

Oil & Natural Gas Technology

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Post Retort, Pre Hydro-treat Upgrading of Shale Oil



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None

EXECUTIVE SUMMARY

Ceramatec was awarded a grant by the National Energy Technology Laboratory (NETL), Department of Energy (DOE) to conduct a project titled: *Post Retort, Pre Hydro-treat Upgrading of Shale Oil*. After the program award October 2009, activity began. There are 2 primary areas of the technology development. In the first primary area, a process will be developed which utilizes an alkali metal in combination with limited hydrogen or methane to promote desulfurization, denitrogenation, and demetallization of shale oil or heavy oil streams not suitable for refining prior to treatment. In the second primary area an electrolysis process will be developed to regenerate the alkali metal and separate sulfur and metals. Alkali metal conductive ceramic membranes will be utilized in the electrolytic process.

Since this was the first quarter of the program, the focus has been to assemble the team and setup the laboratory. 2 new positions were created as a result of the award. The recruiting process was initiated and 2 new personnel have accepted offers to join the team in the next quarter. A laboratory was selected for this program and preparations began to transform the lab for the specific requirements of this program including moving equipment out equipment used for other programs. Planning the laboratory layout, ordering cabinets, ventilation apparatus, and equipment. In addition, analytical equipment needed to conduct the experiments has been ordered.

Two members of the team, John Gordon (PI) and Mukund Karanjikar attended the Oil Shale Symposium at the Colorado School of Mines in October which provided an excellent opportunity to discuss with parties about the technology and obtaining commitments for providing samples for testing.

A program kick-off meeting was held at the NETL office in Sugarland, TX on November 17, 2009 where John Gordon was provided an opportunity to meet with the Program Manager and other individuals in the office and to provide a presentation on the development program. The program currently is on schedule.

The program expenses were much lower in the 1st quarter than planned but they are expected to substantially catch up in the 2nd quarter as equipment orders are placed.

PROGRESS, RESULTS, DISCUSSION

Task 1.0: Project Management Plan

The PMP was updated within 30 days and submitted to the Project Manager.

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

To decrease the turnaround time of obtaining analytic results necessary for determining the quality of the oil product after a treatment, Ceramatec has ordered a CHNS analyzer for Carbon, hydrogen, nitrogen and sulfur analysis and an Inductive Coupled Plasma (ICP) analyzer to be used for determining the heavy metals content in the oil before and after treatment. A systematic process consisting of seeking multiple quotes, assessing technical merits and performing cost-to-benefit analysis of each vendor was followed. Both these instruments are ordered from Perkin-Elmer. The model of CHNS analyzer is CHNS 2400 and that of ICP is Optima 7000 DV. Both these instruments are expected to be delivered by second week of January.

An online gas chromatograph for measuring gas composition of the gas phase stream vented from the reactor will be ordered in the first week of January. An off-line gas chromatograph consisting of Simulated Distillation software would also be ordered shortly.

Sample Analysis at Vendor Location

Two different samples; San Joaquin Heavy oil (supplied by Chevron Corp) and Shale oil (supplied by Oil Shale Exploration Co of Utah, OSEC, ATP Retort Process) were sent out for CHNS and ICP analysis to prospective vendors. All the samples were sent out in triplicate and the vendors were instructed to run each sample a minimum of three times to minimize measurement errors. While the primary goal of the program is to develop a process for Shale Oil, initially few large samples could be obtained. But heavy oil could readily be obtained and has some similar characteristics to shale oil in that there is nitrogen, sulfur and heavy metal content that must be removed.

Sub-task 2.2: Upgrading Reactor and Separation setup

The experimental apparatus is being set up. The process flow diagram of the experimental set up is shown in Figure 1. Figure 2 shows the laboratory lay-out for the upgrading work. The laboratory area is being modified in order to safely handle hydrogen sulfide. Primary and secondary enclosures are being provided for safe operation of the reactor. A material take-off sheet has

been prepared and most of the items have been ordered. Documentation involving operating procedure, start-up and emergency shut-down procedure are being prepared. A detailed hazard analysis (HAZOP) study will be performed early next month.

Red Leaf, a shale oil development company in Utah, has offered to provide a large fresh sample from their slow, low temperature surface retort process but shipment has not been confirmed. These sources are sufficient to last through phase 1 of the research.

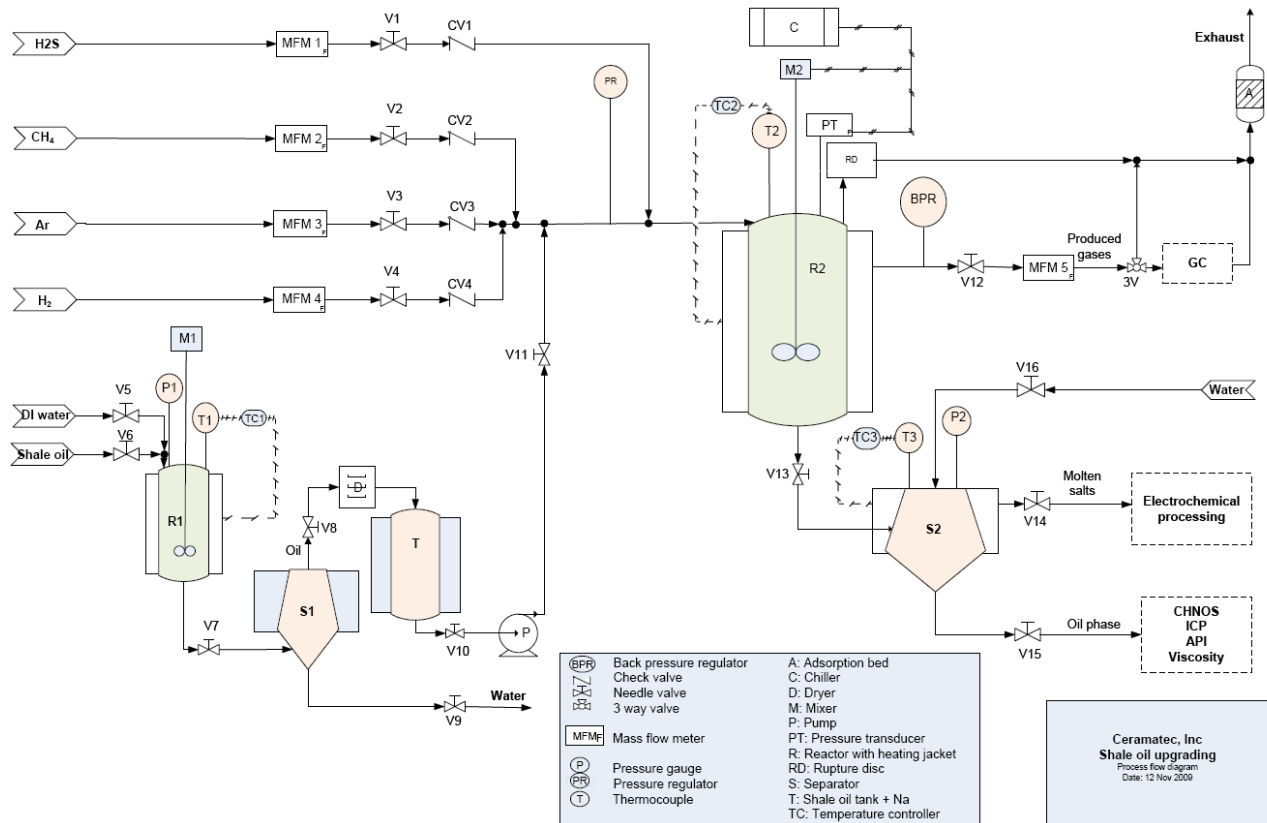


Figure 1: Upgrading Process Flow Diagram

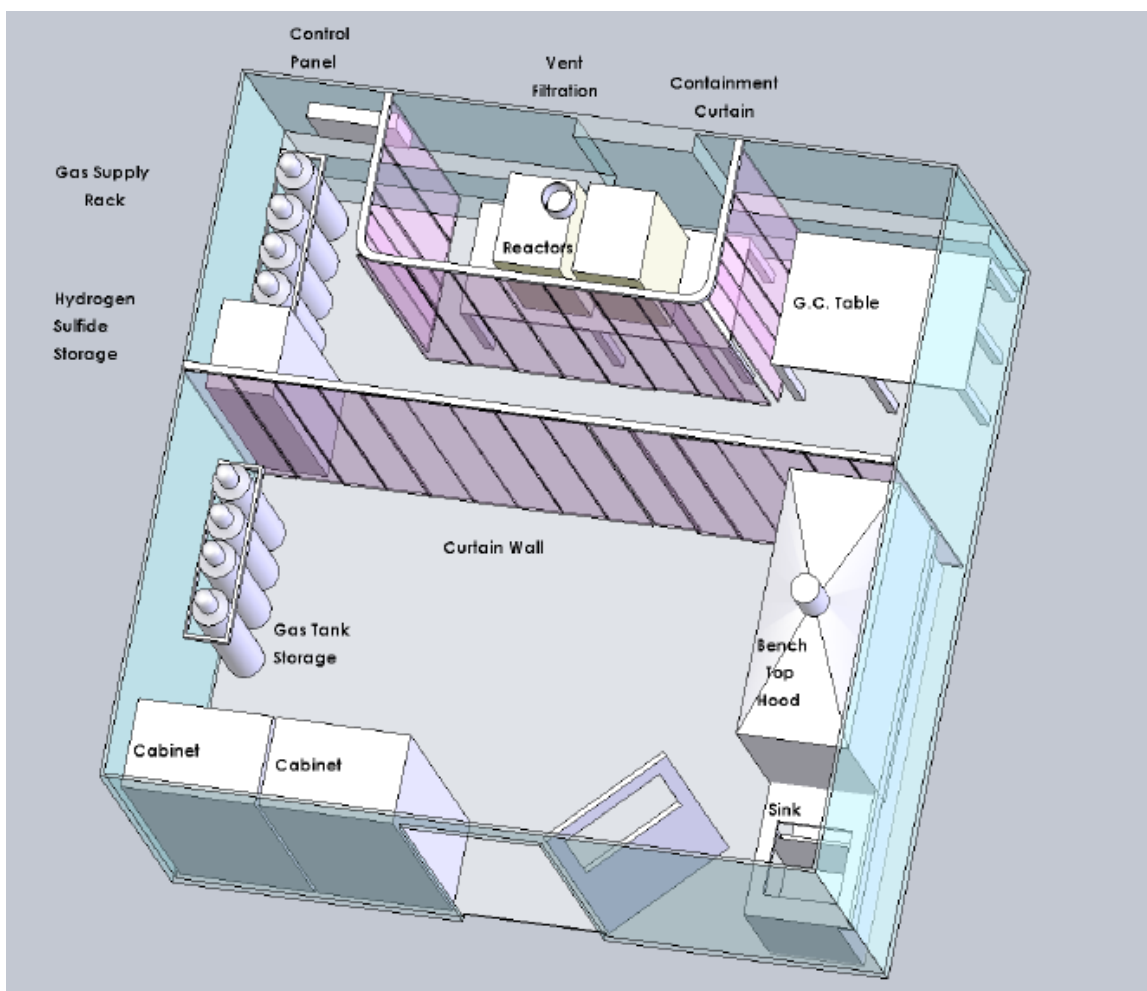


Figure 2: Laboratory Lay out

Schedule

The progress of Task 2 is as per schedule. The two milestones of Analytical Laboratory set up and Experimental set up will be reached on or before the scheduled period of 5 months and 6 months respectively.

Task 3.0 – Electrolysis Development

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 3.1 – Membrane fabrication

Ceramatec shall fabricate at least 20 sodium conductive and at least 20 lithium conductive membranes. In some cases the membranes will be coated to improve compatibility with the alkali metal.

Work has been focused on improving the fitness of Lisicon membranes.

Non-porous sodium conductive membranes have been achieved but the lithium conductive membranes have not reached that level of development. In this quarter sodium conductive ceramic powders were milled to two particle size distributions so that they may be combined together with improved unsintered (green) packing and then reduced porosity after sintering.

Also, to reduce electronic conductivity and chemical stability of the membrane in direct contact with lithium 3 quotations have been obtained for applying a thin lithium phospho-oxy-nitride (LiPON) to the Lisicon membranes.

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.

Lab space

Lab 214 within Ceramatec has been designated as the lab in which the majority of the work for this program will be performed. The lab has been cleared of all other project equipment. The floors were re-surfaced and the walls were painted. The lab is currently ready for project occupancy.

We have designed the layout of the lab for increased functionality. Cabinets are ordered and will be installed at the end of January. We have ordered a fume hood that is a benchtop hood for safety and protection of the personnel. We have identified an anticipated equipment list, including tools, balances, hot plates, etc. that will be required for use during this research project. Many of these items have been ordered for use. The lab will be equipped with a “dry box” for working with water sensitive materials. Ceramatec’s house supplied air with a typical dew point of -40C has been determined to be dry enough for use with these materials in a safe and effective

manner. Desiccant canisters will serve to additionally dry the incoming air in the event of process upsets. Lab 214 is equipped with house air supply lines.

Fabrication of electrochemical test cells

We have designed a test cell setup for quickly ascertaining the viability of Na ion removal from a sodium polysulfide within an organic electrolyte. These cells are designed to accommodate a Nasicon or a Lisicon membrane, and a small volume of anolyte and catholyte. The cells will initially be using stainless steel cathodes and anodes, but can accommodate other materials as well, such as pure Ni, Cu, etc. These cells will allow us to do some baseline testing of the proposed Na or Li stripping for electrochemical recovery of these metals.

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.

Initial Testing of Nasicon Stability in the presence of Molten Na

Three potential operating temperatures were identified for this program; however, only one of them (110°C) is hot enough to cause the metallic sodium to be in a liquid form and metallic lithium will never be molten. During the electrolysis process, Na ions removed from the heavy oil will be stripped for recycling, and at an operating temperature of 110°C, it is possible, depending on cell design, that molten sodium will be in contact with the Nasicon ceramic separator. Therefore, characterization of the stability of the Nasicon membrane in the presence of molten sodium is required. Due to the reactivity of Na metal with moisture and with oxygen when in the molten state, we must use a glovebox with less than 10 ppm of combined oxygen or water present to work with this material. Ceramatec has two gloveboxes in which this experiment could be performed.

To quantify the stability of the Nasicon membrane in the presence of molten Na, we setup an experiment in which molten Na was placed on both sides of a ceramic membrane. A picture of the experimental setup is shown in Figure 3. A Pt wire anode (having a large surface area) was placed into the center of a quartz tube along with some molten Na metal (@120°C). A NaSICON (GY type) was epoxied to the end of the tube, which was then cured at 150°C for 24 hours. This not only cures the epoxy resin, but it also served to drive out any residual water contained within the ceramic piece. After curing, a leak test was performed to ensure that there were no holes or cracks in the ceramic that the Na metal could pass through. The dried sample was then transferred into the glovebox for assembly into the cell. As mentioned, a pool of Na metal at 120°C was placed on either side of the ceramic membrane. The counter electrode was a Ni wire in the form of a coil for increased surface area. A jacketed flask was wrapped in heat tape and brought to 120°C to ensure even heating throughout the experiment.

The Arbin battery tester leads were attached to the Pt and Ni wires, and a constant current of 50 mA/cm² was applied to the cell. The voltage as a function of time was recorded. After a 4-hour

period the current direction was reversed to drive the Na ions across the NaSICON membrane in the opposite direction. The program was set to switch back and forth between + and -50 mA/cm² for 1000 cycles or until the membrane failed (whichever occurred first).

The membrane appears to be stable in the presence of molten Na, as evidenced by the continuous operation of this cell for almost 700 hours now. The data for the cell is shown in Figure 4 below. Initially the cell voltage is quite high +/- 7V, however after 80 or so hours the voltage appears to come to a steady state voltage of +2 and -3V. Possibly the decrease in voltage is due to a wetting phenomena between the NaSICON materials and the Na metal, another possibility is a minor crack in the membrane has developed. Once the system comes to an equilibrium it appears to hold this voltage steady for another 200hours or so, after which the voltage decreases again. At this point it is unclear why the voltage decreases to roughly +1 and -1 V. One possibility is a hairline crack in the membrane that has reduced the resistance of the cell somewhat, but has not caused catastrophic failure of the membrane.

The results of this test are very encouraging but will be better understood when the test is complete and the membrane examined. They demonstrate that the NaSICON membrane is stable in the presence of molten Na, and therefore can operate at these temperatures for recovery of Na ions from oil shale. Additional tests using a similar setup will be performed to verify these results, and to further characterize the stability of the membrane in the presence of molten Na.



Figure 3. Image cell for testing Nasicon membrane in molten Na

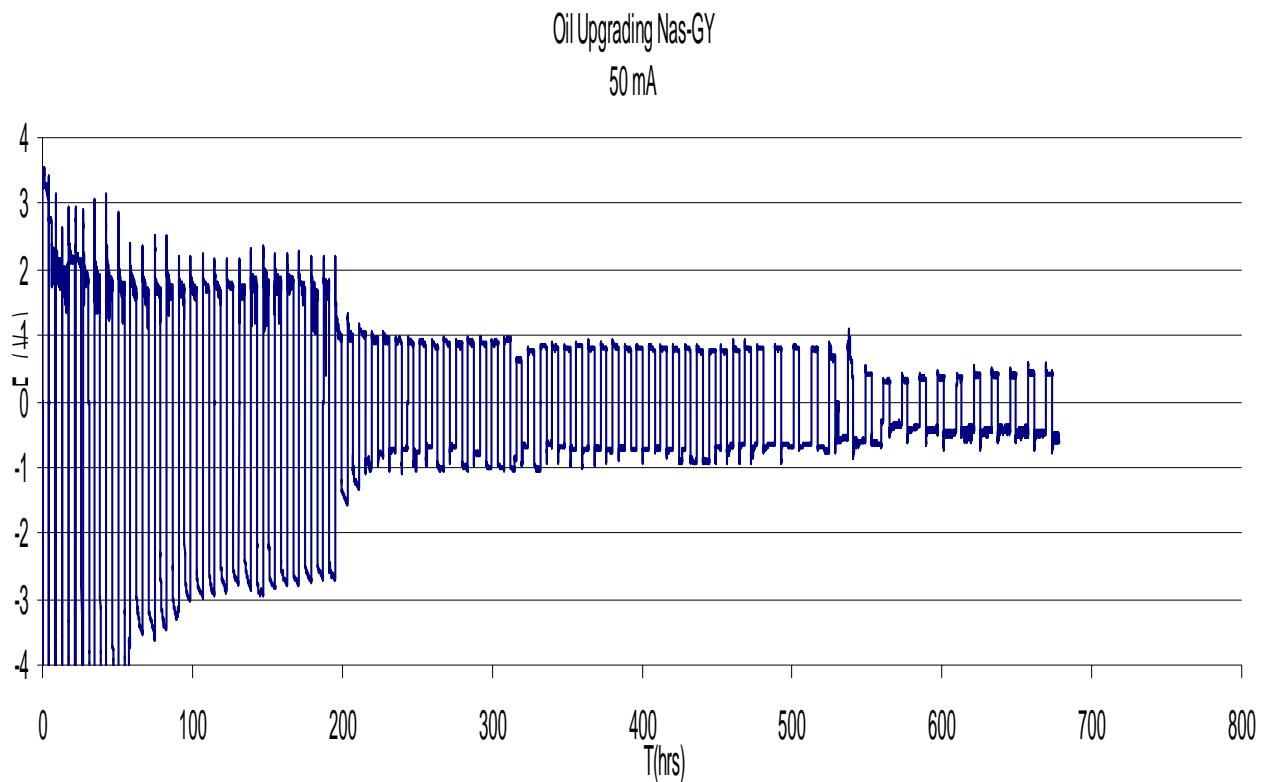


Figure 4. NaSICON membrane stability test in the presence of molten Na metal

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 1st 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

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

Table 1. Project costing profile for the 1st Quarter

	Oct-09		Nov-09		Dec-09		Q1		
	Projected	Actual	Projected	Actual	Projected	Actual	Projected	Actual	
Direct Labor		17,044.34		21,829.62		11,992.45		50,866.41	
Benefits	32%	5,454.19		6,985.48		3,837.58		16,277.25	
Overhead	41%	6,988.18		8,950.14		4,916.90		20,855.23	
Total Burdened Labor		29,486.71		37,765.24		20,746.94		87,998.89	
Direct Materials / Spec Test		20,686.49		19,749.66		17,624.11		58,060.26	
Equipment								-	
Travel				946.14		860.13		1,806.27	
Subtotal		50,173.20		58,461.04		39,231.18		147,865.42	
G&A	29%	14,550.23		16,953.70		11,377.04		42,880.97	
Total monthly		217,379.00	64,723.43	221,331.00	75,414.74	243,639.00	50,608.22	682,349.00	190,746.39

Our costs in the 1st quarter were much lower than the projection. This was primarily due to a slow start getting the program ramped up and equipment ordered and secondarily due to December being a month in which there were only 17 scheduled work days and high incidence of year end vacation which reduced the billing to the program. Also, individuals recruited will not impact the program until the 2nd quarter. Approximately \$130,000 of materials and equipment were on order at the time of this report writing and approximately \$150,000 more will be ordered by the end of the 2nd quarter. Thus, while the program costs have begun slower than projected. They will partially catch up in the 2nd quarter and should fully catch up by the end of the 3rd quarter.

Figure 5 shows a plot of the total monthly costs and the initially projected costs versus time and figure 6 shows the cumulative monthly costs versus time.

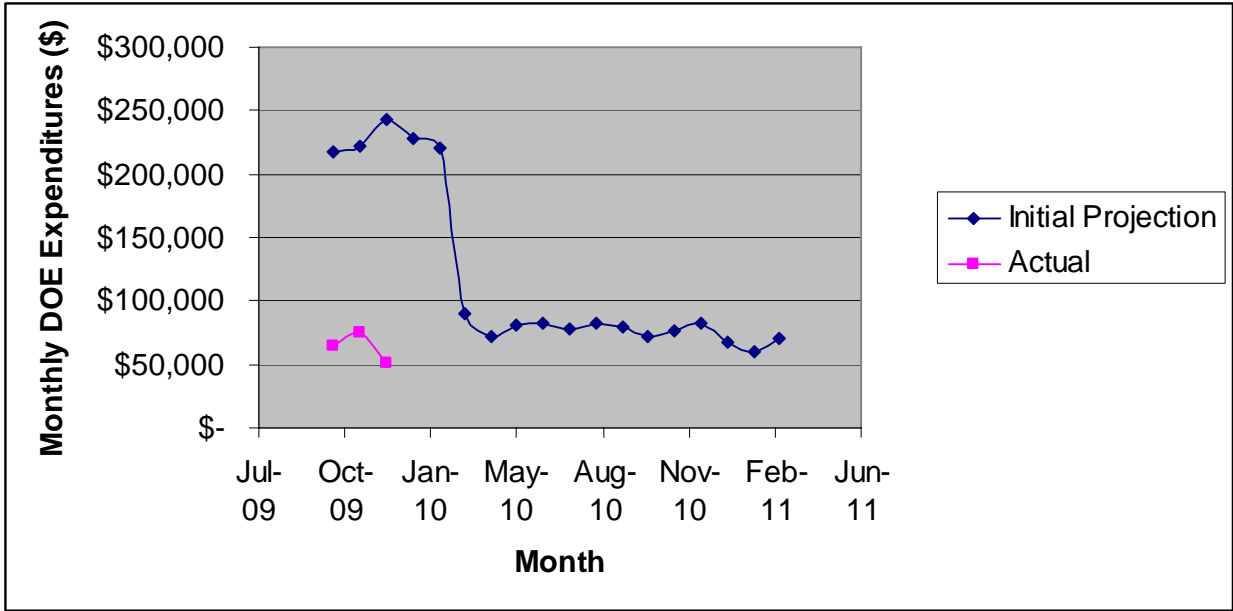


Figure 5: Projected and actual monthly costs over time

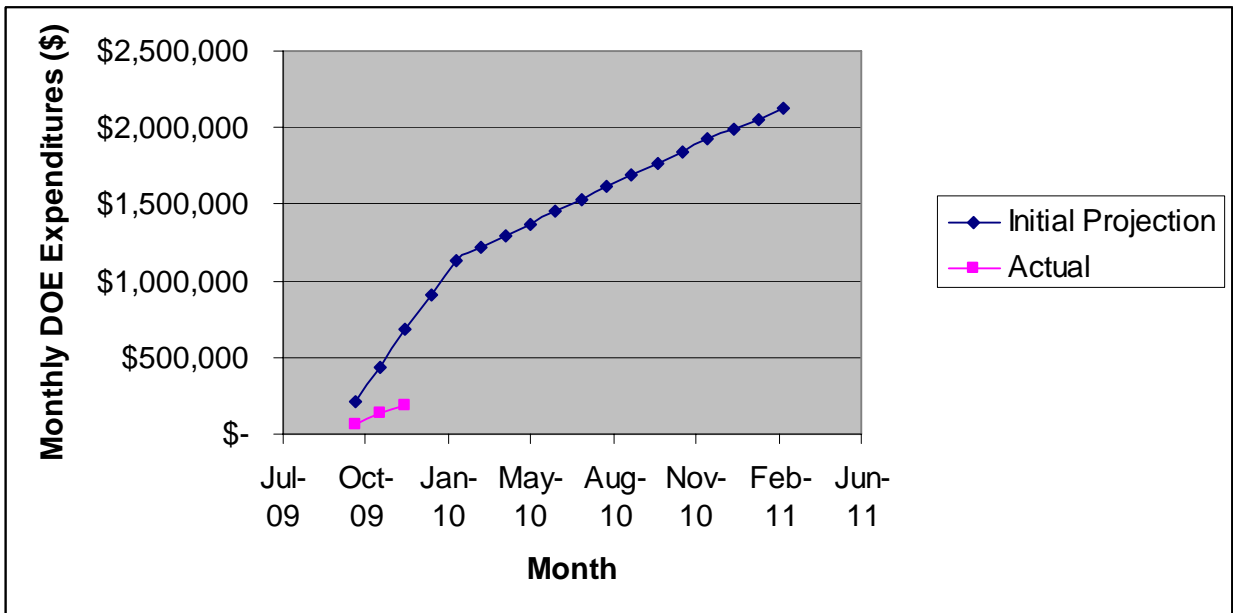


Figure 6: Projected and actual cumulative costs over time

MILESTONE STATUS

Table 2: Milestone log for 1st 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	2.2	Complete upgrading exp. Setup	9/29/09	3/29/09	9/29/09		
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			
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

- ✓ Detailed process flow diagram for reactor process.
- ✓ Selected laboratory for program and cleared out unneeded equipment.
- ✓ Completed laboratory layout.
- ✓ Recruited personnel for 2 positions – to begin working in Q2.

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. The specification of equipment occurred in the 1st quarter and will result in orders placed in the 2nd quarter.

PRODUCTS

No products to report at this time.

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