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RESULTS OF SCOPING STUDIES FOR DETERMINING RADIOLYTIC HYDROGEN PRODUCTION FROM MOIST CST AND CST SLURRIES

N. E. Bibler, C. L. Crawford, and C. R. Biddle

**Westinghouse Savannah River Company
Savannah River Technology Center**

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Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

SAVANNAH RIVER SITE

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Approvals

E. W. Holtzscheiter

E. W. Holtzscheiter

10-5-98

Date

W. L. Tamosaitis

W. L. Tamosaitis

10/5/98

Date

Technical Review

John R. Harbour

10/5/98

Date

INTRODUCTION AND SUMMARY

In support of the Salt Disposition team, scoping studies have been performed on the radiolysis of moist and aqueous slurries of Crystalline Silicotitanate(CST). If CST is used for removal of Cs-137 from SRS salt solutions, radiolysis of the water by Cs-137 on the CST will produce H₂. Also it has been shown that the presence of a solid in the system can enhance the production of H₂ by transferring absorbed energy from the solid to the water (1). As indicated in the test plan (2) for this scoping study, it is the intent of this study to determine if CST enhances the radiolytic production of H₂ and to estimate the radiolytic hydrogen generation rate from an aqueous CST slurry in a column at the maximum expected Cs-137 loading on the CST.

Initially several CST slurry systems were irradiated with Co-60 gamma rays and the radiolytic yield of H₂ measured in terms of its G value (molecules of H₂ produced per 100 eV of energy absorbed). Based on the results of these tests it was determined that CST did not enhance the radiolytic production of H₂ by transferring energy to the water and causing it to decompose.

Calculations were then performed to estimate the rate of H₂ production from a process column 16ft. long by 5ft. in diameter containing CST that was fully loaded with Cs-137. The maximum rate of H₂ production based on the G values measured in this study was one liter per minute at STP (0.04 cfm). This was for a 63% water/CST slurry with a G value of 0.2 molecules/100eV for H₂ production and a loading of 1 gram of Cs-137 per 100 grams of resin. The present work also indicates that for a column containing salt solution and CST rather than water and CST, the rate would be 4X lower. This lower value is much more realistic.

EXPERIMENTAL METHODS

CST Samples and Systems Irradiated

CST samples were obtained from Batch 4 of D. D. Walker of SRTC (3). The CST was in the form of small spherical beads of nominally 30-60 mesh size. About 100 grams of CST powder was exposed to ambient atmosphere in a shallow dish in order to equilibrate the CST to ambient atmospheric conditions prior to irradiation. This exposed CST was then used in all subsequent irradiations. The moisture content of the resulting CST powder was measured to be 13±1% by drying 4 gram triplicate samples at 250°C for overnight. It has been shown that temperatures this high are necessary to completely dry the CST (4). This experimentally determined moisture content of 13 % water is within the range of similar

results reported by Walker(3). Walker measured moisture contents of various batches of CST to be 2.7 to 13.0 wt% water upon drying overnight at 100 °C.

Initially, duplicate samples of the moist CST were irradiated without addition of any liquid. Next, two CST-liquid slurry systems were irradiated. The liquid used in these tests was either deionized water or 1M NaOH. In these slurries, known amounts of dry CST were contacted with the liquid and allowed to stand for approximately 1 hour. After this contact period, excess liquid was decanted from the settled CST slurries and known amounts of the damp slurry were added to the irradiation vessels. The CST pretreatment step simulates a CST conditioning step with alkaline solution that might be used in actual processing. Known amounts of fresh solutions of either the deionized water or 1M NaOH were then added to the damp CST in the radiation vessel to give the final CST-liquid slurries (37% CST/63% water or 1M NaOH). The systems were then sealed, leak tested, and irradiated. Two different slurries were used in a third irradiation. These slurries were a 61% CST/ 39% salt solution and 17% CST/83% deionized water. The salt solution contained Na^+ , NO_3^- , NO_2^- and OH^- ions.

Irradiation Methods

Irradiations were carried out in a Co-60 gamma ray source submerged beneath 30 ft. of water for shielding purposes. The temperature of slurries during the irradiations was ~ 35 °C due to gamma heating. A diagram of the irradiation apparatus is shown in Figure 1. Two samples could be irradiated simultaneously. For each experiment, a known amount of CST or CST/liquid slurry was placed in a 45 ml stainless steel vessel (1 in. diameter and 4.5 in. length). The vessel was connected via 4 ft. of 1/8 in. O.D. stainless steel tubing and 24 ft. of 1/8 inch O.D. nylon pressure tubing to a calibrated pressure transducer located outside of the radiation field. A gas sampling septum was located ~ 4 ft. above the steel vessel at the stainless steel/nylon pressure tube interface. This gas sampling septum was used to calibrate the void volume of the apparatus before the irradiations. To determine the void volume in the free gas in the system, successive 5-cc additions of air were added to the sealed system and the pressure increases recorded. Using the ideal gas law and the pressure increases, the constant void volume of the apparatus could be calculated. After the apparatus was leak checked and its void volume determined, the apparatus was then resealed and was ready for irradiation. For irradiation, both vessels had to be placed in a larger stainless steel cylindrical vessel (4" diameter and 12" length) which was attached to cables used to lower them into the Co-60 source. The slurries were irradiated for typically 2-6 days. During this time, the gas pressure generated in each apparatus was recorded periodically throughout the irradiation time.

Figure 1. Diagram of Irradiation Apparatus Used to Measure Radiolytic Pressure Production.

Gas Analyses

After the sample vessels were removed from the radiation field, a 1-L evacuated glass bulb was connected to the gas collection port valve of each apparatus. The 1-L bulbs were evacuated with a standard mechanical pump by pulling a vacuum on them for a few minutes prior to use. The gas contained in the void volume of each apparatus was then expanded into each evacuated 1-L bulb by slowly opening the system needle-valve. The 1-L bulbs were purposely made much larger than the <100 cc void volume in each apparatus to ensure that at least 95% of the total gas was removed from each irradiation apparatus. The 1-L glass bulb was then sealed and disconnected from the radiation vessel system. The 1-L bulb was then brought up to atmospheric pressure by briefly opening the 1-L bulb to the atmosphere. This dilution of radiolytic gases with air was accounted for in subsequent gas component calculations using measured volumes of both the original sealed system and the total volume of the original sealed system plus 1-L bulb. The 1-L bulb was sealed after equilibration with atmosphere and transported to a gas chromatograph for gaseous analyses. Gases produced from irradiation of CST and CST slurries were analyzed by gas chromatography with a Varian Model 3400 gas chromatograph (thermal conductivity detector, chromosorb-101 and molecular sieve columns, argon carrier gas). Gases detected and analyzed for were H_2 , O_2 , N_2 . Standard gases (Scott Specialty Gases, accuracy = $\pm 2\%$) containing these components in the range of 1-10 vol% were used for calibration. Moles of H_2 produced were then calculated from the ideal gas law by knowing the measured H_2 vol% in air, the final system pressure just prior to removal from the radiation source, the total system void volume and a nominal temperature of 30 °C.

Radiation Dosimetry

The radiation dose rate of the Co-60 source was measured using a standard dosimetry method that was based on measuring gas production from radiolytic decomposition of water (5). The dosimeter solution is 0.0001M potassium iodide (KI). The KI prevents the primary radiolytic products H_2 and H_2O_2 from recombining in the radiation field. Figure 2 shows the pressures produced when two identical 0.0001M KI systems were irradiated in sealed vessels (In Figure 2, the lines are drawn by the computer software). After ~ 2 days irradiation, the systems were removed from the source and gas was analyzed.

Compositions of hydrogen gas and experimental details are given in Table 1. Table 1 shows the total dose rate calculated from moles of H_2 produced and the reference G value for H_2 . The reference $G(H_2)$ value for KI dosimeter is 0.383 molecules/100eV (5). This dose rate is in excellent agreement with that measured earlier using the thin film dosimeters (6) after decaying the Co-60 radiation to the time of the current experiments. Table 1 data also shows the precision of measured dose rates (%RSD < 4%) from duplicate samples irradiated simultaneously is very good.

Figure 2. Pressures Produced from Radiolysis of Potassium Iodide Dosimetry System.

TABLE 1. FINAL HYDROGEN GAS COMPOSITION AND CALCULATED DOSE RATES FROM RADIOLYSIS OF 0.0001 M KI DOSIMETER SOLUTIONS

Experimental Details	Vessel 1	Vessel 2
Initial Pressure, PSIA	14.58	14.58
Final Pressure, PSIA	16.88	17.32
Irradiation Time, h	49.25	49.25
Mass Solution, g	39.5	39.7
Void Volume, cc	48.8±0.3	50.8±0.4

Final Gas Compositions	Vessel 1	Vessel 2	Average	St. Dev.	% R.S.D
Vol% Hydrogen	12.7	12.0	12.4	0.5	4.0

Calculated Dose Rates	Vessel 1	Vessel 2	Average	St. Dev.	% R.S.D
Dose Rate, rad/h	4.06E+05	4.25E+05	4.16E+05	0.14E+05	3.3

Methods for Calculating G Values

Radiolytic G values (molecules produced per 100 eV absorbed) for hydrogen were calculated knowing the moles of H₂ produced and the gamma ray energy absorbed by the system based on the dosimetry. Two different G values were calculated. One was based on the energy absorbed by the total mass of the CST slurry being irradiated. This includes both the CST and the water. The second was based on energy absorbed by only the mass of water present. If the CST enhances the radiolytic production of H₂ from the water, the second G value should be greater than 0.45 molecules per 100eV, the maximum G value for H₂ production from pure water (7).

RESULTS AND DISCUSSION

RESULTS FROM IRRADIATION TESTS

Moist CST and CST/Water Slurries

The purpose of these tests was to determine if the presence of CST in the slurries increased the G value for H₂ production by transferring energy absorbed by the CST to cause water to decompose to give H₂. These systems were as received CST that contained 13 wt% water, a slurry that was 63% water slurry and a slurry that was 83% water. The slurry that was 63% water was intended to simulate the slurry in a column of CST resin that could be used for Cs removal from SRS supernates. The 83% water slurry simulated a slurry that could be pumped or might be present in a storage tank. Calculated G values for H₂ based on energy absorbed by the total slurry and on energy absorbed by the water are given in Table 2 and radiolytic pressure changes for these three systems are shown in Figure 3. (In Figure 3, the lines are drawn by the computer software.)

TABLE 2. G VALUES FOR HYDROGEN PRODUCTION FROM RADIOLYSIS OF MOIST CST AND CST-WATER SLURRIES

<u>System</u>	<u>G(H₂) Based on CST+H₂O</u>	<u>G(H₂) Based on Water</u>
Moist CST (13% H ₂ O)	0.019±0.005	0.14±0.01
CST-H ₂ O (63% H ₂ O) ^{a,b}	0.20	0.32
CST-H ₂ O (83% H ₂ O) ^{a,c}	0.15	0.18

^a Corrected for water in moist CST.

^b Calculated percent water in a processing column of CST.

^c Calculated percent water in CST slurry that can be pumped.

Figure 3. Pressure Changes Produced from Irradiation of CST and CST-Water Slurries

For the as received moist CST the pressure decreased initially and then gradually increased after about 50 hours of irradiation. The final pressure of these systems remained below atmospheric pressure. This CST appeared dry and was an easily flowing powder. This type of radiolytic induced pressure decrease has been observed previously when as received zeolites were irradiated (8) or organic resins are irradiated (9). This pressure decrease is most likely due to O_2 depletion in the air initially sealed in the system. Trapped electrons are formed in the CST by the radiation and these electrons can easily react with O_2 to produce oxide species. Depletion of O_2 causes a pressure decrease. The fact that this depletion eventually ceases may indicate that this O_2 reaction occurs primarily on the surface of the particles.

A test was performed to determine if the observed pressure decreases were indeed due to radiolysis or if the CST in the sealed system was just absorbing water vapor and decreasing the pressure. To do this test, moist CST was sealed in the system and it was allowed to sit in the absence or radiation for several days. There was no indication of gas depletion and the sealed system pressure remained at 14.4 ± 0.2 PSIA over approximately nine days of testing.

As shown in Table 2, the G value for H_2 based on energy absorbed by the total system is very small. However, when based on the energy absorbed by the water only the value is increased in proportion to the mass fraction of the water present. This value of 0.14 molecules/100 eV is smaller than 0.45 (the value for pure water (7)) indicating that CST is not transferring energy to the water and enhancing H_2 production. If energy transfer were occurring, the G value based on energy absorbed by the water would be larger than 0.45 molecules/100eV.

The 63% water slurry resembled damp CST and was intended to simulate the CST slurry in a processing column through which supernate would be passed to remove Cs-137. For this system, the pressure increased linearly within experimental error with time or radiation dose. The G value for H_2 for the 63% water slurry was 0.20 molecules/100eV based on energy absorbed by the entire system and 0.32 based on the energy absorbed by the water. The value based on energy absorbed by the water is still lower than 0.45 – again indicating that energy absorbed by the CST is not transferred to the water and causing it to decompose to give H_2 .

The 83% water slurry could easily be poured and was intended to simulate a CST slurry that could be pumped or a slurry that might be stored in a tank until transfer to the DWPF. As shown in Figure 3, the pressure increased linearly within experimental error as with the 63% slurry. The G value for H_2 based on energy absorbed by the water is 0.18 molecules/100eV which is lower than 0.45 indicating that energy absorbed by the CST is not transferred to the water to make H_2 .

The G value for H_2 based on energy absorbed by the both the CST and the water is 0.15 which is lower than the value found for the 63% water system. This is consistent with the fact that in this system there is more free water or water that is not associated with the CST. In fact, in this system the CST settles and there is definitely clear water above the CST. This was undoubtedly the configuration during most of the time that the system was being irradiated. In this water during radiolysis, dissolved H_2 could react with the OH radicals being produced by the radiation and thus decrease the amount of H_2 being released from the solution to cause a pressure increase. In fact, when pure water is irradiated there is no pressure increase due to back reactions in the water to reoxidize the H_2 (7). The mechanism for this has been well documented in the literature of radiation chemistry (7,10).

Irradiation of a CST/1M NaOH Slurry

Based on the radiation chemistry of water it is expected the G value for H_2 production is not dependent on pH (7,10). A test was performed with 37% CST/63% 1M NaOH slurry. In this test the G value for H_2 based on energy absorbed by the entire slurry was 0.24 molecules/100eV in agreement with that determined with CST/63% water. Based on energy absorbed by the 1M NaOH, the G value was 0.35 in agreement with that determined for the CST/63% water slurry based on the energy was absorbed by the water. As expected, the pH of the solution did not affect the radiolytic production of H_2 .

Irradiation of a CST/ NO_3^- , NO_2^- Salt Solution/ Slurry

To determine the effect of nitrate and nitrite in the salt solution on H_2 production, a 61% CST/ 39% salt solution slurry was irradiated. Previous studies have shown that these two ions in solution decrease the G values for H_2 production (7,10). The salt solution was 5.6 M Na^+ , 2.1M NO_3^- , 0.5M NO_2^- and 1.9M OH^- . This 39% slurry was to simulate the packed CST slurry that would be in a column as the salt solution was passing through it to remove the Cs-137. Based on energy absorbed by the total system during a 136 hour irradiation and the final H_2 concentration in the gas, the G value for H_2 production was 0.05 molecules/100eV. This is 4X lower than the G value for H_2 production from the CST/63% water system and CST/63% NaOH system.

RESULTS OF CALCULATIONS TO ESTIMATE H_2 PRODUCTION FROM A PROCESS
COLUMN CONTAINING Cs-137 AND CST

The following calculations were performed assuming that the Cs-137 concentration on the CST was one weight percent and using the maximum G value of 0.2 molecules/100eV determined in this study for energy absorbed by the CST slurry. One weight percent is probably the maximum loading of Cs-137 on the resin (11).

Radioactivity Loading per Gram of Fully Loaded CST

Cs-137 has a specific activity of 87 Ci/g (12). With a loading is one gram of Cs-137 per 100 grams of CST; thus, the Cs-137 Curie loading of the resin is 0.87 Curies per gram of resin. The Cs-137 decays to Ba-137m and to stable Ba-137. Ninety five percent of the Cs-137 decays to radioactive Ba-137m (12) which has a very short half life compared to that of Cs-137. Ba-137m decays to stable Ba-137. Thus the Cs-137 is in secular equilibrium with its radioactive daughter Ba-137m. This means that there are 0.95 Curies of Ba-137m for each Curie of Cs-137. The total Curie loading to the resin is then 1.7 Curies/g. Cs-137 is a beta emitter and decays emitting a total of 1.01 watts per 1000 Ci (12). Ba-137m is a gamma emitter and the decay energy is 3.94 watts per 1000 Ci (12). The beta heat load per gram of resin is then, $8.8E-04$ watts. If all the gamma energy is absorbed, the gamma heat loading is $3.3E-03$ watts per gram of resin. (Obviously not all the gamma energy is absorbed in a gram of resin, but in a processing column or tank it probably is due to the large size of the vessel.) In this case the total heat loading is $4.1E-03$ watts per gram of resin.

Radioactivity Loading per Processing Column of CST

For this calculation it was assumed that a processing column was 16 feet long and 5 feet in diameter (11). With these dimensions and a density of 1 Kg of CST per liter of resin bed (13), the processing column contains $8.9E+06$ grams of resin. The total Curies on the resin including those of Cs-137 and Ba-137m, is $1.5E+07$ Curies. With a column this size it can be shown that greater than 95% of all the gamma energy is absorbed; thus, the total wattage in the column is 37 kilowatts.

Rate of Radiolytic H₂ Production per Gram of Fully Loaded CST

The rate of H₂ production can be calculated using a G value of H₂ production of 0.2 molecules per 100eV of energy absorbed. The necessary conversion factors are, 1 eV/sec equals 1.6E-19 watts and one mole (6.0E+23 molecules) of H₂ occupies 22.4L at STP. If the loading is 4.2E-03 watts per gram of resin, then 1.1E-07 liters(STP) of H₂ will be produced per minute.

Rate of H₂ Production per Processing Column of CST

The processing column contains 8.9E+06 grams of resin, thus H₂ will be produced at a rate of one liter per min or 0.04 standard cubic feet per minute. Presuming that this H₂ diffuses out of the column to the head space above it, the purge rate to ensure that the concentration of H₂ remains below the flammability limit for H₂ would have to be 1 scfm.

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