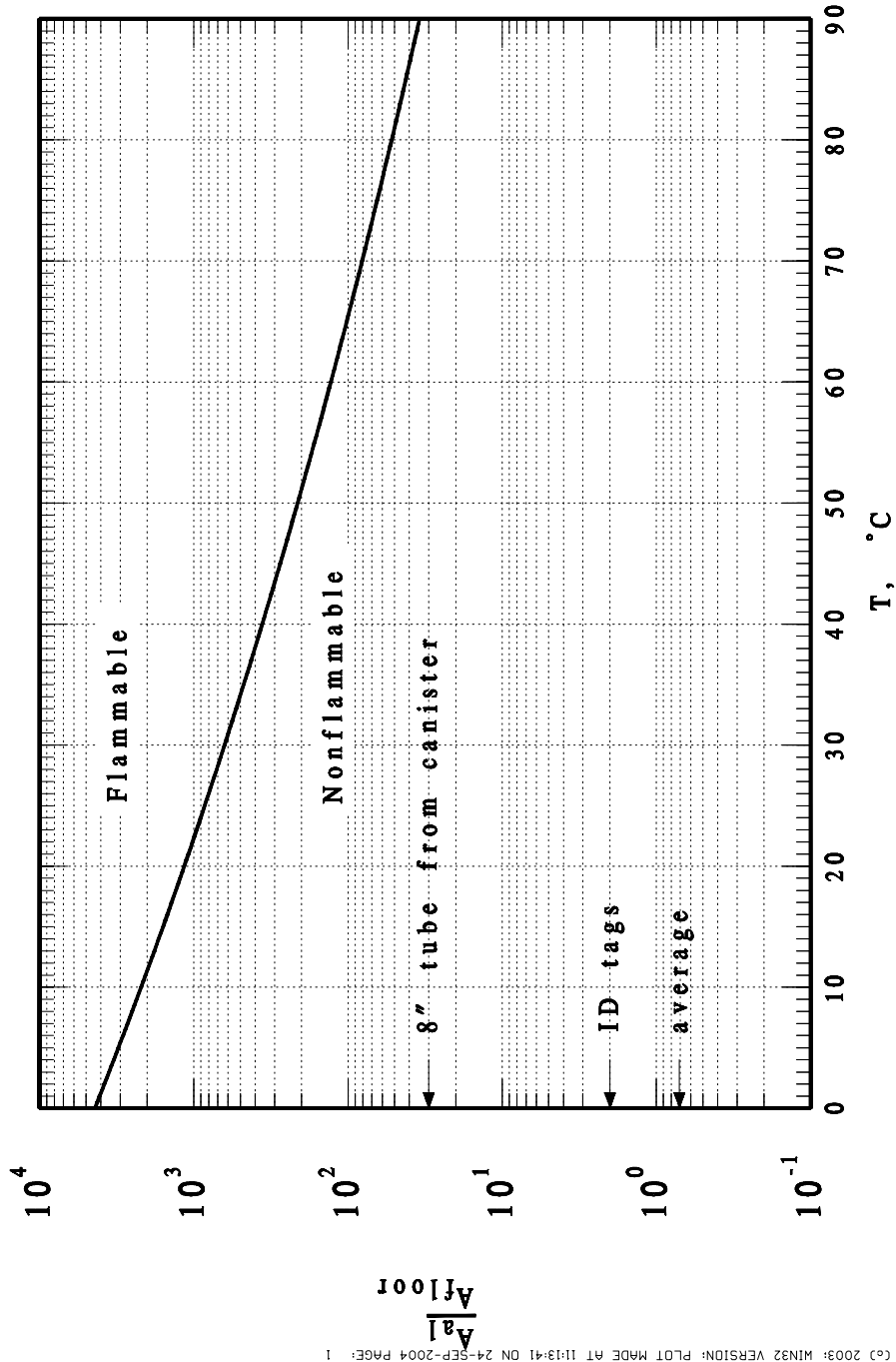
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FAI GRAPHICS, VS.1, (c) 2003: MIN2 VERSION: PLOT MADE AT 11:13:41 ON 24-SEP-2004 PAGE: 1
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Figure 1 Critical aluminum surface area ratio for flammable condition at surface of K Basin pool versus grout temperature.

Appendix C

Thermal Analysis of Basin Water Temperature with the Addition of Grout

Thermal Analysis of Basin Water Temperature with the Addition of Grout

Brian M. Parker

Introduction

During grouting of the KE Basin it is preferable to cover all of the aluminum metal during a single uninterrupted pour of grout to minimize the generation of hydrogen from exposure of the aluminum metal to leached $\text{Ca}(\text{OH})_2$. However, it is possible that this “first” grout pour may be interrupted for operational or other reasons. After interrupt of the grout pour, the temperature of the basin water will rise as a result of heat transfer from the grout to the water. Experimental analyses have shown that the higher the temperature, the faster the corrosion rate of the aluminum metal and, thus, the faster the hydrogen generation rate. The purpose of this appendix is to perform a thermal analysis to determine the potential rise of 105-KE Basin water temperature due to the addition of grout.

Assumptions

This analysis conservatively assumes that the 105-KE Basin is partially filled with grout to a height of 28-in to immobilize equipment and debris (the same height as an upright fuel canister). A total height (grout plus water) of 12-17 feet is maintained as the grout is being added to the basin.

A list of physical and material properties used in the analysis is provided below. Values for the material properties of the grout are dependant on the composition of the grout mixture. For these values, a range of typical values is listed and a conservative value is chosen in the calculations.

Basin Area

The area of the basin is assumed to be $8,375 \text{ ft}^2$ (HNF-SD-WM-SAR-062). The basin walls are assumed to be straight in the vertical direction so that the grout and water volume vary linearly with height.

Mass

The maximum mass of the grout is assumed to be the floor area of the 105-K basin multiplied by it's maximum height (28-in.) multiplied by the density of the concrete. The density of concrete is dependant on the type of concrete used. A typical value of cement mixture density is $80 - 120 \text{ lbm/ft}^3$, to ensure conservatism in the calculation, a density (ρ_g) of 120 lbm/ft^3 is assumed. The density of water (ρ_w) at 50°F is 62.4 lbm/ft^3 . The mass of water is dependant on the total height, of the grout and water (h).

$$\begin{aligned} m_{\text{grout}} &= (8,375 \text{ ft}^2) \cdot (2.33 \text{ ft}) \cdot (120 \text{ lbm/ft}^3) \\ m_{\text{water}} &= (8,375 \text{ ft}^2) \cdot (h - 2.33 \text{ ft}) \cdot (62.4 \text{ lbm/ft}^3) \end{aligned}$$

Specific Heat

The specific heat of concrete is dependant on the type of concrete used. Typical values range from 0.15-0.25 Btu/(lbm·ft). To ensure conservatism, the specific heat of concrete is assumed to be 0.25 Btu/(lbm·ft). The specific heat of water is 1.0 Btu/(lbm·ft).

Temperature

The initial temperature of the as-poured grout is assumed to be 120°F. This temperature is conservative since the grout is expected to be poured at less than 90°F per project specifications (SNF-18734). Results are calculated for initial basin water temperatures of 50°F, 60°F, 70°F, 80°F, and 90°F.

Analysis Methodology

The basin contents, including grout and water, are represented as a closed system. No heat loss is assumed through the basin walls or to the air at the basin surface. The 1st law of thermodynamics, the conservation of energy, is applied:

$$Q - W = \Delta U + \Delta KE + \Delta PE$$

Q = net energy transfer to the system as heat

W = net energy transfer to the system as work

ΔU = net increase (or decrease) in the internal energy of the system

ΔKE = net change in kinetic energy

ΔPE = net change in potential energy

Heat Transfer

Heat is added to the system during the curing process of the concrete through the heat of hydration. The heat of hydration of cement is the heat evolved by chemical reactions with water and is dependant on the constituents present in the cement mix. Normally, the greatest rate of heat liberation is within the first 24 hours. Because the rate of heat of hydration is highly dependant on the type of cement and the mix, a total heat of hydration over a seven day period is conservatively used (the rise in water temperature during the first three hours after interrupt of the grout pour is the period of concern for hydrogen generation).

Heats of hydration for various mixes of types and samples of cement are presented in tabular form in "Portland Cement, Concrete, and Heat of Hydration", *Concrete Technology Today*, Volume 18, Number 2, July 1997. The heat of hydration rates were calculated using ASTM C 186, *Standard Test Method for Heat of Hydration of Hydraulic Cement*. The grout added to the basin is assumed to be similar to a type of portland cement. The highest value for heat release due to hydration for any type of cement over a seven day period is used for this calculation, and is as follows:

$$\bar{Q} = 89.0 \text{ cal} / \text{g} \quad (160.1 \text{ Btu/lbm})$$

The total heat of hydration during the initial seven days is dependant on the heat of hydration per unit mass, the density, and volume.

$$Q = \bar{Q} \cdot \rho_g \cdot V_{\max,gr} = (160.1 \text{ Btu/lbm}) \cdot (120 \text{ lbm/ft}^3) \cdot (8375 \text{ ft}^2) \cdot (2.33 \text{ ft})$$

Q = heat of hydration

ρ_g = density of grout

$V_{\max,gr}$ = volume of grout at height of 28-in.

There are assumed to be no other sources of heat generation to the system that would be of significant value.

Internal Energy

Both the water and grout can be approximated as incompressible substances. The change in internal energy can then be calculated from the equation below.

$$\Delta U = m \cdot C \cdot (T_f - T_i)$$

m = mass

C = specific heat

T_f = final temperature

T_i = initial temperature

Work, Potential Energy, and Kinetic Energy

The change in potential energy is assumed to be negligible and there are assumed to be no sources of work or kinetic energy added to the system.

Final Solution

The final equilibrium temperature of the closed system can be determined by the energy conservation equation.

$$Q = \Delta U(\text{grout}) + \Delta U(\text{water})$$

$$Q \cdot m_{\text{grout}} = [m \cdot C \cdot (T_f - T_i)]_{\text{grout}} + [m \cdot C \cdot (T_f - T_i)]_{\text{water}}$$

or

$$T_f = [Q + (m \cdot C \cdot T_i)_{\text{grout}} + (m \cdot C \cdot T_i)_{\text{water}}] / [(m \cdot C)_{\text{grout}} + (m \cdot C)_{\text{water}}]$$

Results

Final basin temperatures were calculated for a range of total heights (grout plus water) as well as for a range of initial basin water temperatures. All other properties were assumed to remain constant. An example calculation is shown below with the initial conditions of a total height of 12 feet and initial basin water temperature of 50°F.

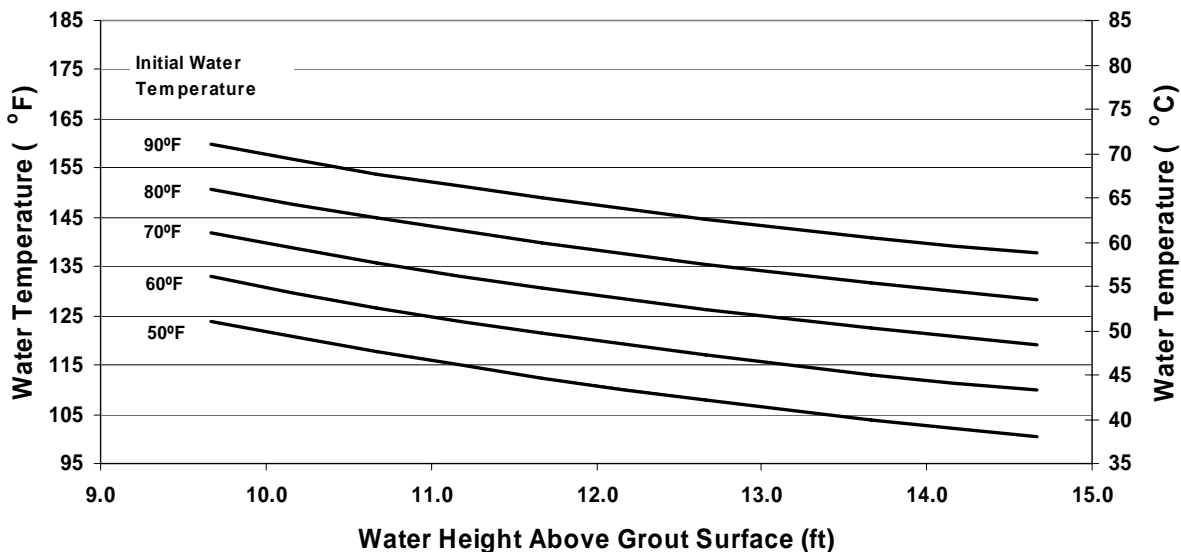
$$T_f = [3.749 \times 10^8 \text{ Btu} + (2.342 \times 10^6 \text{ lbm}) \cdot (0.25 \text{ Btu/lbm} \cdot \text{F}) \cdot (120 \text{ F}) + (5.052 \times 10^6 \text{ lbm}) \cdot (1 \text{ Btu/lbm} \cdot \text{F}) \cdot (50 \text{ F})] / [(2.342 \times 10^6 \text{ lbm}) \cdot (0.25 \text{ Btu/lbm} \cdot \text{F}) + (5.052 \times 10^6 \text{ lbm}) \cdot (1 \text{ Btu/lbm} \cdot \text{F})]$$

$$T_f = 123.8^\circ\text{F}$$

The table below summarizes the analysis results for the different total heights and initial basin water temperatures calculated via this same methodology.

$T_{i(\text{water})}$ (°F)	50	60	70	80	90
$T_{i(\text{grout})}$ (°F)	120	120	120	120	120
Total Height (ft)	$T_{f(\text{basin})}$ (°F)	$T_{f(\text{basin})}$ (°F)	$T_{f(\text{basin})}$ (°F)	$T_{f(\text{basin})}$ (°F)	$T_{f(\text{basin})}$ (°F)
12	123.9	132.9	141.8	150.8	159.8
13	117.6	126.7	135.7	144.8	153.8
14	112.4	121.5	130.6	139.7	148.8
15	107.8	117.0	126.2	135.4	144.6
16	103.9	113.2	122.4	131.6	140.9
17	100.5	109.8	119.1	128.4	137.7

The graph below shows the final basin water temperature as a function of initial temperature and water height above the grout surface.



CHECKLIST FOR TECHNICAL PEER REVIEW

Document Reviewed -

Title: Thermal Analysis of Basin Water Temperature After Grouting Operation

Author: Brian M. Parker

Date: 04/11/05 Scope of Review: Review calculation of estimated heat load/heat up of KE basin due to heat of hydration from grouting the basin floor.

<u>Yes</u>	<u>No*</u>	<u>NA</u>	
[X]	[]	[]	Referenced analyses appropriate.
[X]	[]	[]	Problem completely defined and all potential configurations considered.
[X]	[]	[]	Accident scenarios developed in a clear and logical manner.
[X]	[]	[]	Necessary assumptions explicitly stated and supported.
[]	[]	[X]	Computer codes and data files documented.
[X]	[]	[]	Data used in calculations explicitly stated in document.
[X]	[]	[]	Data checked for consistency with original source information as applicable.
[X]	[]	[]	Mathematical derivations checked including dimensional consistency of results
[X]	[]	[]	Models appropriate and used within range of validity, or use outside range of established validity justified.
[X]	[]	[]	Hand calculations checked for errors. Spreadsheet results should be treated exactly the same as hand calculations.
[]	[]	[X]	Software input correct and consistent with document reviewed.
[]	[]	[X]	Software output consistent with input and with results reported in document reviewed.
[X]	[]	[]	Limits/criteria/guidelines applied to analysis results are appropriate and referenced. Limits/criteria/guidelines checked against references.
[X]	[]	[]	Safety margins consistent with good engineering practices.
[X]	[]	[]	Conclusions consistent with analytical results and applicable limits.
[X]	[]	[]	Results and conclusions address all points required in the problem statement.
[]	[]	[X]	Format consistent with applicable guides or other standards.
[X]	[]	[]	** Review calculations, comments, and/or notes are attached.
[X]	[]	[]	Document approved (for example, the reviewer affirms the technical accuracy of the document).

Brian M. Parker
 Technical Peer Reviewer (printed name and signature)

4-11-05
 Date

* All "no" responses must be explained below or on an additional sheet.

** Any calculations, comments, or notes generated as part of this review should be signed, dated and attached to this checklist. The material should be labeled and recorded in such a manner as to be understandable to a technically qualified third party.

Independent check of calculation for basin water heatup due to grout hydration. The primary assumptions are:

- 1) The grout is assumed to be Type III cement. Type III cement typically has the highest hydration heat release.
- 2) The grout is assumed to be 2/3 cement, 1/3 water mix (by mass). This minimizes the effective Cp and maximizes the initial cement temperature (and basin heatup)
- 3) The hydration heat is averaged over a 7 day period. This is assumed to be released in an adiabatic mode in the pool with no heat losses to the environment.
- 4) The initial 'dry' grout temperature is assumed to be 120 F, and the water 80 F. The initial mix temperature is then ~92 F, bounded by using 100F.

$$Cp_{\text{water}} := 1 \cdot \frac{\text{BTU}}{\text{lb} \cdot \text{R}} \quad \text{Basin Level} := \begin{bmatrix} 12 \\ 13 \\ 14 \\ 15 \\ 16 \\ 17 \end{bmatrix} \cdot \text{ft} \quad \text{Area} := 8375 \cdot \text{ft}^2$$

$$\rho_{\text{water}} := 1 \cdot \frac{\text{gm}}{\text{cm}^3}$$

Assumed cement properties

$$Cp_{\text{cement}} := 0.92 \cdot \frac{\text{J}}{\text{gm} \cdot \text{K}} \quad \text{depth} := 28 \cdot \text{in}$$

$$Cp_{\text{cement}} = 0.22 \cdot \frac{\text{BTU}}{\text{lb} \cdot \text{R}} \quad \rho_{\text{cement}} := 150.0 \cdot \frac{\text{lb}}{\text{ft}^3}$$

$$dH := 89 \cdot \frac{\text{cal}}{\text{gm}} \quad \rho_{\text{cement}} = 2.403 \cdot \frac{\text{gm}}{\text{cm}^3}$$

$$n := \frac{2}{3} \quad i := 0..5$$

$$Cp_{\text{mix}} := \frac{Cp_{\text{cement}} \cdot n \cdot \text{kg} + Cp_{\text{water}} \cdot (1 - n) \cdot \text{kg}}{1 \cdot \text{kg}} \quad Cp_{\text{mix}} = 2.009 \cdot \frac{\text{J}}{\text{K} \cdot \text{gm}}$$

$$\rho_{\text{mix}} := n \cdot \rho_{\text{cement}} + (1 - n) \cdot \rho_{\text{water}} \quad \rho_{\text{mix}} = 1.935 \cdot \frac{\text{gm}}{\text{cm}^3}$$

$$dH_{\text{available}} := \text{Area} \cdot (\text{Basin Level} - \text{depth}) \cdot \rho_{\text{water}} \cdot Cp_{\text{water}} + \text{Area} \cdot \text{depth} \cdot \rho_{\text{mix}} \cdot Cp_{\text{mix}}$$

$$dH_{\text{available}} = \begin{bmatrix} 2.806 \cdot 10^9 \\ 3.043 \cdot 10^9 \\ 3.281 \cdot 10^9 \\ 3.518 \cdot 10^9 \\ 3.755 \cdot 10^9 \\ 3.992 \cdot 10^9 \end{bmatrix} \frac{\text{cal}}{\text{K}} \quad \frac{dH \cdot (\text{Area} \cdot \text{depth} \cdot \rho_{\text{mix}})}{dH_{\text{available}}} = \begin{bmatrix} 33.961 \\ 31.315 \\ 29.051 \\ 27.093 \\ 25.381 \\ 23.874 \end{bmatrix} \text{K}$$

Estimate the cement initial temperature

$$\frac{120 \cdot R \cdot C_p_{\text{cement}} \cdot n \cdot \text{kg} + 80 \cdot R \cdot C_p_{\text{water}} \cdot (1 - n) \cdot \text{kg}}{C_p_{\text{cement}} \cdot n \cdot \text{kg} + C_p_{\text{water}} \cdot (1 - n) \cdot \text{kg}} = 92.212 \cdot R \quad \text{Use 100 F as bounding}$$

Calculate the maximum allowable initial basin temperature versus basin water level that precludes reaching 140 F for 7 days.

$$T_{\text{basin}} := 100 \cdot R \quad \text{Level} := 17 \cdot \text{ft} \quad T_{\text{cement}} := 100 \cdot R \quad T_{\text{Max}} := 140 \cdot R$$

Given

$$T_{\text{Max}} = \frac{T_{\text{cement}} \cdot \text{Area} \cdot \text{depth} \cdot \rho_{\text{mix}} \cdot C_p_{\text{mix}} + T_{\text{basin}} \cdot \text{Area} \cdot (\text{Level} - \text{depth}) \cdot \rho_{\text{water}} \cdot C_p_{\text{water}} + dH \cdot (\text{Area} \cdot \text{depth} \cdot \rho_{\text{mix}})}{\text{Area} \cdot \text{depth} \cdot \rho_{\text{mix}} \cdot C_p_{\text{mix}} + \text{Area} \cdot (\text{Level} - \text{depth}) \cdot \rho_{\text{water}} \cdot C_p_{\text{water}}}$$

$$\text{Sol}(\text{Level}) := \text{Find}(T_{\text{basin}})$$

$$T_{\text{basin}_i} := \text{Sol}(\text{Basin Level}_i)$$

Maximum allowable initial basin water temperature versus water level above the grout

$$T_{\text{basin}} = \begin{bmatrix} 74.134 \\ 80.309 \\ 85.425 \\ 89.734 \\ 93.412 \\ 96.588 \end{bmatrix} \cdot R \quad \text{Basin Level} - \text{depth} = \begin{bmatrix} 9.667 \\ 10.667 \\ 11.667 \\ 12.667 \\ 13.667 \\ 14.667 \end{bmatrix} \cdot \text{ft}$$