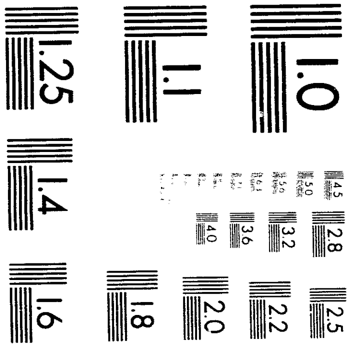
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WSRC-RP-93-688

LATE WASH/NITRIC ACID FLOWSHEET HYDROGEN GENERATION BASES FOR SIMULATION OF A DEFLAGRATION/DETONATION IN THE DWPF CPC (U)

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LATE WASH/NITRIC ACID FLOWSHEET HYDROGEN GENERATION BASES FOR SIMULATION OF A DEFLAGRATION/DETONATION IN THE DWPF CPC (U)

SUMMARY

Hydrogen generation data obtained from IDMS runs PX4 and PX5 will be used to determine a bases for a deflagration/detonation simulation in the DWPF CPC. This simulation is necessary due to the new chemistry associated with the Late Wash/Nitric Acid flowsheet and process modifications associated with the presence of H_2 in the offgas. The simulation will be performed by Professor Van Brunt from the University of South Carolina. The scenario which leads up to the deflagration/detonation simulation will be chosen such that the following conditions apply.

The SRAT is filled to its maximum operating level with 9,600 gal of sludge, which corresponds to the minimum vapor space above the sludge. The SRAT is at the boiling point, producing H_2 at a very low rate (about 10 % of the peak) and 15 scfm of air inleakage is entering the SRAT. Then, the H_2 generation rate will be allowed to increase exponentially (catalyst activation) until it reaches the peak H_2 generation rate of the IDMS run, after which the H_2 generation rate will be allowed to decay exponentially (catalyst deactivation) until the total amount of H_2 produced is between 85 and 100 % of that produced during the IDMS run.

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INTRODUCTION

The Late Wash/Nitric Acid (LW/NA) flowsheet changed not only the amount of H_2 being generated in the DWPF CPC but also the peak H_2 generation level and induction period compared to the HAN/Formic Acid (FA) flowsheet.[1,2] In all of the bench and IDMS demonstrations of the LW/NA flowsheet the total amount of H_2 produced and the peak H_2 generation rate were less and the induction period was greater when compared to comparable HAN/FA flowsheet runs.[2,3] Nevertheless, the possibility of a deflagration/detonation occurring in the PVV of the DWPF CPC still exists as a result of process modifications.

The modifications planned for the PVV of the DWPF CPC are the result of the H_2 design basis for radioactive operations. This design basis requires that a significant amount of purge air be supplied to the CPC vessels in order to control the H_2 concentration by fuel dilution.[1] This purge air, in turn, resulted in an increase in the piping size (from 3 to 6 in diameter) throughout the PVV in order to minimize the pressure drop in the lines. This piping size change coupled with the changes in the flowsheet warranted revisiting the deflagration/detonation issue in the PVV of the DWPF CPC.[4]

The objective of this report is to generate the bases for a simulation of a deflagration/detonation in the DWPF CPC. The simulation will be performed by Professor Van Brunt from the University of South Carolina. LW/NA flowsheet data from the IDMS facility are presented here for this purpose. IDMS run PX5 represents extremely conservative conditions as this run considered all the possible credible deviations from nominal operating conditions that could increase the H_2 generation rate. IDMS run PX4, on the other hand, represents a run that was operated at conditions much closer to the nominal operating conditions, but slightly less H_2 was generated compared to what may be expected under truly nominal conditions.

BASES FOR DEFLAGRATION/DETONATION SIMULATION

For both the HAN/FA and LW/NA flowsheets, the generation of H_2 in the SRAT follows a consistent trend of catalyst activation followed by catalyst deactivation. The catalyst has been observed to activate in a somewhat exponential fashion, where the H_2 generation rate continuously increases and reaches a peak. Then, catalyst deactivation occurs and the H_2 generation rate begins to decrease according to a first order or exponential relationship in time. Based on this experimental evidence, for the LW/NA flowsheet, the scenario which leads up to the deflagration/detonation simulation will be chosen such that the following conditions apply.

The SRAT is filled to its maximum operating level with 9,600 gal of sludge, which corresponds to the minimum vapor space above the sludge. The SRAT is at the boiling point, producing H_2 at a very low rate (about 10 % of the peak) and 15 scfm of air inleakage is entering the SRAT. Then, the H_2 generation rate will be allowed to increase exponentially (catalyst activation) until it reaches the peak H_2 generation rate of the

IDMS run, after which the H_2 generation rate will be allowed to decay exponentially (catalyst deactivation) until the total amount of H_2 produced is between 85 and 100 % of that produced during the IDMS run.

The data for the H_2 generation rate exponentially increasing, peaking and undergoing a first order decay were obtained from two IDMS demonstrations of the LW/NA flowsheet. As mentioned previously, IDMS PX5 represents a very conservative upper limit on the generation of H_2 from the LW/NA flowsheet, whereas IDMS PX4 represents a nominal situation. The main differences between these two runs were operational differences that affected the H_2 generation rate.[1]

IDMS PX4 was operated at nearly nominal operating conditions except for the way in which the addition/concentration of the PHA was carried out. The batchwise addition/concentration procedure coupled with the low boil-up rate more than likely resulted in a lower peak H_2 generation rate compared to that which would have resulted if truly nominal operating conditions were employed. PX5, on the other hand, was operated in such a way as to account for all of the known credible deviations from the nominal operating conditions that could increase the H_2 generation rate. This included an over-batching of the PHA added by 30 %, using a continuous PHA addition/concentration procedure and using a 72 % higher than normal boil-up rate. For these reasons, a truly nominal peak H_2 generation rate along with the corresponding induction period should lie somewhere between that observed from these two IDMS runs.

RESULTS AND DISCUSSION

The data presented graphically below are given in terms of the IDMS scale, only. This includes the exponential functions displayed in each of the figures. To convert the IDMS H_2 generation rate data to the DWPF scale, the following scaling factor must be used: H_2 (lb/hr DWPF) = 7.4 * H_2 (lb/hr IDMS). This scaling factor was based on 6,000 gal of sludge in the DWPF SRAT compared to 1,100 gal in the IDMS SRAT, and a factor to scale the wt % solids to that expected as an upper limit at DWPF (i.e., from about 14 to 19 wt % solids).

The H_2 generation rate and temperature profiles obtained during PHA addition/concentration of IDMS PX5 are shown in Figure 1. Note that the elapsed time corresponds to the start of nitric acid addition. This graph shows that the peak H_2 generation rate occurred at about 45 hr and was 0.088 lb/hr (IDMS scale). Just before that time the H_2 generation rate was increasing in a somewhat exponential fashion (Box A). Just after that time and a brief process interruption (indicated by the decrease in temperature and sharp drop in the H_2 generation rate), the characteristic first order decay of the H_2 generation rate was exhibited (Box B). The data sets in Boxes A and B were fitted to exponential functions-one function to correlate the increasing H_2 generation rate and the other function to correlate the decreasing H_2 generation rate. The results are shown in Figures 2 and 3, respectively.

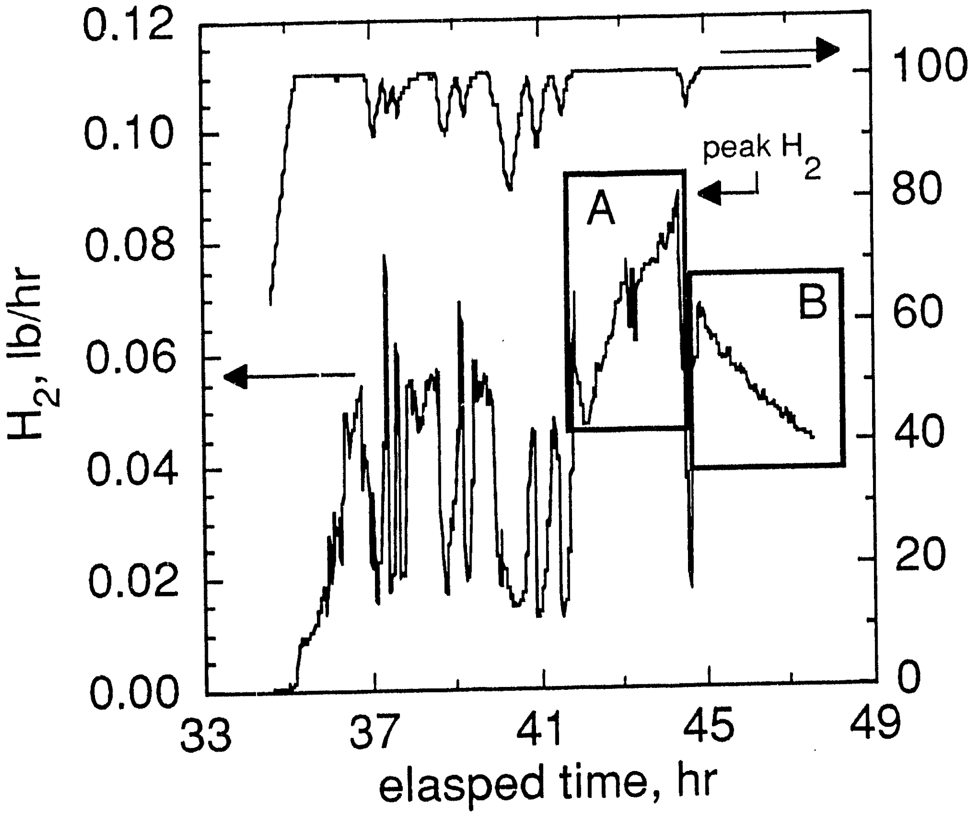

Figure 1. IDMS PX5: hydrogen generation rate and SRAT temperature. Box A corresponds to data shown in Figure 2 and Box B corresponds to data shown in Figure 3.

Figure 2 displays a representative sampling of the data from Box A in Figure 1. These data were fitted to an exponential function which resulted in a first order time constant of $3.77\text{x}10^{-3}$ min^{-1}. This function should be used until the H_2 generation rate peaks at $8.83\text{x}10^{-2}$ lb/hr (see Figure 1). In order to start the simulation, the H_2 generation rate at t=0 must be selected. It is suggested that the H_2 generation rate at t=0 correspond to about 10 % of the observed peak H_2 generation rate.

Figure 3 displays a representative sampling of the data from Box B in Figure 1. These data were fitted to an exponential function which resulted in a first order time constant of $-2.45\text{x}10^{-3}$ min^{-1}. With the aforementioned assumption that a first order decay of the H_2 generation rate always occurs after the H_2 generation rate peaks, this time constant and the peak H_2 generation rate ($8.83\text{x}10^{-2}$ lb/hr, see Figure 1) were combined to obtain the exponential function indicated and plotted as the heavy solid line in Figure 3.

The exponential functions shown in Figures 2 and 3 represent the increase, peak and decrease in the H_2 generation rate for the extreme case in the simulation of a deflagration/detonation in the PVV of the DWPF CPC. For this case, the total production of H_2 integrated over the entire SRAT cycle was 7.4 lb (DWPF scale) and the peak H_2 generation rate was 0.64 lb/hr (DWPF scale). The nearly nominal case corresponds to the data from PX4, where 5.2 lb of H_2 (DWPF scale) were produced during the entire cycle and the peak was only 0.2 lb/hr (DWPF scale). This data is shown in Figure 4.

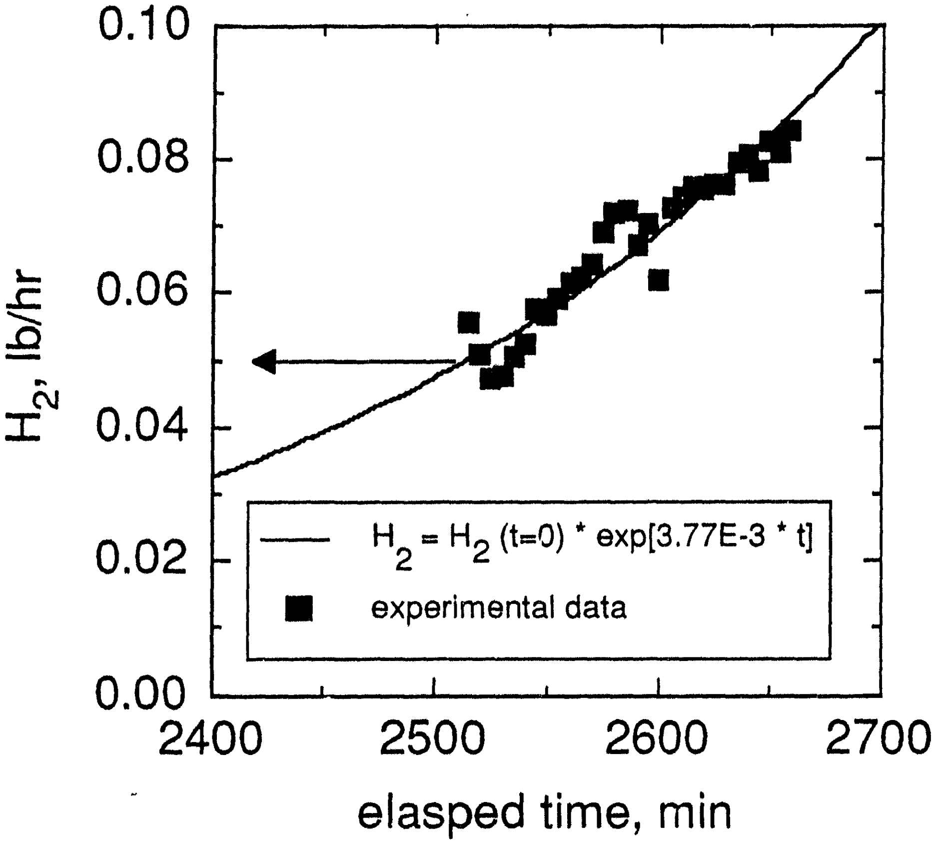

Figure 2. IDMS PX5: increase in the hydrogen generation rate at boiling conditions just before peak occurred (data correspond to Box A in Figure 1). For an assummed t=0, the preexponential coefficient of the function for the hydrogen generation rate should be selected from the curve, e.g., the arrow in the figure indicates H_2 (at t=0) = 0.05.

Figure 4 shows the H_2 generation rate and temperature profiles obtained during PHA addition/concentration of IDMS PX4. Note that the elapsed time corresponds to the start of nitric acid addition. This graph shows that the peak H_2 generation rate occurred at about 80 hr compared to 45 hr for PX5. Moreover, the peak H_2 generation rate was much less. The suspected causes of the differences between these two runs were given earlier. As with PX5, the data sets in Boxes A and B were fitted to exponential functions. The results are shown in Figures 5 and 6, respectively.

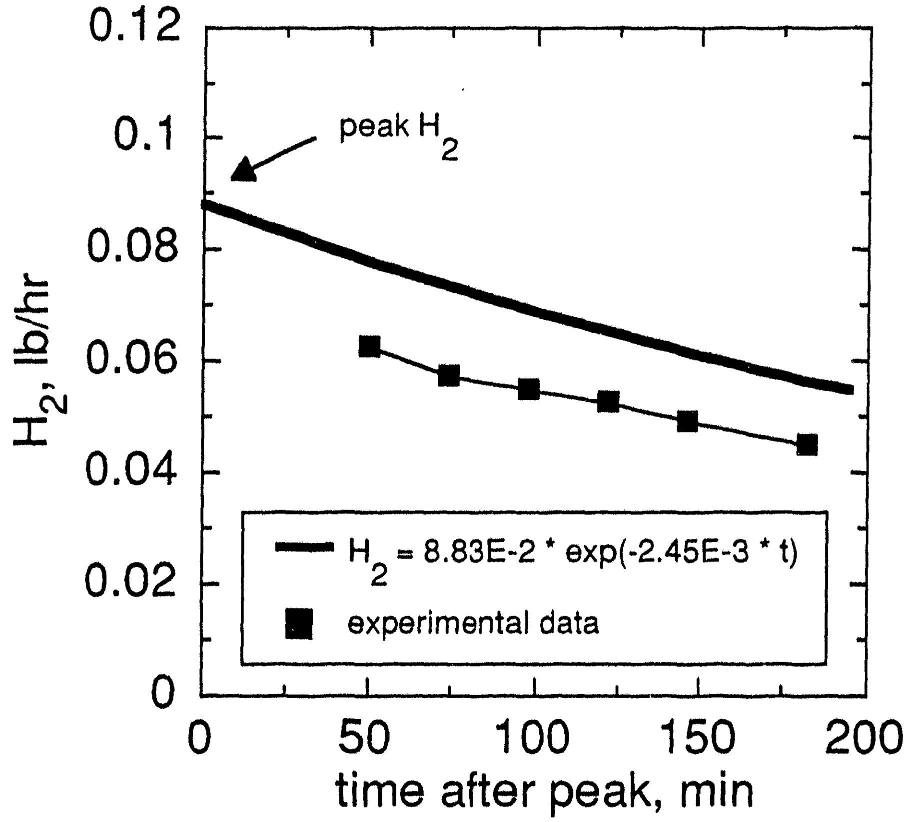

Figure 3. IDMS PX5: Lower curve and symbols represent the decay of the hydrogen generation rate at boiling just after peak occurred data correspond toBox B in Figure 1). Upper curve corresponds to same decay rate as data but adjusted for the peak hydrogen generation rate at t = 0 (see Figure 1, peak H_2 arrow).

Figure 5 displays a representative sampling of the data from Box A in Figure 4. These data were fitted to an exponential function which resulted in a first order time constant of 4.94×10^{-3} min^{-1}. This function should be used until the H_2 generation rate peaks at 2.20×10^{-2} lb/hr (see Figure 4). Once again, in order to start the simulation, the H_2 generation rate at t=0 must be selected. It is again suggested that the H_2 generation rate at t=0 correspond to about 10 % of the observed peak H_2 generation rate.

Figure 6 displays a representative sampling of the data from Box B in Figure 4. These data were fitted to an exponential function which resulted in a first order time constant of -1.71×10^{-3} min^{-1}. Because there was no interruption in the process just after the peak H_2 generation rate occurred, there was no need to adjust the data and the peak H_2 generation rate (2.20×10^{-2} lb/hr) was used directly in the correlation.

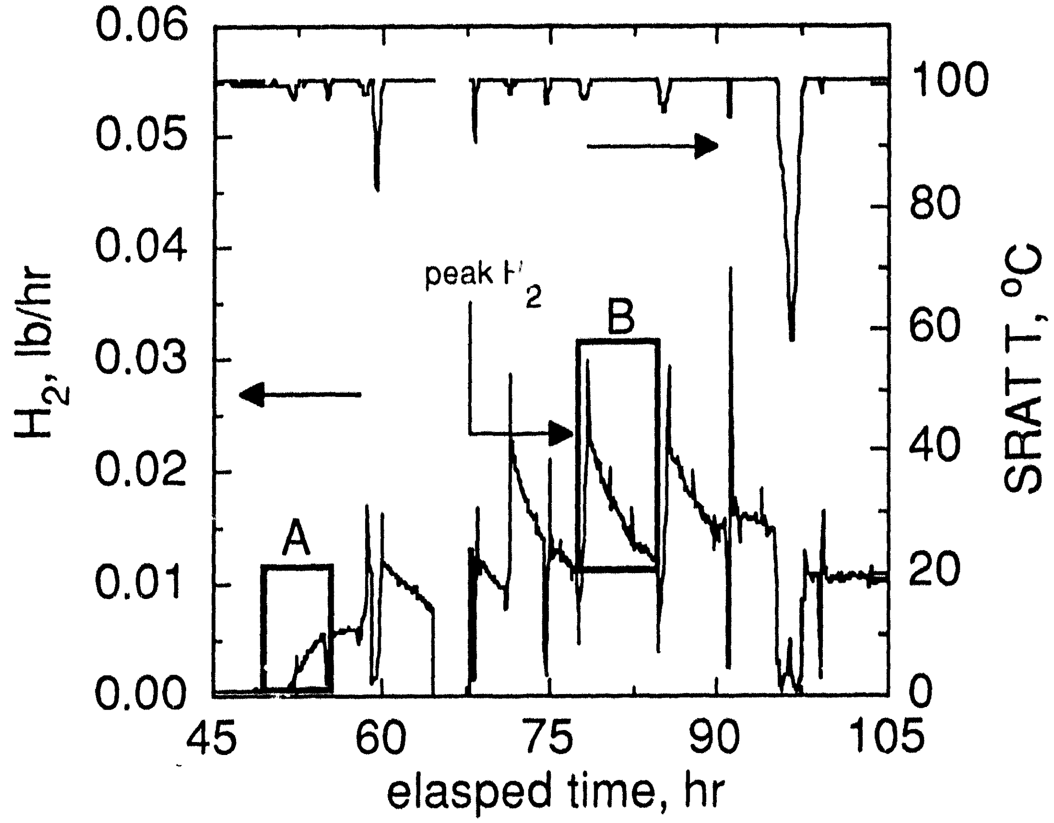

Figure 4. IDMS PX4: hydrogen generation rate and SRAT temperature. Box A corresponds to data shown in Figure 5 and Box B corresponds to data shown in Figure 6.

It should be noted that the time constant for the increasing H_2 generation rate during PX4 was about 30 % larger than that for PX5. This result was an artifact of the arbitrary selection of the data chosen for the correlation of PX4 (see Figure 4). It is clear from the data shown in Figures 1 and 4 that PX5 exhibited well behaved data that increased and decreased around the peak H_2 generation rate. This was not the case for PX4. So, for PX4, the data was chosen at the onset of the H_2 generation rate. The effect of this choice on the simulation should be minimal, however, and only makes the simulation using PX4 data more conservative.

The correlations generated from the IDMS PX5 data were used to create the profiles shown in Figure 7 for the H_2 generation rate and cumulative amount of H_2 generated in the SRAT during PHA transfer. For this scenario, the H_2 generation rate at t=0 was arbitrarily chosen as 0.074 lb/hr (DWPF scale), which was only slightly larger than 10 % of the peak H_2 generation rate. The peak H_2 generation rate and the total amount of H_2 generated both corresponded to that actually generated during IDMS PX5, scaled to DWPF. Also, the 30 hr time span corresponded to a typical PHA transfer time, if 12,000 gal of PHA are added at about 7 gal/min. It should be emphasized that this simple but realistic scenario only serves as an example that may be (but need not be) followed by Van Brunt in his study.[4]

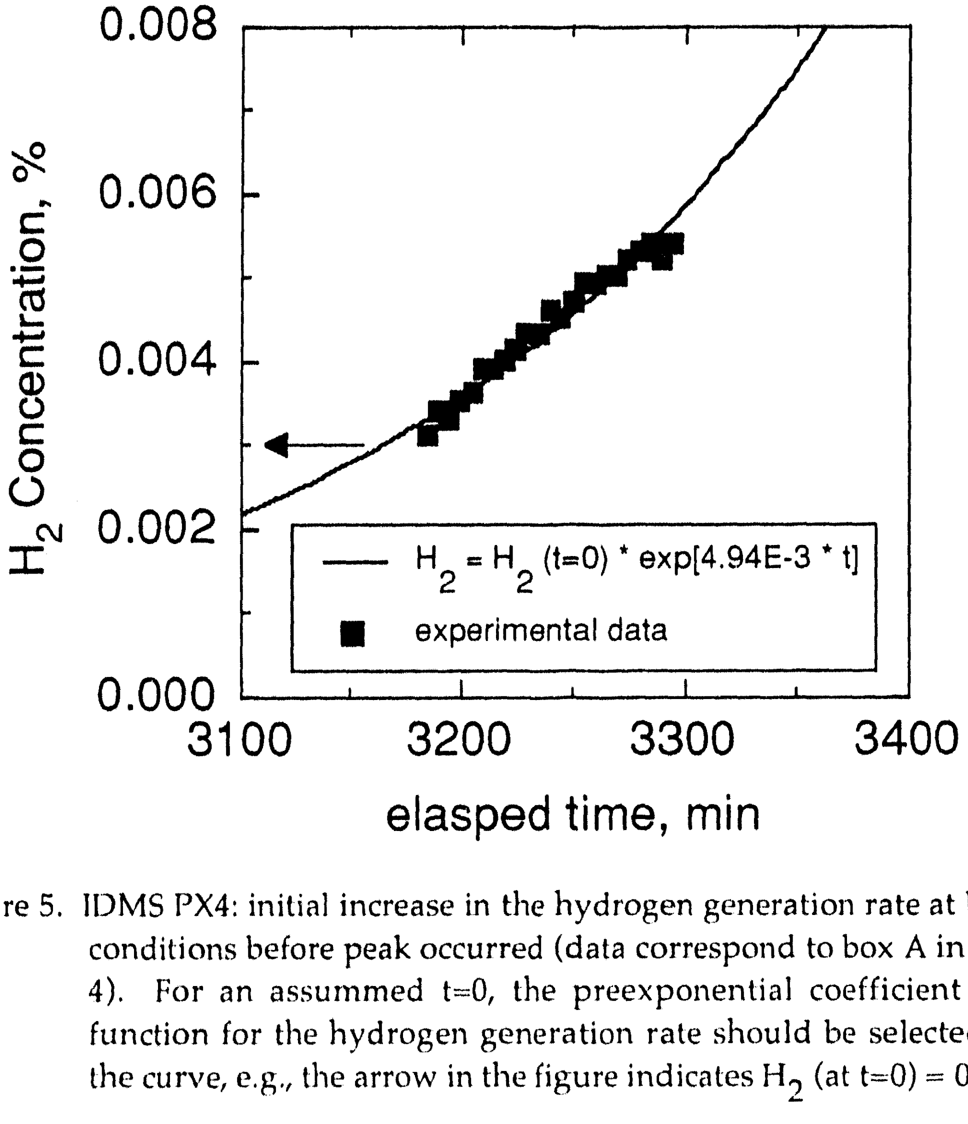

Figure 5. IDMS PX4: initial increase in the hydrogen generation rate at boiling conditions before peak occurred (data correspond to box A in Figure 4). For an assummed t=0, the preexponential coefficient of the function for the hydrogen generation rate should be selected from the curve, e.g., the arrow in the figure indicates H_2 (at t=0) = 0.003.

CONCLUSION

Data obtained from IDMS runs PX4 and PX5 for the generation of H_2 were used to determine a bases for a deflagration/detonation simulation in the DWPF CPC. The simulation will be performed by Professor Van Brunt from the University of South Carolina. This simulation is necessary due to the new chemistry associated with the Late Wash/Nitric Acid flowsheet and process modifications associated with the presence of H_2 in the offgas. IDMS PX5 represented extremely conservative conditions, whereas IDMS PX4 represented conditions much closer to the nominal. For both IDMS runs, exponential functions were correlated with the increasing and decreasing H_2 generation rate data. Prior to performing the deflagration/detonation simulation, these functions will be used to determine the peak H_2 concentration and the total amount of H_2 in the system , based on a scenario similar to that described in the text.

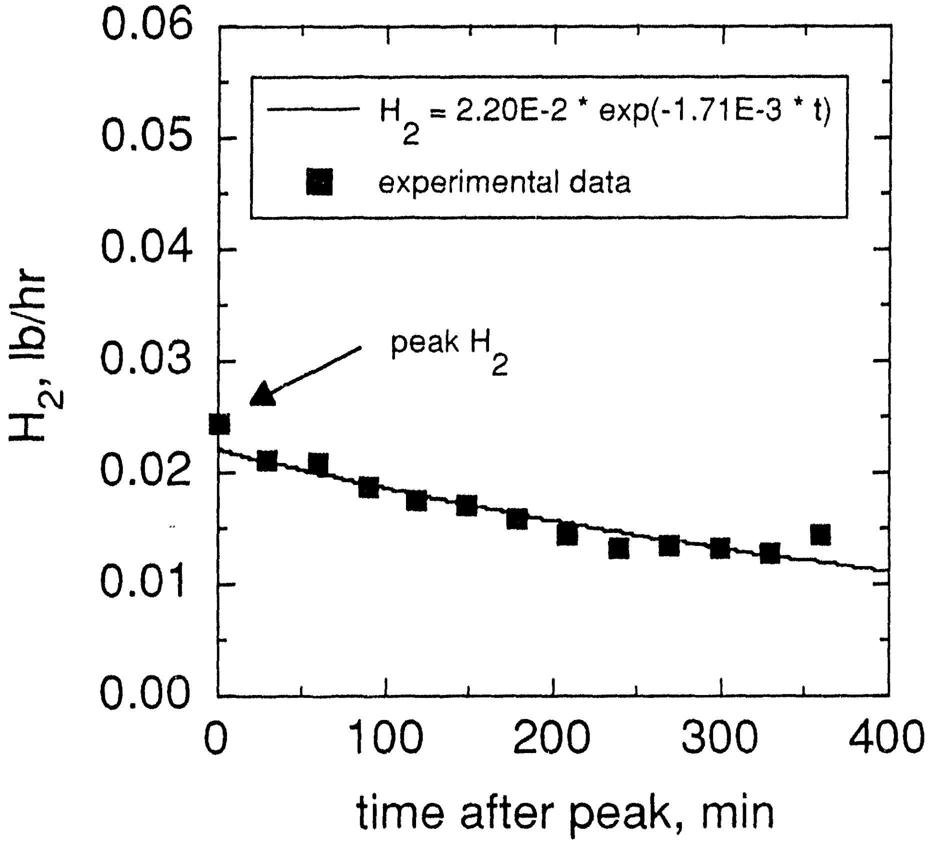

Figure 6. IDMS PX4: decay of the hydrogen generation rate at boiling just after highest peak occurred (data correspond to Box B in Figure 4). At t = 0, the preexponential coefficient corresponds to the peak value (see Figure 4).

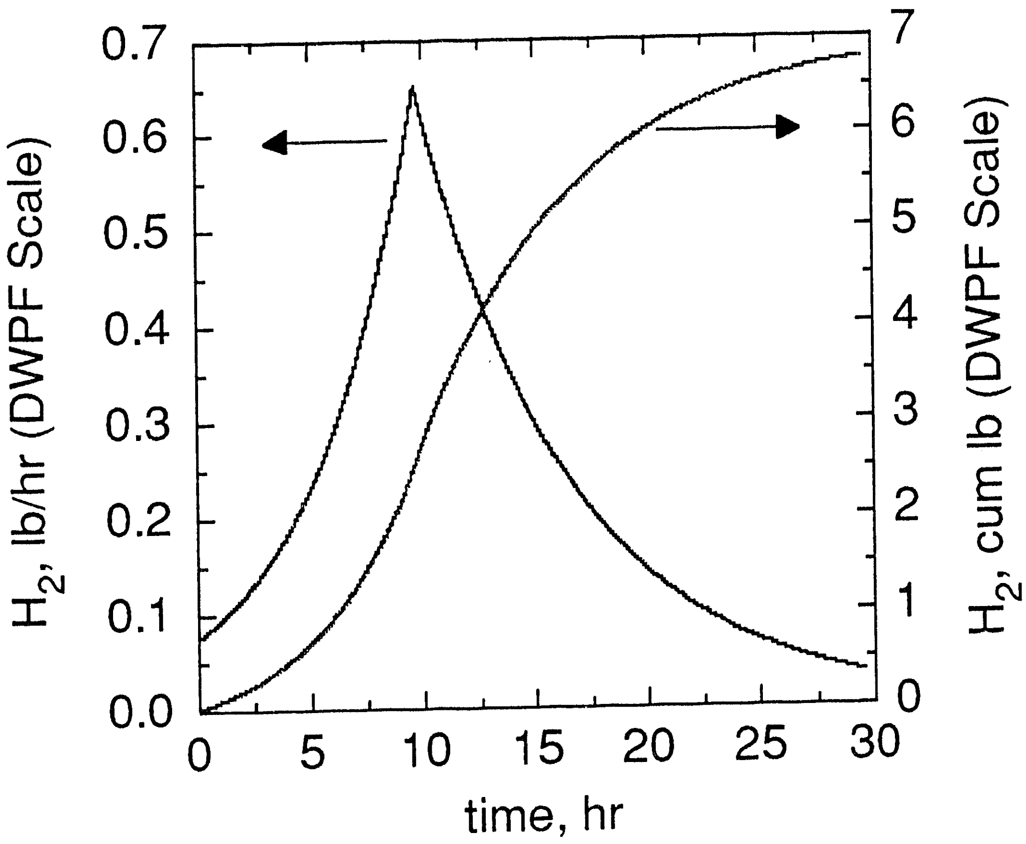

Figure 7. A typical scenario representing the H_2 generation rate and cummulative amount of H_2 generated in the SRAT during PHA transfer, based on the IDMS PX5 functions scaled to DWPF conditions (the H_2 generation rate at t=0 was abitrarily chosen as 0.074 lb/hr DWPF scale).

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