

Gas Retention and Release Experiments with Low Yield Stress Fluids - 10137

R. Patel, G. Tachiev, V. Sharma, N. Yadav, D. McDaniel, D. Roelant
Applied Research Center, Florida International University
10555 W. Flagler St, EC 2100, Miami, Florida 33174

ABSTRACT

The U.S. Department of Energy (DOE) Waste Treatment and Immobilization Plant (WTP) will pretreat and vitrify the waste retrieved from Hanford's underground storage tanks. The WTP facilities generate process streams, which are characterized with relatively high concentrations of solids and non-Newtonian rheology (generally described with a Bingham plastic model). The current flow sheet of the WTP includes the use of pulse jet mixers throughout the plant to provide adequate mixing of the process fluids. During normal operation, the mixing systems (pulse jet mixers and/or air spargers) in the WTP vessels (including non-Newtonian waste slurries) must achieve safe, controllable release of flammable gases including hydrogen). During design basis events, the pulse jet mixers may be operated intermittently on backup power for extended periods, which may result in gelling of the slurry and accumulation of hydrogen or other flammable gas in the gelled slurry. Upon restart of the pulse jet mixers, the mass of released hydrogen gas and rate of release must not create flammable conditions in the vessel headspace. Florida International University has conducted an experimental program to investigate the gas retention and release properties of selected non-Newtonian fluids in the gelled state relevant to waste streams of the Waste Treatment and Immobilization Plant at Hanford.. For the most part, bench scale experiments were carried out to compare the gas retention and release behavior of clay-based simulants with that of a precipitated hydroxide QARD simulant, and to provide limited but timely insight for the pilot tests at Battelle. In particular, the tests sought (a) a qualitative understanding the behavior of the simulants during gas retention and release, and (b) to determine the release rates from mixing of entrapped gas in the gelled simulants. The experimental program was carried out using oxygen generated in-situ using hydrogen peroxide catalyzed by iron, which is "free" or complexed with a strong ligand (in order to provide the desired degradation rates in simulants with high pH). The composition of released gas which was purged from the headspace using nitrogen or other inert gas was measured to provide information about the rates and volumes of gas retention and release in the gelled simulant. The retention potential of each simulant and the signature of the released gas (such as total volume, shape, and peak intensity) were determined. The experimental data was correlated with the physicochemical and colloidal properties of the selected simulants to provide better understanding of the governing factors for gas retention and release rates as well as volumes of fluids with yield stress parameters in the range of 0-30 Pa.

INTRODUCTION

The WTP design calls for the use of pulse jet mixer technology in tanks that require mixing of solid suspensions and fluid blending, and release of hydrogen gas from radiolysis. These mixers are driven by jet pump pairs that use compressed air for drive energy. The suspension or the liquid phase is drawn into the PJM during the suction phase and then discharged back into the tank during the compression or drive phase of operation. The energy for mixing is imparted to the bulk fluid as momentum added to the suspension in the form of a high discharge velocity during the drive phase. These two phases (suction and drive) together constitute a mixing cycle. Computational Fluid Dynamics (CFD) analysis has been able to validate the efficacy of PJM mixing of tanks for suspensions that behave essentially as Newtonian fluids. However, this approach has been limited in its capability to reflect accurately the behavior for non-Newtonian fluids.

Two principal concerns were identified, even if adequate mixing was accomplished by pulse jet mixers in WTP vessels. The first related to retention of hydrogen in the fluid phase under steady-state operating conditions. The amount of gas retained in the fluid was relevant to estimating the tank volume requirements during normal operation. The second concern related to the release rate of accumulated hydrogen from the gelled contents of the tanks in case of a design basis event. The design basis event provided the conditions for defining the safety envelope required, should there be a major power failure that paralyzed the pulse jet mixer operation for a prolonged length of time. In particular, hydrogen was expected to accumulate in the gelled fluid phase over the duration of design basis event, and it was essential to quantify the release rate of entrapped hydrogen from the gel when mixing resumed. The specific danger from a design basis event was that a spontaneous or high release rate of hydrogen could flood the vent system beyond the design safety envelope, if the purge capability is undersized.

The current control strategy is to maintain hydrogen concentrations below 25 percent of the lower flammability limit¹. The design approach involves providing sufficient dilution ventilation during all plant conditions (e.g., normal operating and design basis event conditions) and therefore requires an accurate understanding of hydrogen generation rates within each WTP vessel. Dilution air is provided by the process vessel purge system. The gas generation rate, together with the retention characteristics of mixed sludge waste was used to determine how much gas can accumulate in the waste in WTP vessels. Furthermore, the volume and rate of a gas released into a vessel headspace, not the generation rate, was used to determine whether flammable concentrations result.

OBJECTIVE

The main objective of the tests at Florida International University was to determine and compare the release rate of gas from bubbles generated in situ in the from the “gelled” state in selected simulants. The test consisted of a bench-scale mechanically agitated gas hold-up setup. The oxygen was generated in situ by decomposition of hydrogen peroxide incorporated into the simulant. These tests were carried out with 3 simulants: (i) AZ-101 high level waste pretreated precipitated hydroxide “QARD” simulant, (ii) “27 % Clay” simulant and (iii) a “Diluted Clay” simulant to determine the projected bounds of gas hold-up as a function of simulant type, particle morphology and sizes, etc. The purpose was to observe relative hold-up in the simulants relevant to the pulse jet mixing tests and actual waste so that the limited number of tests completed at a larger scale with fewer simulants can be shown to be technically defensible. A range of appropriate simulants in a mechanically agitated system using bubble injection near the impellers to ‘beat’ the gas into the simulant was used. The selection of the materials was based on their respective fluid properties using the following requirements:

1. The simulant should provide a realistic but conservative bound on the design of a pulse jet mixing system. More specifically, the shear strength and viscosity (consistency) of the selected simulants must approximate the behavior of the waste to be mixed.
2. The pulse jet mixing design and optimization criteria (number, layout, operation of pulse jet mixing within the tank) may affect the flow regime and correspondingly the selection of simulants.
3. Mixing conditions in the tanks may affect the steady state release rates (when the amount generated equals the amount released) of hydrogen gas.

¹The lower flammability limit has been defined as 2.5% H₂

4. The experimental configuration and the evaluation of the results is another important factor that must be evaluated in order to show that there is good mixing for solids and gases in the system.

The in-situ gas retention and release tests consisted of:

- a) Addition of hydrogen peroxide (H₂O₂) to the simulant and mixing it over a period of about 2 minutes to assimilate the peroxide into the simulant. The mixing is then ceased and the oxygen generated in-situ from peroxide decomposition was allowed to accumulate in the simulant. The simulant was allowed to gel for 18 hours.
- b) At the end of the 18-hour gel period, it was mixed to measure the gas release rate. The physical characteristics of the in-situ generated gas through peroxide decomposition was presumed to resemble that of hydrogen accumulated from radiolysis in the gelled waste.

The key assumptions in opting for a well-mixed vessel for testing were:

- A well mixed condition provides bounding conditions of gas release for comparison of simulants.
- Gas injection with controlled bubble size provides a measure of the steady-state hold-up and release rates. Computations had indicated that gas bubbles approximately 1.0 mm in diameter will freeze in place (or simulant “gels” instantly relative to bubble buoyancy forces) when mixing is stopped.
- A well-stirred system provides a platform for rapid relative evaluation of simulant behavior.

MATERIALS AND METHODS

Simulants

Hanford’s WTP has specified and provided the simulants (see **Error! Reference source not found.**)

Table I. Selected Simulants.³

Simulant	Yield Stress, Pa	Bingham Plastic, Pa
Clay 27%	16.24	24.48
Clay 27%, post-test	12.04	27.70
Dilute Clay (24%)	7.09	16.63
Dilute Clay(24%), post-test	5.22	16.96
AZ-101 ² QARD pH 13	3.39	15.62
AZ-101 QARD pH 13, post-test	16.38	10.49

Experimental Setup

The experimental setup is shown in **Error! Reference source not found.** and included the following requirements:

²AZ-101 HLW Pretreated Sludge @ 20 wt% Solids, precipitated hydroxide QARD particulate simulant.

1. An approximately 5-gallon range on the test vessel (the taller the better so that a change in level can be easily measured).
2. A suitable mechanical agitator system has been defined and agreed upon with WTP.
3. The ability to inject gas near the axial flow impeller blades so as to 'beat' the gas bubbles into smaller bubbles and disperse them uniformly into the simulant.
4. A millimeter wave level detection probe/system or other similar device to be able to measure a 1/2% level change in the vessel.

The test vessel was constructed using a section of acrylic pipe with 11.5-inch inside diameter and 15-inches high (vessel capacity of approximately 25.5 liters). The vessel was sized to allow a 5-gallon (19-liter) charge of simulant with approximately 30% freeboard or headspace above the simulant. Penetrations in the sidewall were provided for recirculation flow intake (required for gas dispersion) and for a thermocouple to measure the simulant temperature. Even though the vessel was baffled at the beginning, these were removed after the shakedown tests since they seemed to interfere with mixing near the walls. The baffles seemed to prevent shearing of a significant volume of the simulant near the wall over the entire circumference of the vessel.

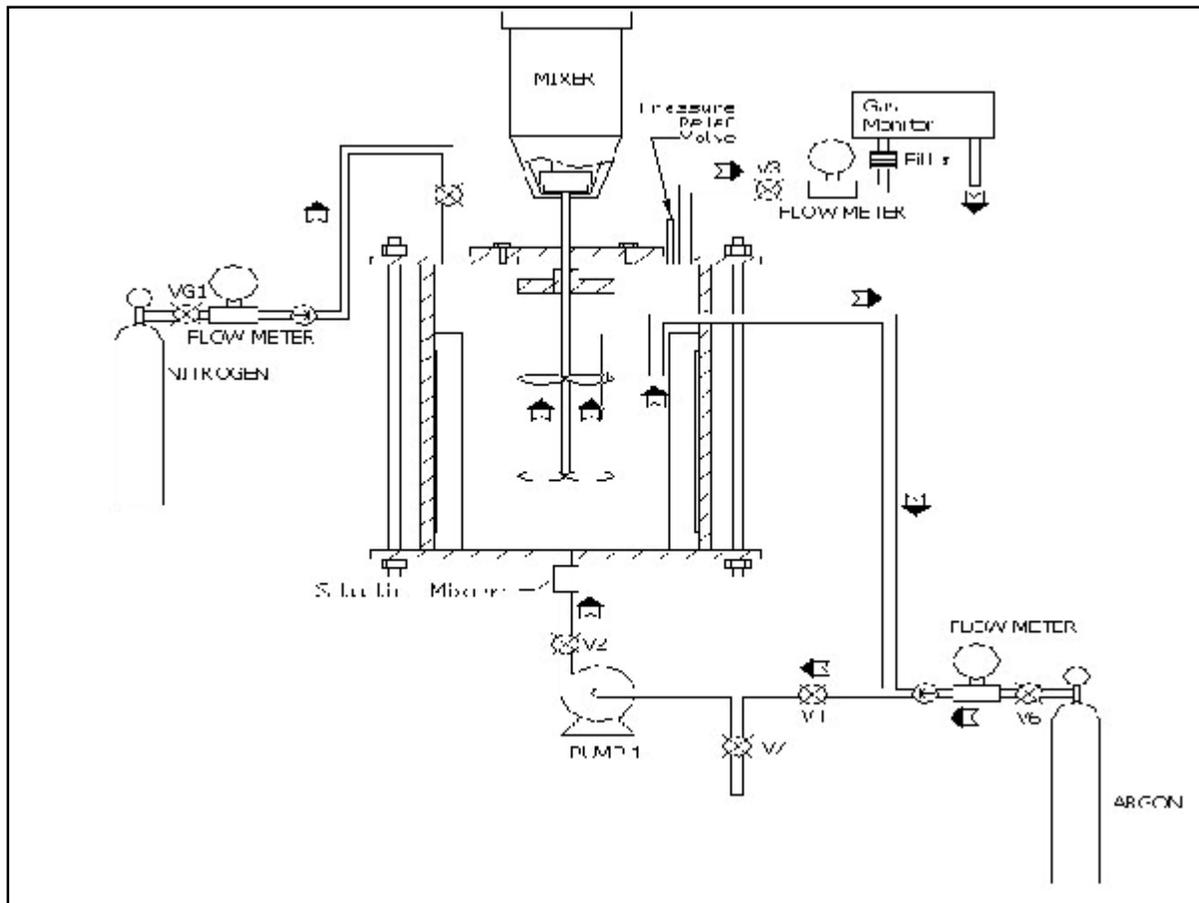


Fig. 1. Experimental diagram (arrows represent the flow of the diagram).

The top and bottom of the vessel were made of 0.5-inch thick acrylic blind flanges. While the bottom flange was cemented to the vessel to form an integral structure with the sidewalls, the top was held by O-ring compression seal. The compression was provided by 4 tie-rods connecting the top and bottom flanges. A graphite-packed seal (similar to pump seals) was installed in the top flange for entry of the

mixer shaft into the vessel. The body of the seal was custom fabricated from teflon stock. The mixer consisted of a 0.5HP variable-speed DC motor controlled electronically that powered two 4.5- inch diameter impellers specially designed for mixing high viscosity fluids (Cole-Parmer Instrument Company, Catalog #:A-04560-63). In addition to the two impellers, a “rake” or sweep-impeller was added below the lower impeller to improve mixing in the volume below the lower impeller. This sweep impeller had a diameter of 9.75 inches with an overall vertical dimension of 3 inches. The impellers were located on a single 1/2-inch shaft supported at the top by the packed seal and at the bottom by a teflon bushing located at the top of the radial flow deflector. The shaft was driven through a flexible coupling to allow for ease of alignment of the motor drive and the shaft.

The pitch orientation for both impellers was selected for upflow displacement of fluid during mixing, and the impellers were located on the shaft to avoid gas entrapment in the vortex under well-mixed conditions. The vessel contents were considered well mixed when movement of fluid at the walls of the vessel could be observed. In other words, the entire fluid volume was fully sheared. In this regards, visual observations of fluid movement at the walls and the shape of the surface vortex were used to guide setting the mixer speed. The mixer shaft speed (RPM) was monitored continuously with a laser tachometer and controlled manually.

The peroxide for in-situ generation of gas (oxygen) was injected below the surface of the simulant using a large syringe and needle, while continuing to mix the simulant and purge the headspace with nitrogen. An injection rate of 40 ml/min was used, assuming 100 times of the maximum hydrogen generation rate. The goal was to inject bubbles with a size of less than 1 mm and preferably less than 0.5 mm.

The mixing rate must be sufficient to mobilize the contents but not over mix (expressed by gas entrainment at the simulant surface, or significant vortex in the system). The simulant must be fully sheared before injection. At least 18 hrs gelling period had to be allowed before release measurements. During the experiment, a number of parameters were monitored, including simulant level, and Ar, N₂ and O₂ concentrations in effluent gas during injection, release and gelling periods. A high headspace purge rate was applied to minimize response time.

IN-SITU GENERATION AND RELEASE TESTS

Oxygen In-situ Generation

Based on observations in qualitative bench-top tests, it was recognized that bubbles evolved insitu in the gel were more uniform in both spatial distribution and bubble diameter. Therefore, a method to generate bubbles insitu was developed in an attempt to represent more closely growth of hydrogen bubbles in gelled waste. The method involved rapid incorporation of hydrogen peroxide (H₂O₂) into the simulant and allowing it to gel. The decomposition of H₂O₂ in the simulant results in oxygen generation insitu in the gel and could serve as a surrogate gas for release tests. The gel hold-up by this method depends on sufficiently slow decomposition rate for H₂O₂, such that bulk of the H₂O₂ added releases the oxygen in the gelled state. Therefore, the strength of the H₂O₂ in the solution added to the simulant was adjusted to slow down decomposition during the addition operation. A comparison of gas bubble diameter and spatial density observed in the gelled simulants during the during insitu tests is shown in the photographs in Fig. 2. In the case of the QARD simulant, because of the presence of transition metal hydroxides and high pH, the decomposition rate of laboratory reagent grade H₂O₂ (30% wt H₂O₂) was violent and the H₂O₂ had to be diluted to slow the decomposition rate and avoid release of oxygen to the headspace during peroxide addition. During tests with the QARD simulant, H₂O₂ solution strengths of 3.4%wt and 6.8%wt were used.

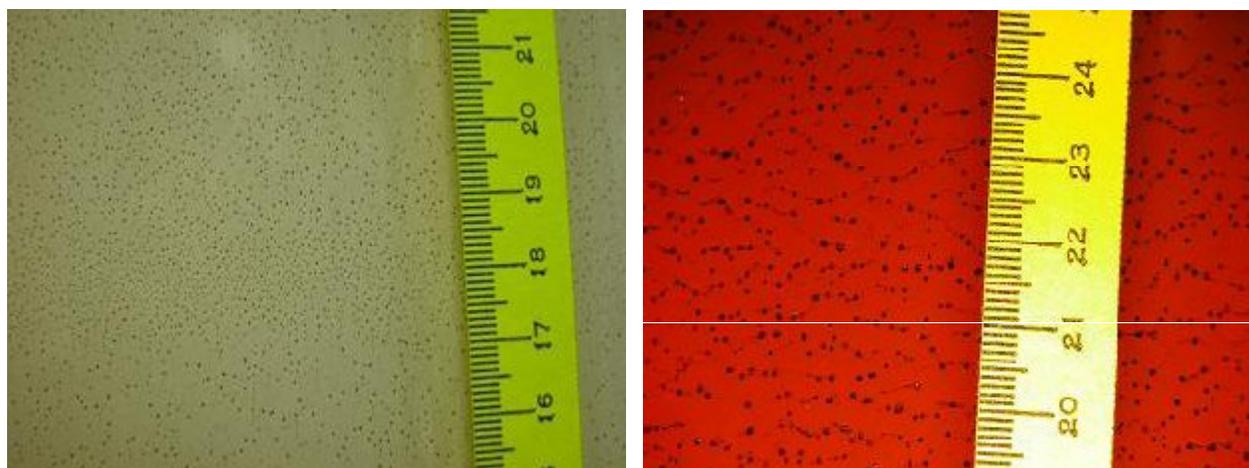


Fig. 2. In-situ generated bubbles in 27% clay (left) and QARD (right).

Test Matrix of In-Situ Generation Tests

The insitu generation and release tests used oxygen generated through decomposition of H_2O_2 as the surrogate gas for hydrogen. The level of oxygen hold-up in the gelled simulant was controlled by the amount of H_2O_2 added to the simulant before gelling. The tests were planned to measure release rates from 2 levels of hold-up for 3 simulants. A total of seven experiments were conducted under different operating conditions. The initial conditions, including the targeted gas hold-up based on stoichiometric calculations assuming completion of hydrogen peroxide decomposition are given in (**Error! Reference source not found.**)

Table II. Test Matrix for In-situ Generation of Oxygen.³

Test	Simulant	V_{simulant}	V_{oxygen}	Holdup, L	Holdup, %	T, °C	Mixer speed, RPM
H01	QARD	17.86	2.51	2.266	12.69	24-25	198-208
H02	QARD	17.86	2.28	1.647	9.25	23-25	196-207
H03	QARD	17.61	4.54	4.069	23.11	22-23	197-207
H04	27% Clay	18.81	2.56	2.232	12.35	23-24	194-200
H05	27% Clay	18.81	2.51	1.096	5.83	25-26	198-212
H06	24% Clay	19.55	2.58	1.733	8.86	23-24	194-200
H07	24% Clay	19.62	1.25	1.060	5.4	22-23	194-203

A typical oxygen concentration profile during hydrogen peroxide injection is shown in Fig. 3. With the exception of the beginning of the experiment, no peaks of oxygen were detected, i.e. the oxygen gas was unable to escape the entrapment into the gelled simulant.

³ Sundar et al has provided a summary of additional parameters not included here.



Fig. 3. Oxygen concentration profile during injection.

Oxygen signatures during release for experiment H03 and the corresponding rates are shown in Fig. 4 below. Red and blue lines in Fig. 4 differentiate the two release parameters obtained.

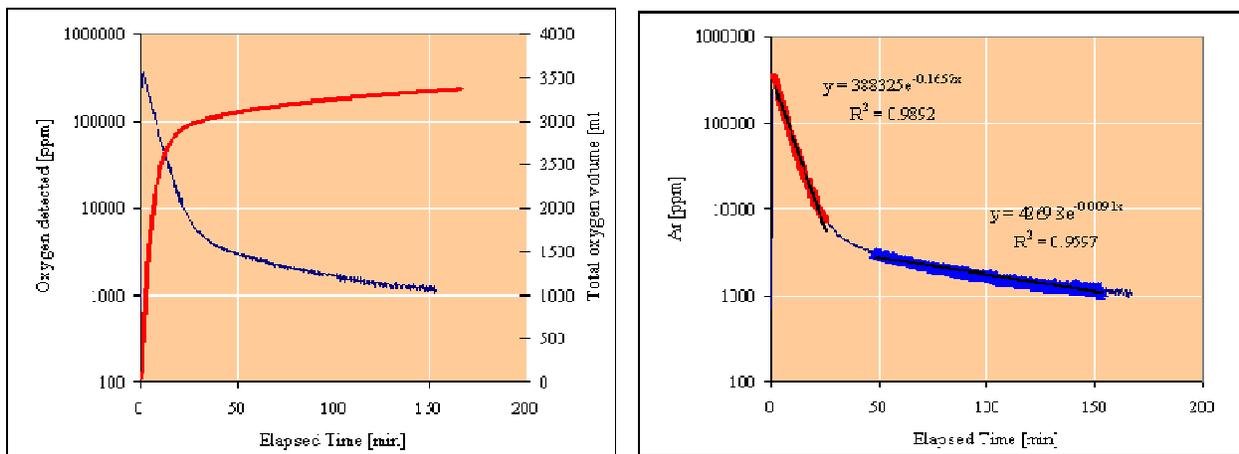


Fig. 4. Oxygen release signature-H03(left) and Oxygen release kinetic parameters (right).

RESULTS AND DISCUSSION

Gas Release from QARD simulant

During the first test with the QARD simulant (designated by H01 and H02), the H_2O_2 solution was added to the surface of the center vortex with the expectation of fast incorporation into the bulk volume of the simulant. However, the decomposition rate of H_2O_2 was violent and occurred near the surface because of the high strength (reagent grade 30% wt H_2O_2) of the peroxide solution used. It is believed that a significant portion of the oxygen released may have been lost to the atmosphere through the open feed port. Therefore, the actual hold-up is very likely lower than the hold-up estimated from the oxygen material balance. While the estimated hold-up was 12.69% vol based on oxygen balance, the hold-up based on simulant level change was only 3.75% vol. Subsequent to this test, the peroxide addition procedure was modified to slow the peroxide decomposition rate. Peroxide was added by injecting a dilute 3.4% wt peroxide solution below the surface of the simulant while mixing vigorously over a 2-minute period. Given this foreword, the three estimated levels of gel hold-up for the tests with the QARD simulant were 9.25% vol, 12.69% vol and 23.11% vol based on oxygen balance (designated by H01, H02 and H03 in Table II). Fig. 6 shows the oxygen profile during the first 10 minutes of the test.

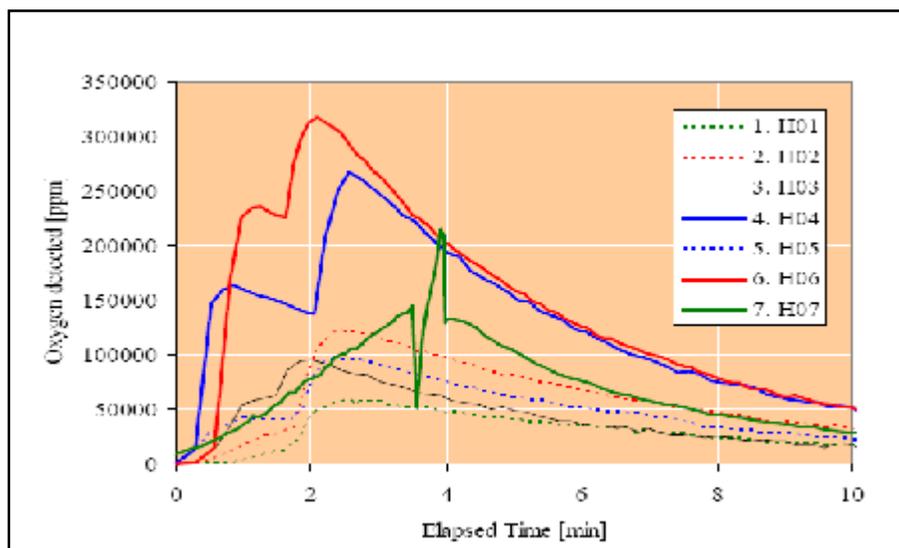


Fig. 5. Oxygen detected in the effluent stream.

The estimated gel release rates for the QARD simulant from the 3 hold-up levels are shown in Fig. 6. Once again, the release rate is normalized relative to the estimated initial gel hold-up prior to commencement of mixing. The gel release rate estimates clearly point to an initial period (on the order of 10 minutes) of relatively higher rates of release, upon commencement of mixing. Furthermore, the estimates indicate that this period was more prolonged at the higher level of hold-up. However, a lower release rate with higher initial hold-up (noted between 23.11% vol and 9.25% vol hold-ups) was unexpected. The higher initial release rate at the higher hold-up is attributed to greater coalescence of the smaller gelled bubbles into larger bubbles, and the higher spatial density of bubbles in the simulant at the commencement of mixing. The gradual drop in the release rate is attributed to depletion of the larger bubbles and to lowered spatial density of the bubbles; this supports the conclusions by Sundar 2004. More experiments are needed with QARD in future as the peroxide degraded rather rapidly in a turbulent manner so that the results truly represent our experimental strategy.

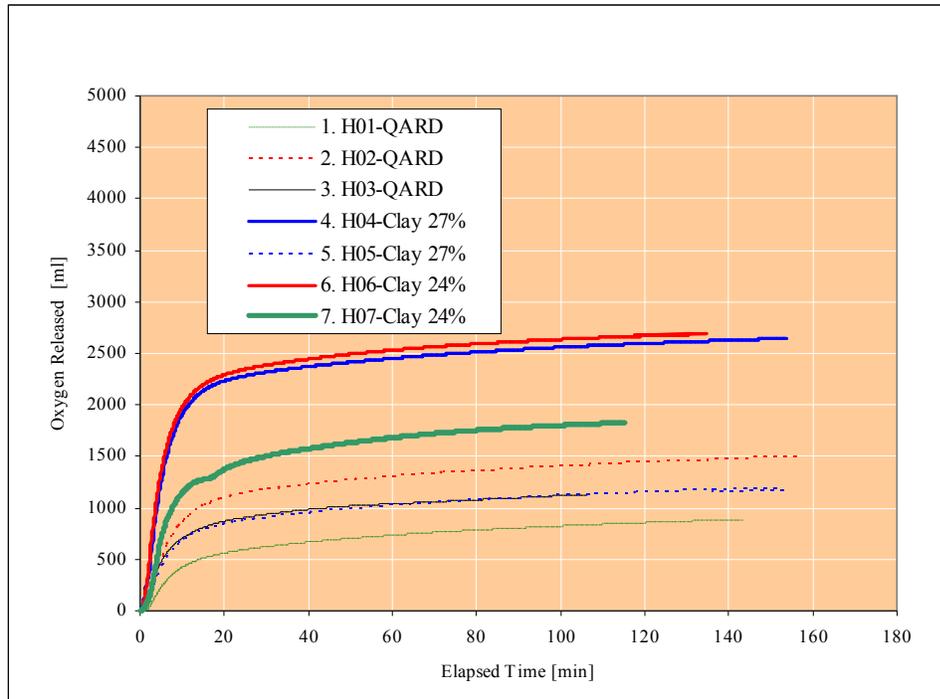


Fig. 6. Total volume of gas detected from release.

Gas Release from Clay simulants

For the estimation of gas release parameter in clay simulants, two clay simulants were tested for gel release behavior: (i) 27% Clay simulant used in the steady state tests and (ii) Diluted Clay simulant believed to be closer in rheology to the QARD simulant. The Diluted Clay simulant has about 50% of the yield strength, and about 67% of the consistency (viscosity) of the 27% Clay simulant. Therefore, it would be reasonable to expect higher release rate from the Dilute Clay simulant than the 27% Clay simulant under similar initial gas hold-up based on bubble rise velocities. This trend cannot be clearly seen in the release rates measured for dilute clay and 27% clay at an initial gel hold-up of about $5.6 \pm 0.2\%$ vol as seen in Fig. 7.

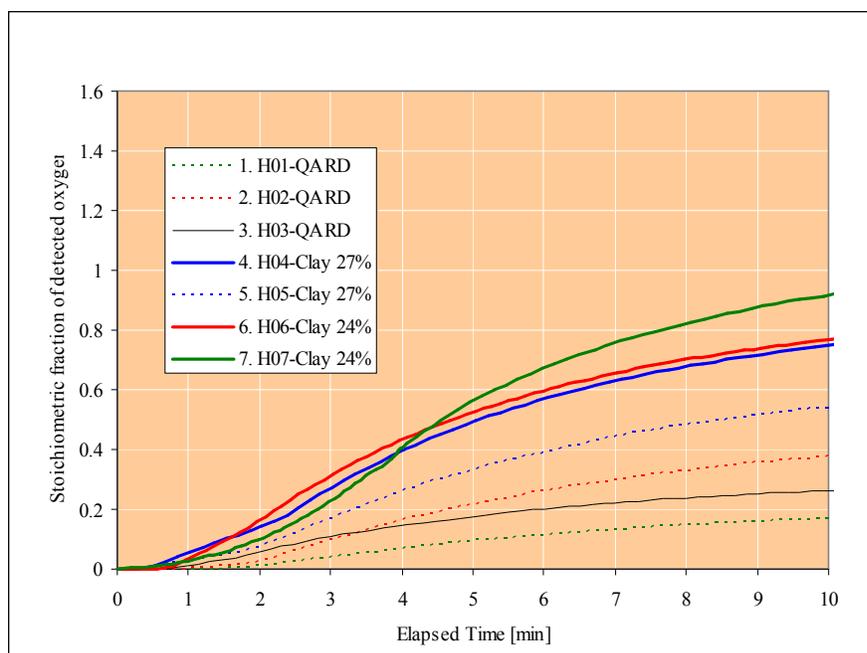


Fig. 7. Fraction of released oxygen during the first 10 minutes.

Table III summarizes the more important parameters that have been determined from the experimental program.

Table III. Summary of Release Parameters.

Experiment	Simulant	k_1 , 1/min	k_2 , 1/min	O ₂ Peak	Volume ¹ , mL	Volumetric Fraction ¹ released
H01	QARD	0.1542	0.011	6%	450	2%
H02	QARD	0.1358	0.0092	12%	855	4%
H03	QARD	0.1657	0.0091	36%	2400	12%
H04	Clay 27 %	0.181	0.0115	27%	1900	10%
H05	Clay 27 %	0.1413	0.0112	10%	1678	8%
H06	Clay 24 %	0.1918	0.0159	31%	1967	10%
H07	Clay 24 %	0.2843	0.0194	21%	1142	6%

1. Values based on oxygen release during the first 10 minutes

CONCLUSIONS

The tests at FIU only sought scooping-level information for the comparison of gas retention and release behavior of clay-based simulants to the precipitated hydroxide QARD simulant. Therefore, the limitations of oxygen as surrogate to hydrogen were acknowledged, but not explored. Also, a mechanically well-mixed vessel was considered to represent the bounding condition of a well-mixed vessel using PJMs (Sundar, 2004).

Under the test conditions, gas release from simulants gelled at steady state retention were observed, and findings conclude that they do not represent the gel release from gas-generated in-situ in gelled simulants. Increased injection did not result in higher retention. Both the QARD and the 27% clay simulants seemed to thicken during the injection period, requiring continual adjustment to the mixer speed. These

adjustments to the mixer speed were followed by a surge in the effluent argon level. This is consistent with the conclusions made by Sundar, 2004.

For the in-situ generated gas, a substantial fraction (65 to 85%) of the gas held up is released in a surge of gas release during the first 10 minutes after the commencement of mixing of the gelled simulant. This initial high rate of gas release appears to depend on the initial hold-up. A higher initial release rate was observed with higher gas hold-up. During design basis events, (DBE), there may be an interruption in utilities for a sufficient time for the tank slurry to gel. If the interruption is for more time the hold-up will be more and so will be the initial rate of gas release and vice versa.

Approximately 95 to 98% of the total gas release occurs in the first 120 minutes from the start of gel mixing. Also, virtually all the gas held up was released within 180 minutes, the test time period used for monitoring the release.

Both the 27% clay simulant and the diluted clay simulant appear to exhibit faster gas release behavior than the QARD simulant. In other words, the clay-based simulants tested may be used to provide an upper bound for the gas release rate from the gelled QARD simulant in the pilot tests at Battelle. Even though significantly different in rheology, the 27% clay simulant and the diluted clay simulant tested exhibit similar gas release behavior within the range of initial gel hold-ups in these tests.

REFERENCES

1. Sundar, P., S., 24590-PTF-RPT-RT-04-0005, Rev 0, Gas Retention and Release Tests in Non-Newtonian., Simulants at the Florida International University in Support of the WTP Project