

# **Laboratory Investigations in Support of Carbon Dioxide-Limestone Sequestration in the Ocean**

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**Dan Golomb, Eugene Barry, David Ryan, Carl Lawton**  
*Co-Principal Investigators*  
**Peter Swett, John Hannon, Huishan Duan**  
*Research Assistants*

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*University of Massachusetts Lowell, Lowell, MA 01854*

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## Laboratory Investigations in Support of Carbon Dioxide-Limestone Sequestration in the Ocean

### ABSTRACT

In the second half of the second contractual year the construction of the High Pressure Flow Reactor (HPFR) was completed, tested, and satisfactory results have been obtained. The major component of the HPFR is a Kenics-type static mixer in which two fluids are thoroughly mixed. In our case the two fluids are liquid or supercritical CO<sub>2</sub> and a slurry of pulverized limestone (CaCO<sub>3</sub>) in pure or artificial seawater. The outflow from the static mixer is an emulsion consisting of CO<sub>2</sub> droplets coated with a sheath of CaCO<sub>3</sub> particles dispersed in water. The coated CO<sub>2</sub> droplets are called *globules*, and the emulsion is called *globulsion*. By adjusting the proportions of the two fluids, carbon dioxide and water, the length and pressure drop across the static mixer, globules with a fairly uniform distribution of diameters can be obtained. By using different particle sizes of CaCO<sub>3</sub>, globules can be obtained that are lighter or heavier than water, thus floating or sinking in a water column. The globulsion ensuing from the static mixer flows into a high pressure cell with windows, where the properties of the globules can be observed, such as their diameter and settling velocity. Using the Stokes' equation, the specific gravity of the globules can be determined.

Also, a second generation High Pressure Batch Reactor (HPBR) was constructed. This reactor allows better mixing of the ingredients, more accurate temperature and pressure control, better illumination and video camera observations. In this reactor we established that CO<sub>2</sub>-in-water globulsions can be formed stabilized by other particles than pulverized limestone. So far, we used flyash obtained from a local coal-fired power plant, and a pulverized magnesium silicate mineral, lizardite, Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>, obtained from DOE's Albany Research Laboratory.

In the reporting period we conducted joint experiments in NETL's high pressure water tunnel facility. Thanks to the longer travel path of the globules, and the excellent optical instrumentation available at NETL, we were able to more accurately obtain globule diameters and settling velocities.

## TABLE OF CONTENTS

ABSTRACT	page 3
EXPERIMENTAL	5
(a) High-Pressure Flow Reactor (HPFR) with Static Mixer	
(b) New High-Pressure Batch-Type Reactor (HPBR)	
(c) Experiments in NETL Water Tunnel Facility	
RESULTS AND DISCUSSION	6
(a) Globulsions in HPFR	
(b) Globulsions in HPBR Using Flyash and Mineral Particles	
(c) Globulsions in NETL Water Tunnel Facility	
PLANS FOR THE NEXT PERIOD	8
CONCLUSION	9
PUBLICATIONS	9
TABLES AND ILLUSTRATIONS	10

## EXPERIMENTAL

### (a) High Pressure Flow Reactor

In the reporting period, the assembly of the High Pressure Flow Reactor (HPFR) was completed and tested. The schematic of the HPFR is presented in Figure 1 at the end of the report. The HPFR mixes a stream of liquid carbon dioxide with a slurry of pulverized limestone ( $\text{CaCO}_3$ ) in water or seawater at pressures up to 2,500 psi.

The heart of the HPFR is a Kenics-type static mixer, which is depicted in greater detail in Figure 2. This is a tubular mixer 11 inch long with  $\frac{1}{4}$  inch OD, with a series of 27 alternating helical baffles inside the mixer. Two fluids are forced into the mixer, one is liquid or supercritical  $\text{CO}_2$ , the other is a slurry of pulverized limestone ( $\text{CaCO}_3$ ). The high velocity in the narrow tube and the shearing and streamline cleaving action of the helical baffles efficiently mix the immiscible liquids, so that at the end of the tube a homogenized emulsion ensues. The emulsion consists of liquid or supercritical  $\text{CO}_2$  droplets coated with a sheath of  $\text{CaCO}_3$  particles dispersed in water. We call this emulsion a *globulsion*. The globulsion flows into the view cell equipped with windows. The size distribution of the globules is measured with a fast-frame video camera using the window dimensions as a scale reference.

We modified a laboratory vertical microscope, so to be able to mount it horizontally on the view cell window. The microstructure of the globules can be seen through the eyepiece up to 40x magnification. We are currently seeking to purchase a microscope with an attached video camera for recording the observations.

### (b) New High Pressure Batch Reactor

In the reporting period a new and improved High Pressure Batch Reactor (HPBR) was constructed. The modified design of the HPBR is shown in Figure 3. Several limitations of the original batch reactor were addressed. As before, the cell comprises the intersection of two cylinders. However, some of the dead volume of the cylinders has been reduced in order to avoid stagnation of the globules outside of the field of view of the windows. Also, a recessed bottom of the reactor allows for higher rotational speeds of the stir bar and better mixing. More ports have been added for the insertion of a high pressure pH electrode assembly and other probes. The window material is tempered borosilicate glass (Pyrex), which permits operation up to 5000 psi (34.5 MPa) and temperature up to 50°C.

### (c) Experiments in NETL Water Tunnel Facility

The new High Pressure Batch Reactor (HPBR) was transported from UML to NETL, re-assembled, and interconnected to the NETL Water Tunnel Facility (WTF). The composite schematic of the WTF/UML experimental set-up is given in Figure 4, and an actual photo of the set-up is shown in Figure 5. The WTF allows the injection of liquid  $\text{CO}_2$  droplets, or in our case calcite-sheathed globules of  $\text{CO}_2$ , into pressurized, temperature controlled, pure or artificial seawater. The water can be stationary or counter-flowing to the injected  $\text{CO}_2$  droplets or globules. The characteristics, transport

and fate of the injected droplets or globules can be observed with still or movie cameras through the spy windows mounted on the walls of the WTF.

The globulsion was formed in the UML batch reactor, transferred via a ball valve into the WTF, where it was accumulated in a rotating cup. Upon rotation of the cup by 90°, the globulsion poured out from the cup toward the bottom of the WTF, while fast frame pictures were taken for the measurement of globule diameter and settling velocity. A typical photo of a falling globule is shown in Figure 6.

## RESULTS AND DISCUSSION

### (a) Globulsion in High Pressure Flow Reactor

The High Pressure Flow Reactor (HPFR) has been fully assembled, and preliminary tests have been completed. Figure 7 shows a globulsion obtained under the following conditions: 1 L min<sup>-1</sup> 3.5% by weight NaCl solution in de-ionized water containing 150 g L<sup>-1</sup> CaCO<sub>3</sub> (Fisher Chemicals C-64 lab grade) with average particle size 10-15 µm; 0.17 L min<sup>-1</sup> liquid CO<sub>2</sub> at 10 MPa; temperature in flow reactor 12-15°C. The globulsion is collected in a view cell, where the globule diameter, settling velocity and stability can be observed with a video camera. The average diameter of the globules is 250 µm, with most globules distributed in the 200-300 µm range. Some globules are still floating in the water column, but most globules have settled in the bottom of the view cell. The globules remained stable in the view cell for about 18 hours before being evacuated.

The HPFR is a prototype of a globulsion forming device that could be used in actual deep ocean releases of CO<sub>2</sub>. Its advantages are that the HPFR has no moving parts; the mixing of the ingredients is accomplished by virtue of the pressure drop across the Kenics-type static mixer, which in the case of a deep ocean release would rely on the hydrostatic pressure of the CO<sub>2</sub> and CaCO<sub>3</sub> slurry columns that enter the mixer, so no additional pumping is required. The HPFR forms a dense plume that will sink farther from the release point. In such a fashion, the release could occur just below 500 m depth, which is approximately the depth where liquid CO<sub>2</sub> flashes into vapor. This will save the cost and energy of transporting liquid CO<sub>2</sub> to greater depths. In addition, the HPFR produces globules with a narrow diameter distribution that is mainly determined by the size of the CaCO<sub>3</sub> particles. This fact enables the estimation of the settling velocity (“rain-out” rate) of the globules once the dense plume reaches neutral buoyancy in respect to the density stratified ocean water.

### (b) Globulsions in High Pressure Batch Reactor

The new improved High Pressure Batch Reactor (HPBR) has been used to explore various particles for forming a globulsion, including flyash and mineral particles.

#### ***Flyash***

A sample of flyash was obtained from the Salem Harbor Station, Massachusetts, operated by the Pacific Gas and Electric Company. This is a 750 MW power plant with three pulverized coal-fired boilers, and one oil-fired boiler. The flyash sample was obtained from one of the coal-fired boilers. The flyash was collected by an Electrostatic

Precipitator (ESP). The coal is a low-sulfur type of Venezuelan origin. The exact composition has not been established, but reputedly it has a fairly high Loss-on-Ignition (LOI) in the 12 – 18% range. Indeed, the color of the flyash is grey-black, indicating a high carbon content. The consistency of the flyash is that of talcum powder.

We mixed 18 mL liquid CO<sub>2</sub>, 10 g flyash, and 3 g NaCl dispersed in 95 mL water at 15°C, 20 MPa, using the cylindrical magnetic mixing bar with a cross-shape on top of the cylinder. Rotational speed was 1500 rpm. Stable globules were formed, some of them heavier than water, hence they sank to the bottom of the view cell (Figure 8).

This experiment demonstrates that flyash can produce a stable globulsion of CO<sub>2</sub> droplets coated with flyash dispersed in water. The significance of this experiment is that in principle the two major waste streams of coal-fired power plants, CO<sub>2</sub> and flyash, could be sequestered simultaneously, either in the deep ocean or in deep saline aquifers.

Further experiments are planned using various types of flyash with known composition and size distribution. Well-characterized flyash samples will be purchased from the National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) program.

### **Mineral Particles**

The calcite and flyash experiments demonstrated that fine particles in general, and specifically particles that are hydrophilic, produce a CO<sub>2</sub>-in-water (C/W) macro-emulsion, which we call globulsion. Therefore, we conducted experiments with two types of mineral matter: olivine and lizardite. Finely pulverized samples (median size of particles about 10 µm) of these minerals were obtained from the DOE Albany Research Center, Albany, OR, by courtesy of Dr. Steve Gerdemann.

Olivine, (Mg,Fe)SiO<sub>4</sub>. This mineral produced ambiguous results. While the meniscus between the water and CO<sub>2</sub> phase disappeared, the sediment in the bottom of the cell showed no clearly discernible globules. We surmise that this mineral interacts with the CO<sub>2</sub>/H<sub>2</sub>O mixture to form a gelatinous or flocculated phase rather than distinct globules. Also, the hydrophilicity of olivine may not be sufficient to form a CO<sub>2</sub>-in-water (C/W) globulsion.

Lizardite, Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>. This mineral produced a fine, stable globulsion (Figure 9). The mineral powder and the globulsion have a greenish color. Since the mineral is found in abundant quantities, it may be used instead of CaCO<sub>3</sub> to form a globulsion for ocean or geologic sequestration. The mineral is soft (hardness 2.5), so it should be easy to grind into fine powder. Furthermore, the composition is completely non-toxic, so its use for CO<sub>2</sub> sequestration should not engender environmental opposition.

### **(c) Globulsion in NETL Water Tunnel Facility**

During the period July 12 – 23, 2004 globulsion experiments were performed at the DOE/NETL Research Center near Pittsburgh, PA, in the Water Tunnel Facility (WTF), designed and operated by Robert Warzinski. The excellent optical and digital recording systems available at WTF allowed accurate measurements of the diameter, settling velocity, and stability of the globules under various experimental conditions.

So far, we analyzed a limited number of runs in the WTF. The results are summarized in Table I. The optically determined diameters of the four examined globules ranged from 680 to 930  $\mu\text{m}$ . The settling velocities ranged from 0.0094 to 0.012  $\text{m s}^{-1}$ .

Using the Stokes equation  $v_s = \frac{g d_g^2 (\rho_g - \rho_{sw})}{18 \mu_{sw}}$ , where  $v_s$  is the settling velocity,  $g$  is the gravitational constant = 9.81  $\text{m s}^{-2}$ ,  $d_g$  is the globule diameter (assumed to be spherical),  $\rho_g$  is the globule density,  $\rho_{sw}$  is the artificial seawater density at 17 MPa and 12°C (1030  $\text{kg m}^{-3}$ ), and  $\mu_{sw}$  is the dynamic viscosity of the artificial seawater ( $1.567 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$ ), the globules' densities  $\rho_g$  can be derived. The densities range from 1059.7 to 1085.2  $\text{kg m}^{-3}$ , with an average density of 1068.7  $\text{kg m}^{-3}$ . These densities are much greater than that of ambient seawater, so such globules will definitely sink toward the ocean bottom.

We assume the following model for a globule. The inner core consists of a droplet of liquid  $\text{CO}_2$ . The core is surrounded by a monolayer of calcite particles, which we call the sheath. If the particles are crystalline, it can be shown that they occupy 70% of the volume of the sheath. Taking the derived densities of the globules, a density of  $\text{CO}_2$  at the experimental conditions  $\rho_{\text{CO}_2} = 950 \text{ kg m}^{-3}$ , a bulk density of  $\text{CaCO}_3$   $\rho_{\text{CaCO}_3} = 2700 \text{ kg m}^{-3}$ , the  $\text{CaCO}_3$  particle sheath thickness is estimated from 12.3 to 14  $\mu\text{m}$ . This compares well with the average diameter of the Sigma reagent grade  $\text{CaCO}_3$  used in the experiments, namely 12.5  $\mu\text{m}$ .

The globules were kept in the rotating cup for tens of minutes without disintegration. Also, in the laboratory, the  $\text{CO}_2/\text{CaCO}_3$  globulsion was stable for a period of up to 18 hours. This is no guarantee that globules will not disintegrate or dissolve during the long fall toward the ocean bottom, or once reached the bottom, due to wave and sediment action. However, the massive acidification of seawater around the release point predicted when unemulsified, liquid  $\text{CO}_2$  is injected would be ameliorated when a globulsion of  $\text{CO}_2/\text{CaCO}_3$  is released. At the experimental conditions in the WTF, the mass ratio  $\text{CaCO}_3 : \text{CO}_2$  in the globules was on the average 0.2 (see bottom line of Table I). For actual ocean releases of a globulsion, the mass ratio may be different depending on the density of liquid  $\text{CO}_2$  at the depth of release, and the particle size and bulk density of the pulverized limestone to be used. A conservative estimate for a 500 m release with limestone particles in the 10 – 15  $\mu\text{m}$  range is 0.5 tons of pulverized limestone per ton of liquid  $\text{CO}_2$ .

## PLANS FOR THE NEXT PERIOD

### (a) Apparatus additions and modifications

- Purchase and install horizontal microscope for observation of microstructure of globules
- Purchase and install high pressure pH probe on high pressure batch reactor
- Purchase and install Jerguson cell with windows on outlet of static mixer for optical observations of globulsion exiting the mixer



### **(b) Measurements in High Pressure Batch Reactor**

- Investigate the effects of impurities on globulsion formation
  - $\text{H}_2\text{S}$
  - $\text{NO}_x$
  - $\text{SO}_2$
  - Monoethanolamine (MEA) as a representative of chemical absorbents
  - Methylalcohol as a representative of physical adsorbents
- Investigate globulsion formation with various grade and particle sizes of pulverized limestone
- Investigate globulsion formation with various pulverized minerals, e.g. pulverized sand ( $\text{SiO}_2$ ), clay, shale, and repeat experiments with olivine
- Obtain Scanning Electron Microscope (SEM) photos of residual sheath particles after evaporation of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  and compare with SEM of original particles

### **(c) Measurements in High Pressure Flow Reactor with Static Mixer**

- Investigate globulsion characteristics ensuing from static mixer using various grade and particle sizes of pulverized limestone
- Investigate globulsion characteristics ensuing from static mixer using various flyashes and pulverized minerals
- Investigate globulsion characteristics ensuing from static mixer using artificial or real seawater
- Make measurements at low temperatures in the regime where hydrate formation may interfere with globulsion formation

## **CONCLUSIONS**

Research in the preceding contractual periods has shown that stable macro-emulsions (globulsions) can be formed when liquid or supercritical carbon dioxide and pulverized limestone ( $\text{CaCO}_3$ ) are mixed with pure or artificial seawater. Globulsions can be formed in a high pressure batch reactor, or in a continuous flow reactor using a Kenics-type static mixer. Globulsions can also be formed using other pulverized materials, such as flyash or lizardite, a magnesium silicon hydroxide. The characteristics of the globules (their size and density) in the globulsion can be adjusted by varying the temperature, pressure, mixing conditions, and especially, particle size and characteristics. The laboratory experiments can be used for the prediction of the behavior of a globulsion plume released in the deep ocean.

## **PUBLICATIONS**

D. Golomb, E. Barry, D. Ryan, C. Lawton, P. Swett, D. Arora “Limestone Emulsion to Alleviate Concerns about Deep Ocean Storage of  $\text{CO}_2$ ” Poster paper presented at the Second Annual Conference on Carbon Sequestration, Alexandria, VA, May 5-9, 2003.

D. Golomb, E. Barry, D. Ryan, C. Lawton, P. Swett "Limestone Particle Stabilized Macro-emulsion of Liquid and Supercritical Carbon Dioxide in Water for Ocean Sequestration," *Environmental Science and Technology*, **38**, 4445-4450, 2004.

P. Swett, D. Golomb, E. Barry, D. Ryan, C. Lawton "Liquid Carbon Dioxide/Pulverized Limestone Globulsion for Deep Ocean Storage," Poster paper presented at the 7th International Conference on Greenhouse Gas Control Technologies, GHGT-7, Vancouver, BC, Canada, Sep 5-9, 2004.

## TABLES AND ILLUSTRATIONS

Table I: Globule Diameter, Settling Velocity, and Density From NETL WTF measurements

	Globule #1	Globule #2	Globule #3	Globule #4	Average of Calculation
Settling Velocity (m/s)	0.012	0.010	0.0099	0.0094	---
Diameter (mm)	0.93	0.86	0.68	0.89	---
Globule Density (kg/m <sup>3</sup> )	1065.4	1064.5	1085.2	1059.7	1068.7
Sheath Thickness (μm)	14.0	12.9	12.3	12.8	13.0

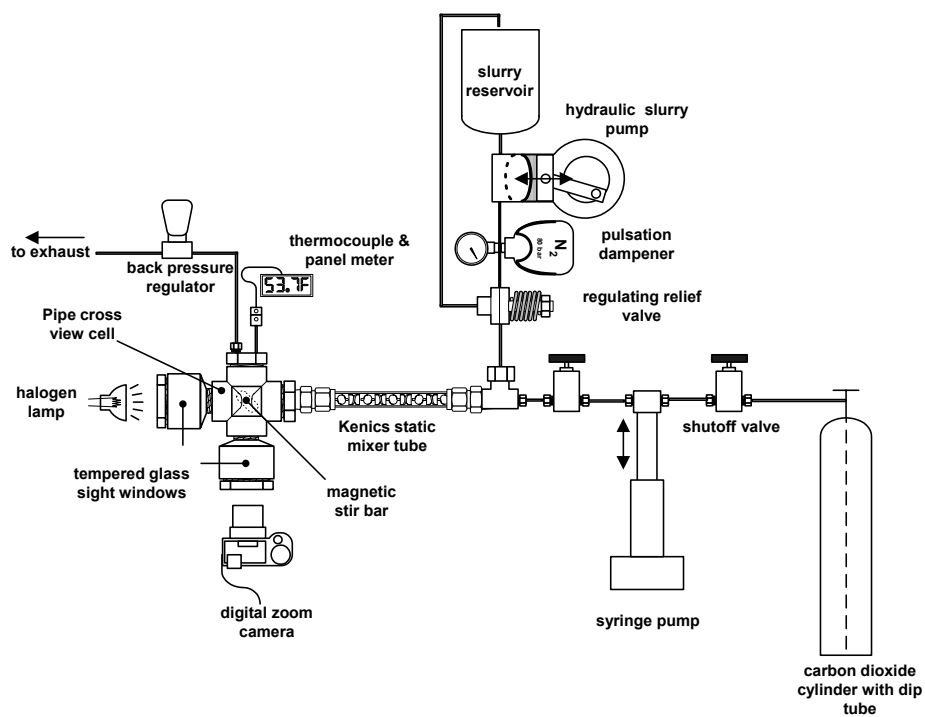


Figure 1: High Pressure Flow Reactor with Static Mixer

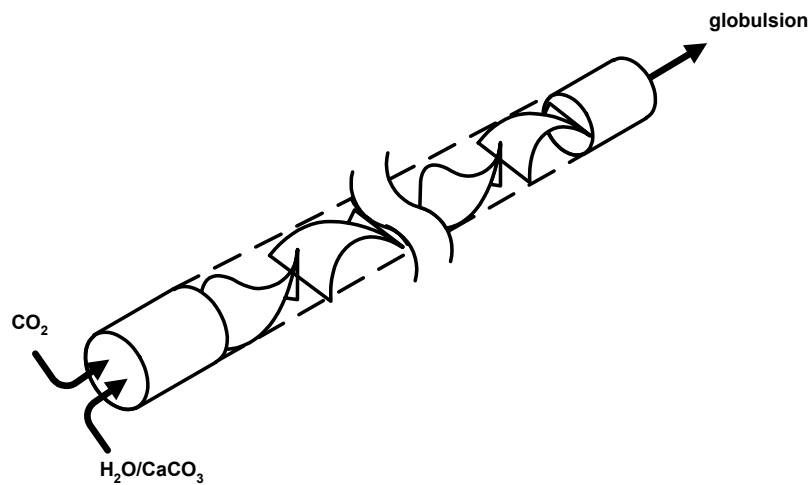


Figure 2: Kenics-Type Static Mixer

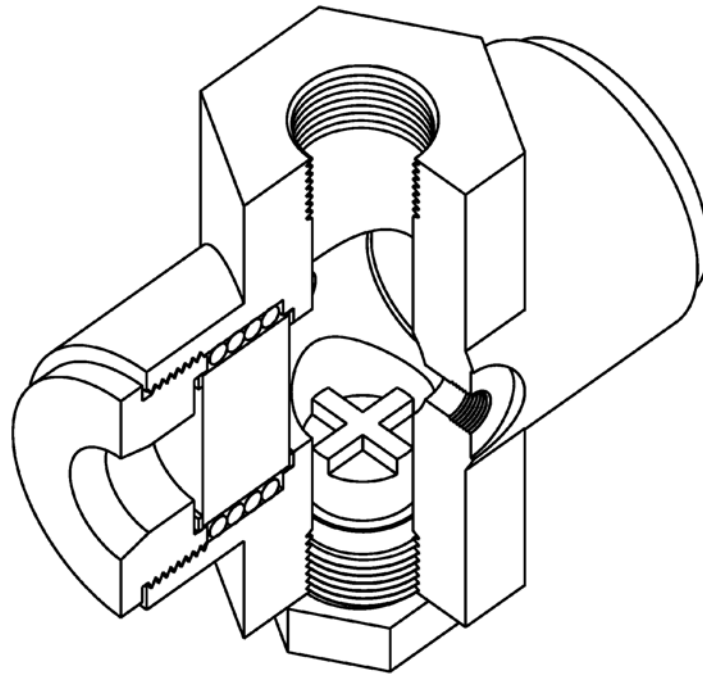


Figure 3: Modified Design of High Pressure Batch Reactor

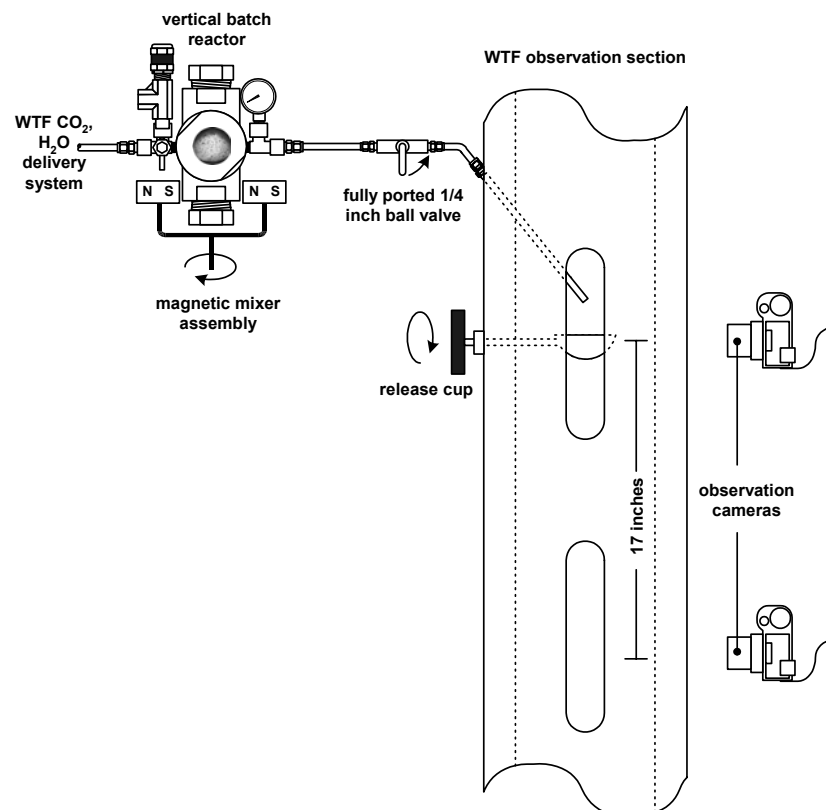


Figure 4: Interconnection of High Pressure Batch Reactor and NETL Water Tunnel Facility



Figure 5: Photograph of HPBR/WTF Setup

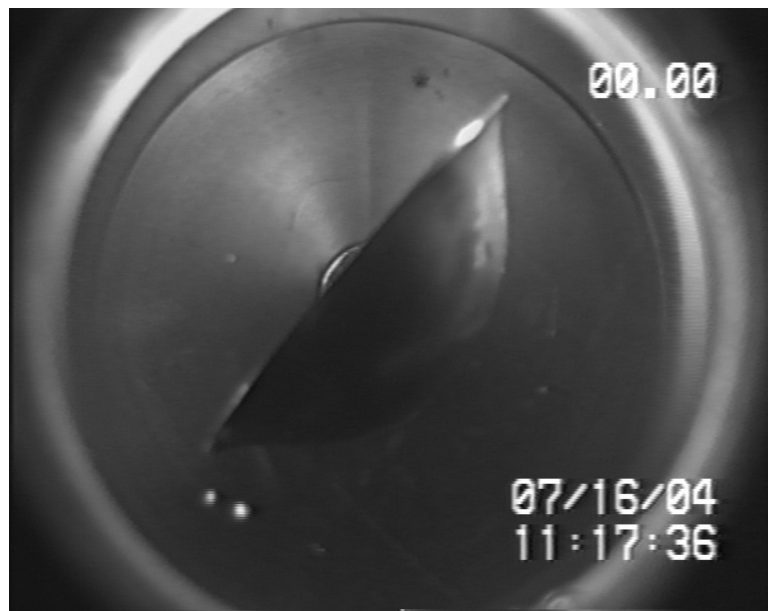


Figure 6: Globule Release Still Frame

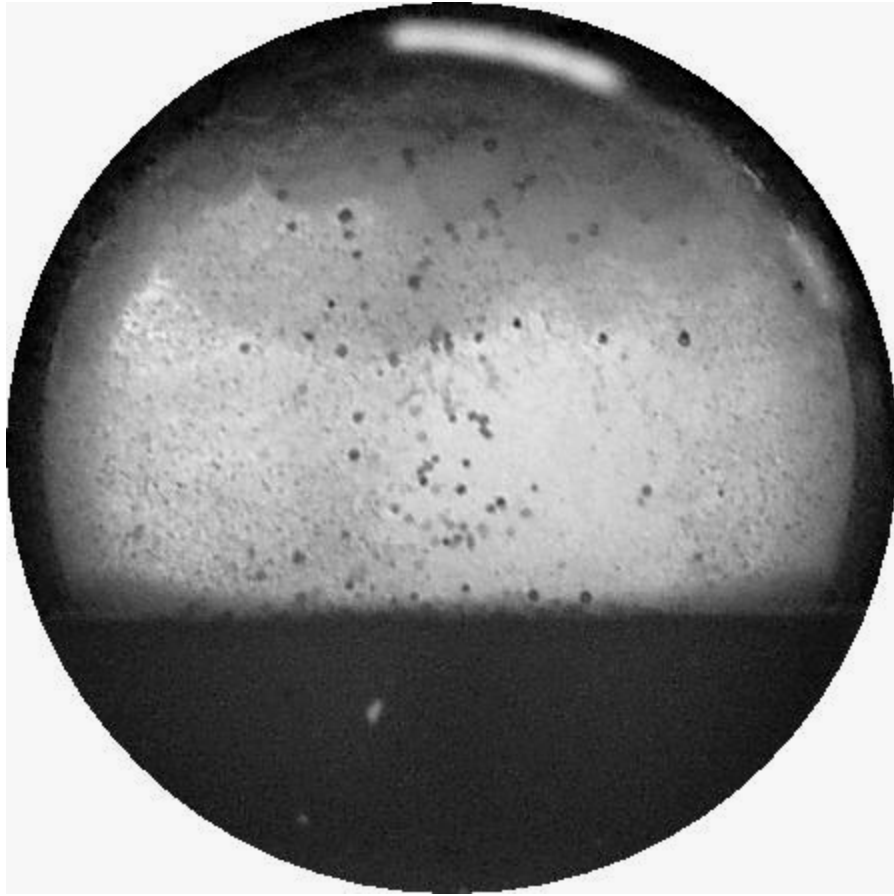


Figure 7: Globulsion Produced by High Pressure Flow Reactor with Static Mixer

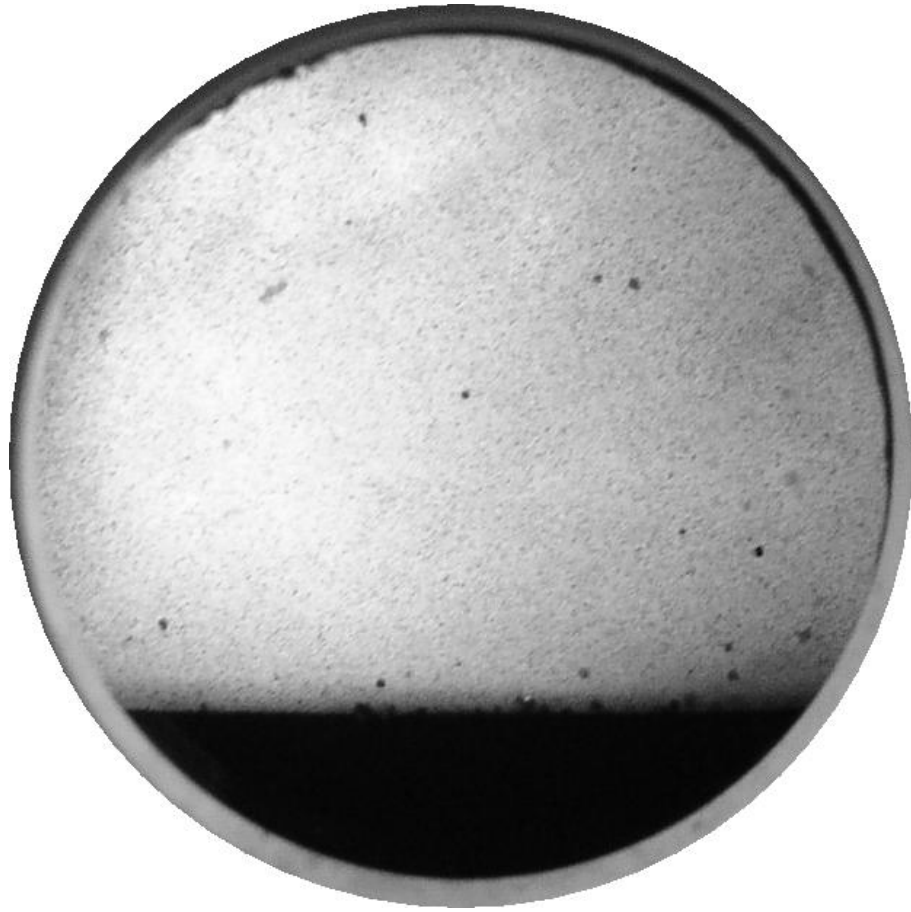


Figure 8: Flyash Globulsion

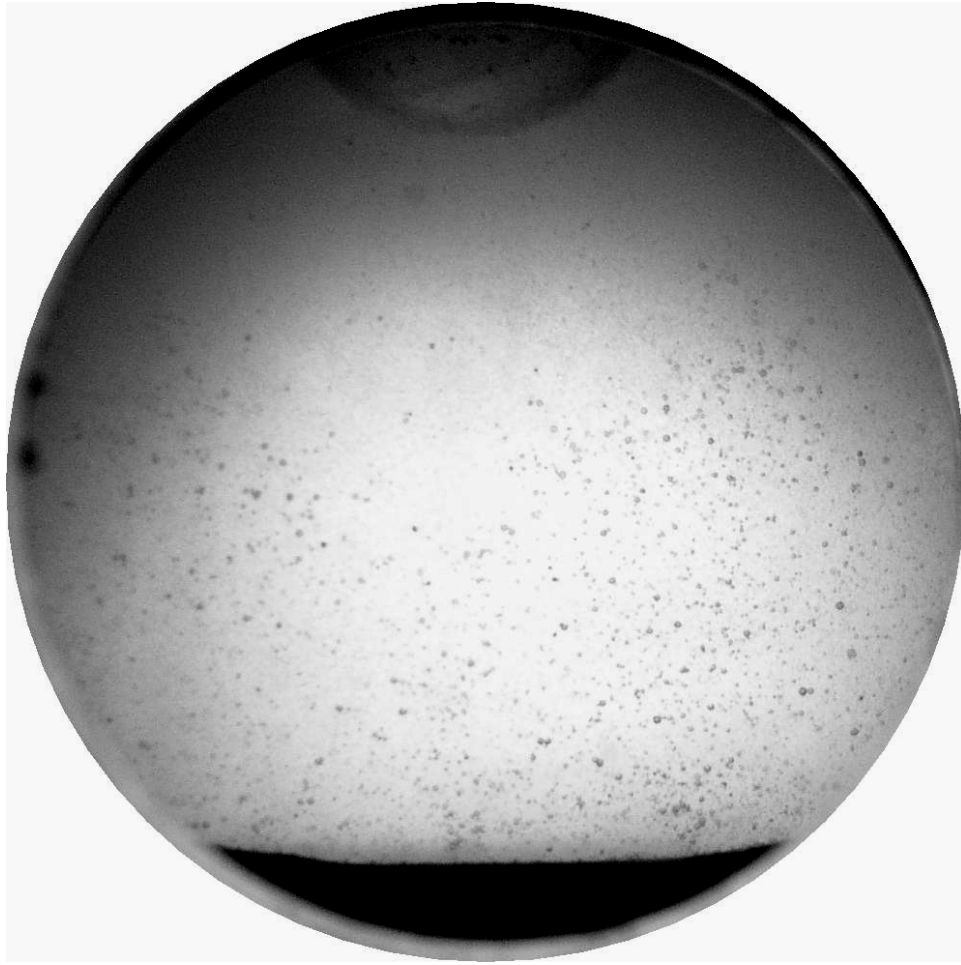


Figure 9: Lizardite Globulsion