

Oil & Natural Gas Technology

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Quarterly Report January 2010– March 2010

Post Retort, Pre Hydro-treat Upgrading of Shale Oil



Submitted by:
Ceramatec Inc
2425 S. 900 W.
Salt Lake City, UT 84119

Prepared by: John H. Gordon, PI

Prepared for:
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National Energy Technology Laboratory

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EXECUTIVE SUMMARY

Analytical capability was established and the reactor was configured to operate anhydrously using hydrogen sulfide by the end of the 2nd quarter so that in the 3rd quarter we may begin to run relevant shale oil treatments and characterize the outcome. In addition the installation and commissioning of a drybox in the 2nd quarter will enable us to begin electrolysis of polysulfides in the 3rd quarter.

Methods were investigated to synthesize alkali metal polysulfides. Conclusion was reached that the simplest method was to electrochemically synthesize the material from sulfur and the alkali metal across an alkali metal ion conductive membrane.

A senior chemical engineer was recruited to lead the development effort on the electrochemical side. He began midway through the second quarter and picked up the effort that had already begun.

Expenditures to date are lagging somewhat that of planned running about 70% cumulative by the end of the 2nd quarter but are expected to further approach the plan in the 3rd quarter.

PROGRESS, RESULTS, DISCUSSION

Task 1.0: Project Management Plan

The PMP was updated within 30 days and submitted to the Project Manager (Quarter 1).

Task 2.0: Upgrading Development

This task is related to developing the process of treating shale oil, or heavy oil at elevated temperature and pressure in the presence of an alkali metal, either sodium or lithium and also a hydrogen source, either hydrogen gas or methane (natural gas) to form an oil stream with reduced levels of sulfur, nitrogen and heavy metals and also in the process reducing the viscosity and increasing the API gravity. The object here is to determine the impact of various reaction parameters on product quality.

Sub task 2.1: Analytical Capability

Analytical Laboratory Set up

The list of major analytical instruments that Ceramatec has procured and successfully installed is shown in Table 1.

Table 1: Major analytical instruments installed

Instrument	Description	Purpose
Inductive coupled plasma	Perkin Elmer 7000DV	To measure metals such as As, Co, Fe, Hg, Mo, Ni, Sb, Se, V and Zn
Elemental CHNS	Perkin Elmer 2400	To measure C, H, N, and S
GC – simdist	HP Agilent 7890	Simulated distillation curves of shale oil before and after treatment
GC – gas phase	HP Agilent 7890	Gas phase composition – C1 through C6 lower hydrocarbons, ammonia
API hydrometer		API gravity measurement
TAN titration		Total acid number measurement

Sub-task 2.2: Upgrading Reactor and Separation setup

The experimental apparatus set up is complete. The laboratory area has been completely modified to safely handle hydrogen sulfide. Primary and secondary enclosures have been provided for safe operation of the reactor. The laboratory has primary and secondary ventilation, both connected to back up power supply. Monitors and alarms were installed. Documentation involving operating procedure, start-up and emergency shut-down procedure were completed. A detailed hazard analysis (HAZOP) study was conducted. Necessary recommendations were incorporated. The reaction set up is now operational. The reactor setup includes a Parr® 0.5 Liter reactor and the separation is performed using centrifuge (Thermo-scientific Sorvall®).

Red Leaf, a shale oil development company in Utah, has provided a large fresh sample from their slow, low temperature surface retort process. These sources are sufficient to last through phase 1 of the research.

Schedule

The progress of Task 2 is as per schedule. The two milestones of Analytical Laboratory set up and Experimental set up have been reached ahead of schedule as shown in milestones log below.

Task 3.0 – Electrolysis Development

Comment [M1]: Javier, pl add your updates under task 3.0

To reduce the overall cost of the upgrading process, an electrolysis process will be developed to regenerate sodium or lithium from the respective polysulfide. The process will feature ceramic ion conductive membranes developed at Ceramatec. The energy cost to regenerate the alkali metals from the polysulfide is expected to be about half that of producing the metals from their respective chlorides.

Subtask 3.2 – Seal testing

Ceramatec shall evaluate various seal approaches for compatibility with the alkali metal and the metal polysulfide at various temperatures.

No work was conducted specifically on this task.

Subtask 3.3 – Cell design and set up

Ceramatec shall design benchtop cells for two types of operation, one where the alkali metal is molten and one where it plates onto a current collector. Reactors and catholyte transfer means will be provided to prepare alkali metal sulfide of differing composition and transfer to the cell. The cells will be designed to accommodate multiple reference electrodes, operate at various elevated temperatures. The cells will have features designed to facilitate sulfur removal and be designed to operate within a dry enclosure.

Dry Box Installation in Lab 214

A dry box for working with water sensitive materials, such as sodium metal, lithium metal and sodium and lithium polysulfides, has been ordered and installed in Lab 214. Ceramatec's house dry supplied air (-40 C dew point) is treated by a regenerative desiccant system to further reduce the inlet air moisture. After conditioning the box for a few days, a dew point of -80 C was reached inside the chamber and antechamber sections of the dry box. This level is more than acceptable for all the operations that will be conducted inside the dry box. Figures 1 and 2 show the chamber and the air supply system, respectively.



Figure 1. Picture of dry box installed in Lab 214



Figure 2. Picture of air supply system with regenerative desiccant air drier system

Process Hazard Analysis

A Process Hazard Analysis (PHA) to identify potential safety hazards and to remediate or minimize their impact was conducted for the dry box. The PHA also included the safety analysis of all the aspects of the work that the researchers will be performing inside the chamber. These include the handling of chemicals, assembly and operation of electrochemical cells, introduction and extraction of objects to and from the dry-box, and others.

Subtask 3.4 – Cell operation

The Recipient shall operate cells under various conditions including variation of the current density, electrode gap, temperature, electrolyte, polysulfide order, and alkali metal. Current will be measured as a function of applied voltage. Periodically cell operation will be interrupted and cell contents analyzed to determine current efficiency. In Phase 1 the alkali metal polysulfide will be synthesized from alkali metal and sulfur and will not contain appreciable impurities which may flow through from an actual upgrading process as will occur in Phase 2.

Synthesis of Polysulfide Compounds in Solution Using Na-S or Li-S Batteries in Discharge Mode

A survey of different methods to synthesize sodium polysulfide from its basic constituents was conducted. The conclusion is that the simplest method, and the one which gives the purest products, has been found to be the controlled discharge of sodium sulfur or lithium sulfur batteries. The battery consists of a sulfur-carbon cathode and a sodium or lithium anode separated by a sodium or lithium ion conductive membrane. As the battery is discharged, the alkali metal is oxidized in the anode electrode and the alkali ions travel across the solid electrolyte. At the same time, the sulfur cathode is reduced and the alkali polysulfide compounds are formed and dissolved in the catholyte compartment. By properly selecting the voltage of the discharged electrical current is possible, in principle, to control the amount of sulfur (x) in the alkali polysulfide blend (Na_2S_x). A polar organic solvent with a relatively high vapor pressure, such as tetraethylene glycol dimethyl ether (tetraglyme), is used as catholyte to dissolve the polysulfides formed. Figure 3 shows the sulfur sodium battery, fitted with a circular 1.5" in diameter Nasicon sodium ion selective membrane, assembled to synthesize small batches of sodium polysulfide. Samples obtained by this method will be used with early proof-of-concept cell prototypes to study the effect of critical operating parameters in the efficiency of the alkali metal recovery process. However, the small volume of the battery's catholyte compartment and the relatively long batch times (100 to 300 hours) significantly limits the amount of polysulfide solution that can be made available by this method.

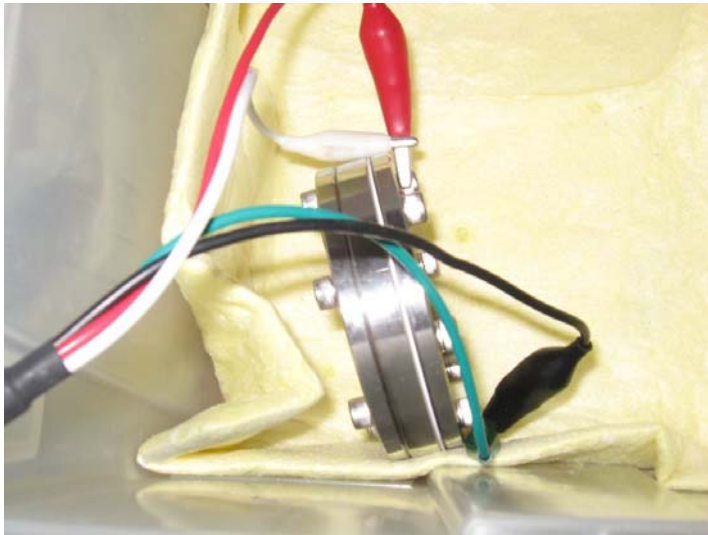


Figure 3. Sulfur sodium battery to synthesize sodium polysulfide

Study of Stability of Catholyte/Anolyte Solvents

The electrochemical stability of a preferred catholyte/anolyte organic solvent (e.g. tetraglyme) under a range of applied DC voltages has been studied. Samples of tetraglyme and a solution of 1M NaI in tetraglyme were added to a glass flask with two Nickel electrodes. The electrodes were connected to the positive and negative leads of a battery tester, where a voltage sweep was applied. Figures 4 and 5 show the measured DC current versus the applied DC voltage for Tetraglyme alone and Tetraglyme +1 M NaI solution, respectively. In both cases, it can be observed that the current measured through the cell, in the expected voltage range of interest (0-4 VDC), is insignificantly small as compared to the large current densities that a large scale alkali metal electrolytic recovery process (up to 100 mA/cm²) would require. Therefore, Tetraglyme seems to be a stable solvent appropriate for the application.

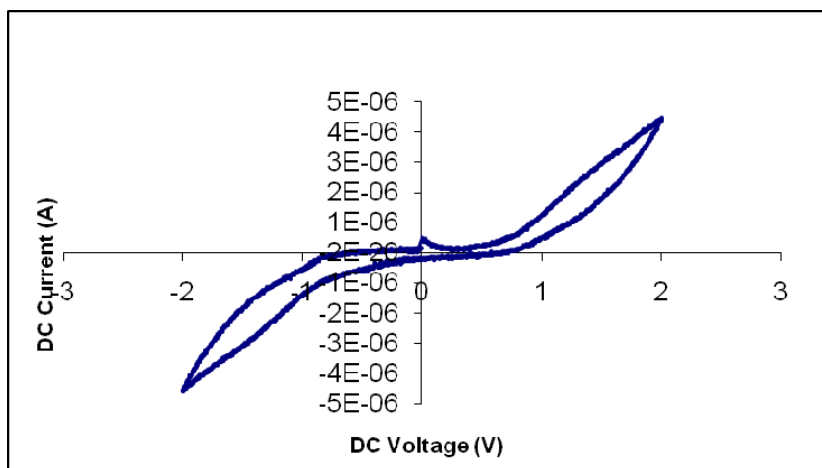


Figure 4. Measured DC current vs. applied DC voltage for Tetraglyme solvent at ambient temperature

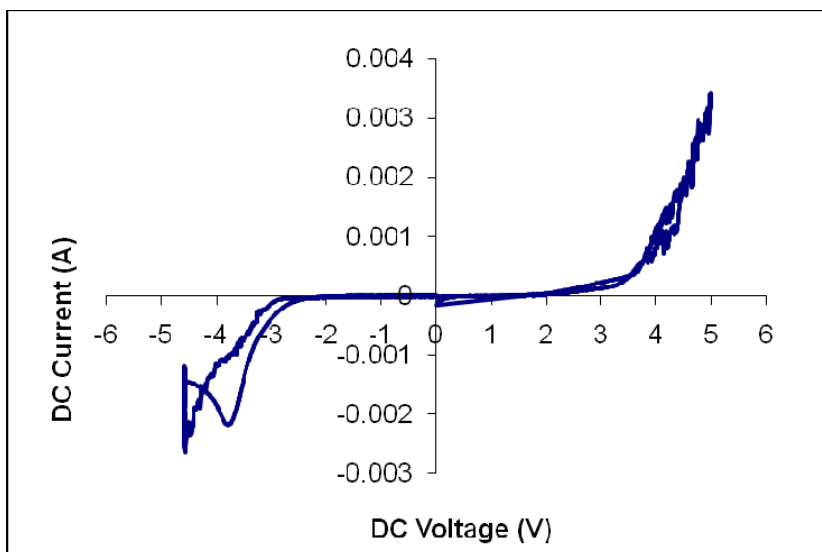


Figure 5. Measured DC current vs. applied DC voltage for a solution of 1M NaI in Tetraglyme at ambient temperature

Review of Analytical Techniques to Characterize Mixtures of Polysulfides in Organic Solvents

A literature survey of available analytical methods to characterize and quantify the composition of mixtures of alkali metal polysulfides in organic solvents has been started. Techniques such as X-Ray Fluorescence Spectrometry, H-NMR, Ion Chromatography, Colorimetry, and Potentiometry have been used with more or less success in the past. Liquid Ion Chromatography methods that combine ionic separation with quantification, via electrochemical techniques, might be the

best option. Dionex Corporation has been contacted to evaluate if one of their Liquid Ionic Chromatographic instruments (ICS-3000 ED with Electrochemical Detector) would be appropriate for this application. Also a potentiometric technique, that uses a sulfide ion selective electrode as measuring electrode, could be proved useful as a rapid and inexpensive way to qualitatively determine the average sulfur composition (x) in the polysulfide mixture (M_2S_x).

Task 4.0 – Analysis

Subtask 4.1 – Develop upgrading process model

Ceramatec shall evaluate several process variables in Task 2 which will impact the effectiveness of impurity removal, saturation, coking, and alkali metal utilization. In addition, the shale oil source and initial composition is likely to be a factor. Extent of hydrogen donation gas added and presence of hydrotreating catalyst will affect the extent of upgrading. A preliminary model based on the data from Task 2 will be constructed.

No progress on this task to date.

Subtask 4.2 – Develop electrolysis process model

Ceramatec shall analyze data from Task 3 and a performance model will be developed. Various factors such as membrane thickness, type of alkali metal, electrode configuration and cell design would be included in the model considerations.

No progress on this task to date.

Subtask 4.3 – Preliminary cost analysis

The Recipient shall incorporate the models from Subtasks 4.1 and 4.2 into a preliminary cost model. Based on the preliminary cost analysis, a selection will be made between sodium and lithium as the most promising alkali metal for further pursuit in Phase 2.

No progress on this task to date.

Task 5.0 – Reporting

The 2nd Quarterly Report is presently submitted.

CONCLUSION

Our conclusion at this point is that the program has been kicked off, underway, and at an early stage of the work plan.

COST STATUS

Comment [M2]: John has access to these numbers?

The monthly costs of the 1st quarter are shown in Table 2, along with the projected costs stated in the Project Management Plan.

Table 2. Project costing profile for the 2nd Quarter

	Jan-10		Feb-10		Mar-10		Q2		
	Projected	Actual	Projected	Actual	Projected	Actual	Projected	Actual	
Direct Labor		26,538.48		31,136.78		37,419.31		95,094.57	
Benefits	32%	8,492.31		9,963.77		11,974.18		30,430.26	
Overhead	41%	10,880.78		12,766.08		15,341.92		38,988.78	
Total Burdened Labor		45,911.57		53,866.63		64,735.41		164,513.61	
Direct Materials / Spec Test		31,592.46		190,805.06		127,880.93		350,278.45	
Equipment		-		-		-		-	
Travel		53.52		846.80		1,223.01		2,123.33	
Subtotal		77,557.55		245,518.49		193,839.35		516,915.39	
G&A	29%	22,491.69		71,200.36		56,213.41		149,905.46	
Total monthly		228,156.81	100,049.24	219,985.58	316,718.85	89,345.45	250,052.76	537,487.84	666,820.85

Our costs in the 2nd quarter were higher than the projection because there was a lag in ordering equipment in the 1st quarter. Approximately \$60,000 of materials and equipment were on order at the time of this report writing. Overall the project was behind in spending by approximately 70% over the first 4 months but is now only 30% behind in spending.

Figure 6 shows a plot of the total monthly costs and the initially projected costs versus time and figure 7 shows the cumulative monthly costs versus time. Also shown in figure 7 is the fraction of actual over planned cumulative expenses.

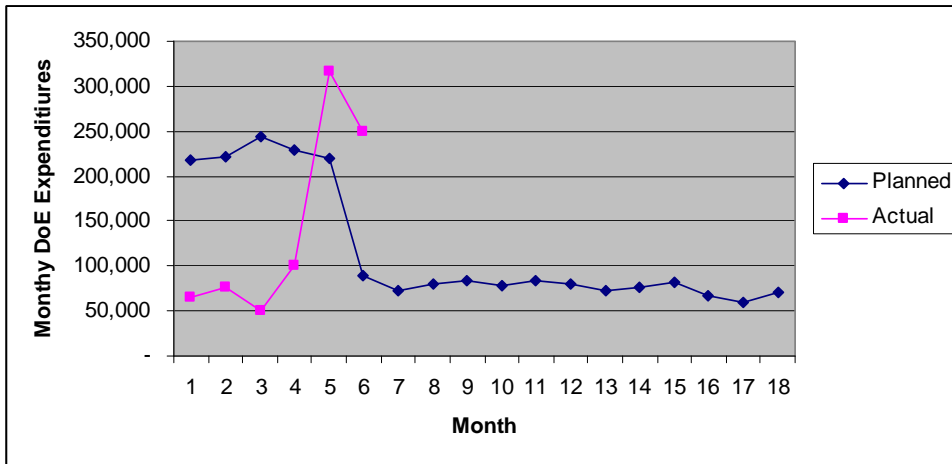


Figure 6: Projected and actual monthly costs over time

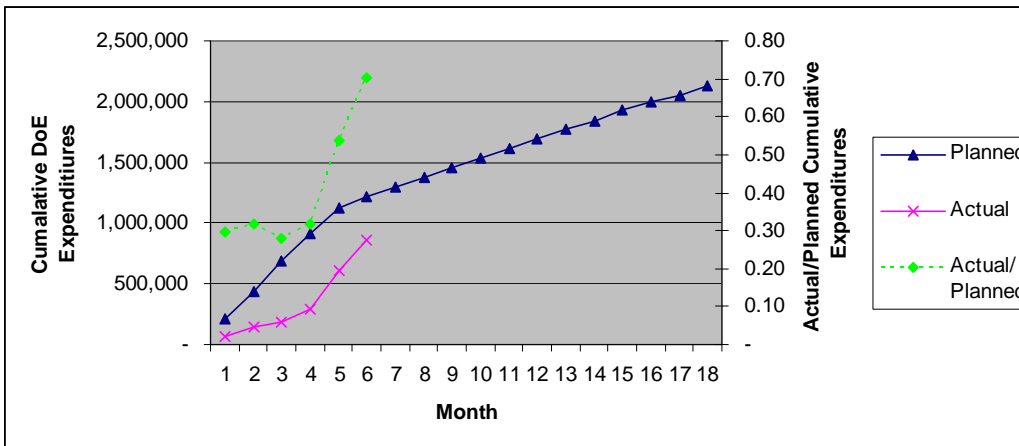


Figure 7: Projected and actual cumulative costs over time

MILESTONE STATUS

Table 3: Milestone log for 2nd Quarter

Milestone No.	Task / Sub-task	Project Milestone Description	Planned Start Date:	Planned End Date:	Actual Start Date:	Actual End Date:	Comments
1	1	Updated PMP	9/29/09	10/29/09	9/29/09	10/26/09	
2	2.1	Analytic capability established	9/29/09	3/1/10	9/29/09	3/23/10	Analytical capability has been established as stated in the PMP. Operators have been trained on GC. ICP and CHNS are operational
3	2.2	Complete upgrading exp. Setup	9/29/09	3/29/09	9/29/09	3/26/09	Upgrading set-up has been completed including HAZOP and pre-start up safety review. The reactor set up has been ready to be operational as of Friday, March 26, 2010.
4	2.3	Complete process runs	3/30/10	1/3/11			
5	3.1.1	Complete membranes for Phase 1	9/29/09	7/5/10	9/29/09		
6	3.3	Cells ready for operation	4/13/10	2/28/11			<p>Installed dry box in Lab 214.</p> <p>Completed PHA hazard review process for all operations inside glove box.</p> <p>Implemented a method to synthesize sodium polysulfide by running S-Na batteries in discharge mode.</p> <p>Studied electrochemical stability of tetraglyme.</p>
7	4.3	Preliminary cost model complete	2/8/11	3/14/11			

Milestone 1 was completed in the 1st quarter. No other milestones were scheduled.

ACCOMPLISHMENTS

- ✓ Analytical laboratory set up is complete.
- ✓ Laboratory modification is complete
- ✓ Experimental set up is complete.
- ✓ Recruited Personnel joined and started working on the project.
- ✓ Installed a glove box in Lab 214 to handle water sensitive materials. Completed PHA hazard review for operation of glove box.
- ✓ Successfully implemented a method to synthesize sodium polysulfides by electrochemically reacting sodium metal with sulfur across a Nasicon membrane.
- ✓ Studied electrochemical stability of Tetraglyme.

PROBLEMS OR DELAYS

There is no significant problem at this point other than the program started slowly. We still expect to meet the milestone schedule. All the necessary resources are available to perform rapid experimentation in the third quarter.

PRODUCTS

No products to report at this time.

National Energy Technology Laboratory

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880

13131 Dairy Ashford, Suite 225
Sugar Land, TX 77478

1450 Queen Avenue SW
Albany, OR 97321-2198

2175 University Ave. South
Suite 201
Fairbanks, AK 99709

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