

Oil & Natural Gas Technology

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Quarterly Report July 2011 – September 2011 Post Retort, Pre Hydro-treat Upgrading of Shale Oil

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1. EXECUTIVE SUMMARY

In the 8th quarter considerable progress was made. This quarter the work extended to processing bitumen in the reactor and focusing on adding in more separation steps to be able to complete a mass balance. The bitumen was more sulfurous and more viscous than the other feed stocks we had processes before. The process again was found to be effective in removal of sulfur, metals less effective removing nitrogen. The electrolysis process development continues to be a highlight. Nearly 3500 hours have been logged on a cell electrolyzing sodium sulfide to form molten sodium at 60 mA/cm² and about 130C using a Nasion membrane. The membrane appears to be very stable under these conditions. The bitumen, bearing about 5% sulfur, after being process yielded considerable sodium sulfide which subsequently was electrolyzed to recover the sodium. The technology was presented to numerous Oil & Gas companies to create awareness and to hopefully create a path to extend the work when the present program ends.

2. PROGRESS, RESULTS AND DISCUSSION

2.1 Task 1.0 -- Project Management Plan

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

2.2 Task 2.0 -- Upgrading Development

It is explained in detail in 6th Quarterly report.

2.3 Task 3.0 -- Electrolysis Development

It is explained in detail in 6th Quarterly report.

2.4 Task 4.0 -- Analysis

It is explained in detail in 6th Quarterly report.

Budget Period 2

2.5 Task 5.0 – 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.

The investigation focus of this task during the 8th quarter was on maximizing the liquid phase yields, working toward a mass balance, and processing a new feedstock - bitumen.

Experimental

The work during this quarter focused upon heavier feedstock. Bitumen was obtained from a third party to upgrade through our process. The experimental work was aimed at parametric optimization considering vastly different properties of such heavy feedstock. All the experiments were performed with using Sodium as the alkali metal, 180 gm (approx.) of oil as raw material unless otherwise specified. Temperature, pressure and modes of operation were varied to improve API rating, decrease viscosity, remove sulfur/nitrogen and remove metals while maximizing the liquid phase yield. Upon reaction, the product was subjected to centrifuging to separate the solid fraction (sulfides and possibly heavy metals) from liquid. The extracted solids were further solvent treated to remove the excess miscible hydrocarbon. Table 1 below shows the list of different experiments.

The reactor set up underwent an improvement. A sodium charging assembly was added to the reactor. This assembly allows for us to add sodium into the oil at the temperature and pressure of reaction. The assembly is a high pressure tube that can be pre-charged with sodium under inert environment. The tube has a heating tape to melt the sodium upon sealing the tube with appropriate high pressure fittings. A ball valve connects the charging tube with the reactor. High pressure inlet gas is used to charge the sodium into the reactor. Table 1 below shows the list of experiments performed.

Table 1: List of experiments Performed with Bitumen samples

Expt #	Quantity of Na (g)	Upgrading gas	Time (hr)	Pressure (psig)	Temp (°C)
1	9.86	H2	2	1500	375
2	10.07	H2	2	1500	400
3	12.75	CH4	2	1500	375
4	13.14	H2	2	1500	375
5	13.42	CH4	1	1500	375
6	13.53	H2	2	1500	425
7	15.97	H2	1	1500	425
8	15.28	H2	1	1500	375
9	16.34	CH4	1	1500	375
10	19.16	H2	1	1500	375
11	16.28	CH4	1	1500	375
12	14.7	H2	1	1500	375
13	14.48	CH4	1	1500	375

Extractive Separation of Sulfides

The solid fraction in the reactor as well as centrifuge contains sodium sulfides along with carbonaceous residue. Sodium sulfides can be separated using solvent extraction. Same experimental apparatus was used for solvent extraction. A 5:1 mixture of solvent and solid residue was heated in the closed vessel under nitrogen. Upon cooling the solvent and solids were separated using centrifuge. CHNS contents of the final solids and initial solids were measured. The loss in sulfur content corresponds to sodium sulfides solubilized in the solvent.

Results and Discussions

1. CHNS

CHNS measurements were performed on raw material samples and product samples. Compositional analysis for SJ raw material samples is shown in Table 2 below and Table 3 lists analysis results for products.

Table 2: C, H, N and S Composition of Raw Materials

Raw material	C (%)	H (%)	N (%)	S (%)
Bitumen	83.18	10.77	0.39	4.96

2. Metals

Metal content as measured by ICP is shown in Table 3 below.

Table 3: Metals contents in bitumen

Raw Material	Ni	V	Fe
Bitumen as received	79	200	16

3. Sulfur Removal

Results of sulfur removal from Bitumen are shown in Figure 1 below. As observed, more than 94% of sulfur was removed from bitumen using hydrogen as the cover gas. When using methane, more than 80% sulfur was removed.

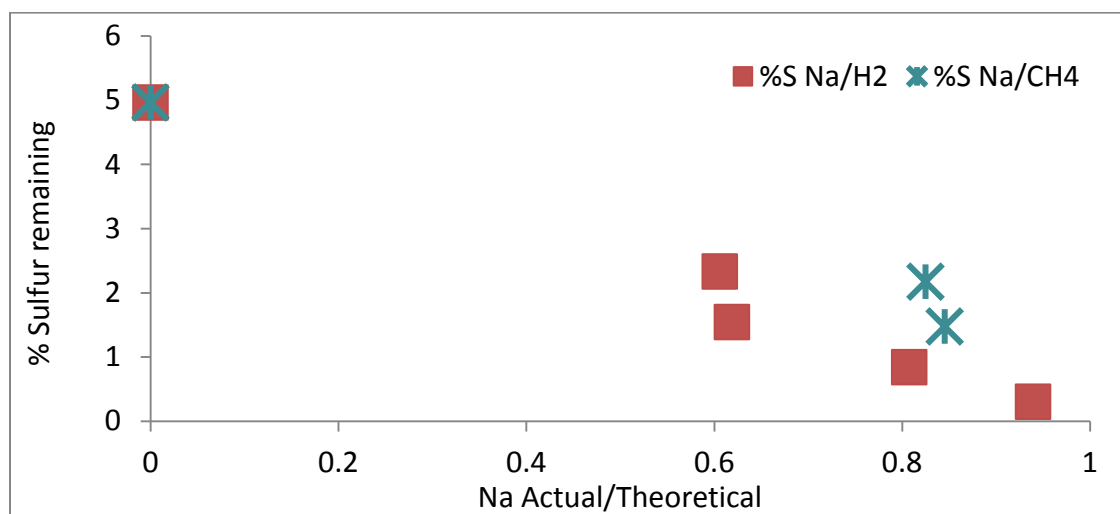


Figure 1: Sulfur removal from bitumen using Na treatment

4. API Changes

API improvements upon processing with Na in presence of hydrogen or methane are shown in Figure 2 below. In most experiments, the API improves from beginning value to 8.8 to approximately 18. In two of the experiments, API of product above 25 was observed. The primary reason for such high API value is higher operating temperatures (425 C or more). Some bitumen cracking is anticipated at these temperatures.

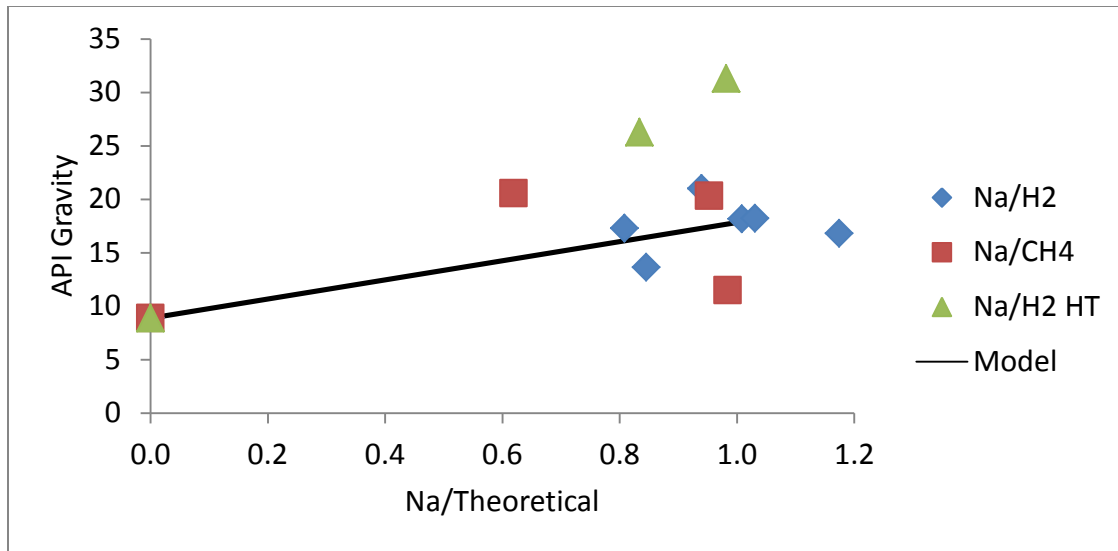


Figure 2: API improvement in bitumen

5. Viscosity Change

Figure 3 below shows the change in viscosity of products. It is observed that the viscosity is reduced and also rises more slowly with temperature upon treating with Na. The viscosity plot also follows Arrhenius behavior.

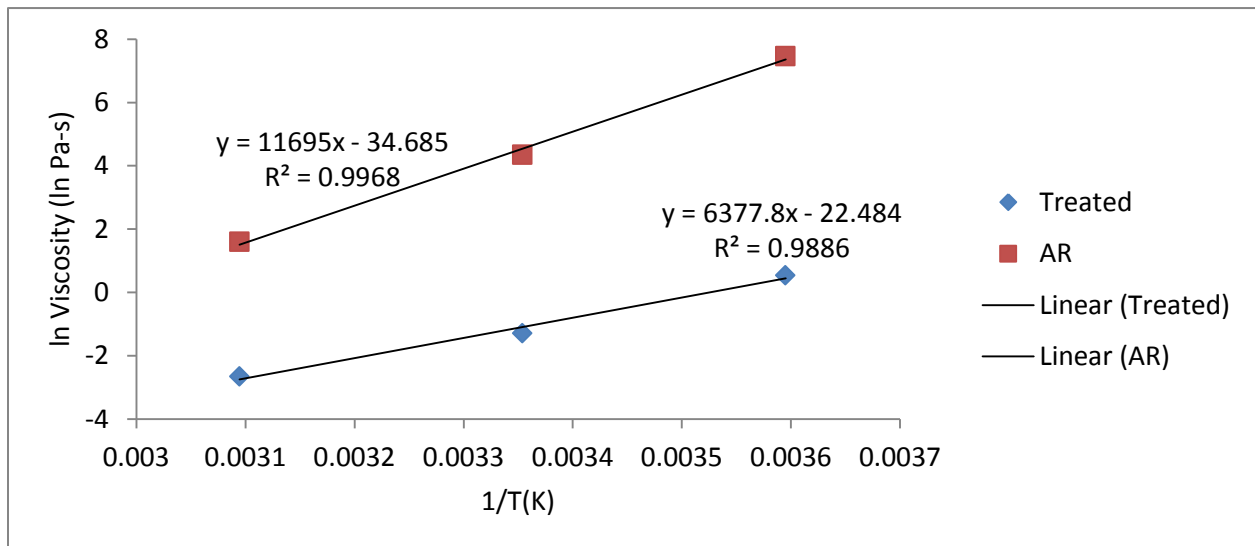


Figure 3: Changes in Viscosity of Bitumen

6. Metals Removal

Figure 4 below shows the effect of Na treatment on metals in bitumen. As observed, V, Ni and Fe drop below detectable levels after processing.

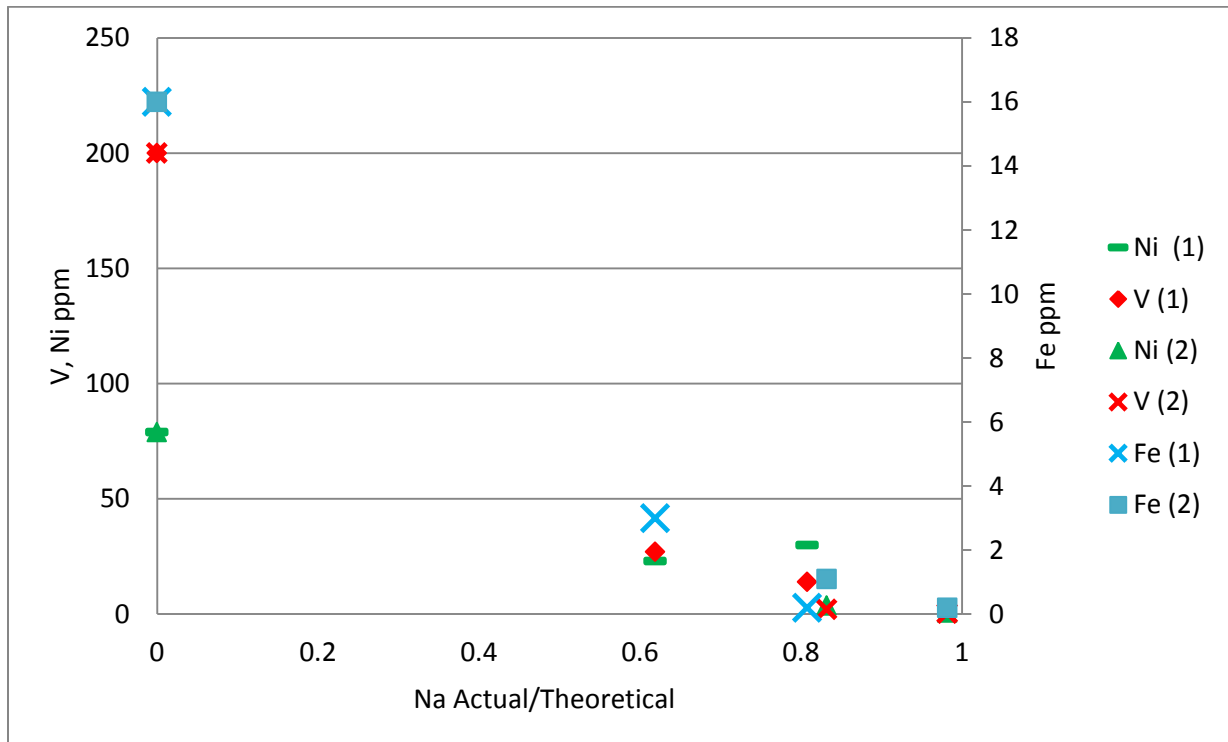


Figure 4: Metals removal from Bitumen

Conclusion

Sodium treatment of bitumen removed up to 94% sulfur, doubled the API, significantly reduced viscosity and dropped metals to below undetectable levels.

2.5.1 Subtask 5.1 - Analysis lab upgrade

The Recipient shall add the capability to further characterize the shale oil in terms of heavy metals, aromatics and other characteristics important to assessing the quality of the upgraded stream to the analysis laboratory. For example the following addition/capability is planned: a Fluorescence Indicator Absorption (FIA) apparatus for composition analysis (The determination of the total volume % of saturates, olefins, and aromatics) (e.g. Koehler Instruments \$10 K) (ASTM: D1319)

Ceramatec is evaluating the need for this equipment and has not yet ordered.

2.6 Task 6.0 –Post reactor / pre electrolysis separation steps

The Recipient shall set up a reactor and centrifugal separator to separate the sodium / lithium sulfide salts and heavy metals from the upgraded shale oil. Individual separation schemes shall be designed for the removal of salts, heavy metals and metal mercaptides shall be identified. The separated products including the upgraded oil, metal mercaptides, metal polysulfides shall be chemically analyzed for efficiency of separation. The separated oil shall be analyzed for CHNS content, metals content, API gravity and boiling point distribution. Further an industrially suitable separation that can be economically scaled up shall be identified and designed

2.6.1 Subtask 6.1-Separations Experimental set up

The recipient shall assemble an experimental set up that shall include a reactor assembly to treat the upgraded oil (Task 5.0 above) with H₂S and the balance of apparatus as described in PMP.

2.6.2 Subtask 6.2-Separation of metal Salts

The recipient shall implement four different separation schemes with the following variables and parameters:

H₂S partial pressure

H₂ partial pressure

Operating temperature

Operating pressure

The operating procedure for these separation schemes is detailed in PMP. The preferred separation technique shall be chosen upon investigation of the proposed schemes.

2.6.3 Subtask 6.3-Separation of metal mercaptides

In order to separate the oil soluble mercaptides the mixture shall be subjected to acid treatment using dilute mineral acids. The acid treated mixture shall be separated and the acidic aqueous phase shall be analyzed using CHNS analyzer.

2.6.4 Sub-task 6.4 - Design

The overall separation scheme shall be designed to include H₂S recycle loop to the separation reactor, sulfur recycle, purge and chosen separation scheme.

2.7 Task 7.0 - 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.

2.7.1 Subtask 7.1 – Membrane fabrication

The Recipient shall fabricate and characterize sodium conductive and lithium conductive membranes.

No more work performed in this area.

2.7.2 Subtask 7.2 – Seal testing

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

A long term cell test is under way in this to determine glass seals.

2.7.3 Subtask 7.3 – 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.

No more work performed in this area.

2.7.4 Subtask 7.4 – 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.

Long term test cell results

One cell has been operated as long term test during this reporting period. Table 4 summarizes the properties of the cell. Sodium polysulfide (Na_2S_4) is periodically added to the anolyte solution in the cell to replenish the sodium as the ions are transported and reduced to sodium metal in the cathode. Cell *Na_molten_20110504* has been in continuous operation for 3390 hours (141 days) at a constant current density of 60 mA/cm^2 . Figure 5 shows the cell voltage and the Open Circuit

Voltage (OCV) during the test. The average cell voltage for the run is equal to 2.96V. The cell's Nernst potential or OCV (Open Circuit Voltage) varied between 2.1 and 2.3V, with an average around 2.2V. Since the temperature is kept very uniform $130 \pm 0.1^\circ\text{C}$, the OCV variations are mostly due to the change in the sodium polysulfide composition and concentration in the anolyte solution. So after each addition of fresh Na_2S_4 to the anolyte, the OCV drops and then slowly increases during the run as richer sulfur polysulfide molecules are formed. Table 5 lists some of the cell's key metrics measured in the test. Out of a total of 1412.7 grams of Na_2S_4 added to the cell, 295.5 grams of sodium have been recovered. This represents approximately 79% of the total sodium added as sodium polysulfide to the cell.

As documented in past quarterly reports, we have detected small amounts hydrogen sulfide gas being generated in the cell. Since the cells are operated inside a glove box in a dry nitrogen environment, we have speculated that the gas comes from decomposition reactions between the anolyte solvent and the sodium polysulfide. Aging of the anolyte solvent is evident as the test goes on and it is manifested as an increase in viscosity and in the reduction of the ionic conductivity. This also explains the slow but steady increase in the cell operating voltage as shown in Figure 5. We have measured the sulfur composition of the anolyte solution during the test. Figure 6 compares the total cumulative sulfur added and the total sulfur measured, expressed as weight percent of the anolyte solution, during the long term test with Anolyte #4. The difference between the sulfur added and the sulfur measured is equal to the sulfur lost as H_2S gas plus the elemental sulfur, which precipitates out of the anolyte solution. The figure indicates that it takes approximately 240 hours (after adding fresh anolyte solution) to reach a 46% difference between sulfur added and measured. Then, this difference is maintained for the remaining of the anolyte life. If we discount the amount of elemental sulfur recovered from the anolyte after separation, the sulfur losses account for 37% of the total sulfur added. A total of five anolyte solutions (four replacements) have been used so far during the 3390 hours of the test. After replacing the anolyte, the cell voltage decreases every time to a value similar to that of the beginning of the test. This is proof of the good condition of the membrane since little or no over potential due to the NaSICON solid electrolyte has been measured. We are investigating two new anolyte solvents that are potentially more stable than MF in the presence of sodium sulfide/polysulfide. Our target is to minimize the amount of sulfur losses as H_2S gas.

Table 4: Summary of sodium recovery test cells tested in long-term mode during the reporting period

Cell ID#	Anolyte	Anode Electrode	Membrane	Catholyte	Cathode Electrode	Seal Type	Operating Conditions
Na Recovery Cell 20110504	Na_2S_4 in MF	Platinized Ti mesh (1.1" diam.)	NaSICON GY (1 mm thick, 0.8" diam.)	Molten Na	Molten Na, Ti rod current collector	Silica-Boria Glass	Temperature=130C Anolyte agitation Cte Current=60 mA/cm ²

Table 5: Summary of performance of sodium recovery test cells run in long-term testing mode during the reporting period

Cell ID	Total Run Time	Avg. Current Density	Avg. Voltage	Number of Anolyte Solution Replacements	Total Na ₂ S ₄ Added	Na Recovered		Notes
	Hours (days)	mA/cm ²	V			g	% out of Na added	
Na Recovery Cell 20110504	3390* (141)	60	2.96	4	1412	296	79	Cell is still in operation with membrane in excellent conditions

* Total time includes short time periods to measure the cell OCV

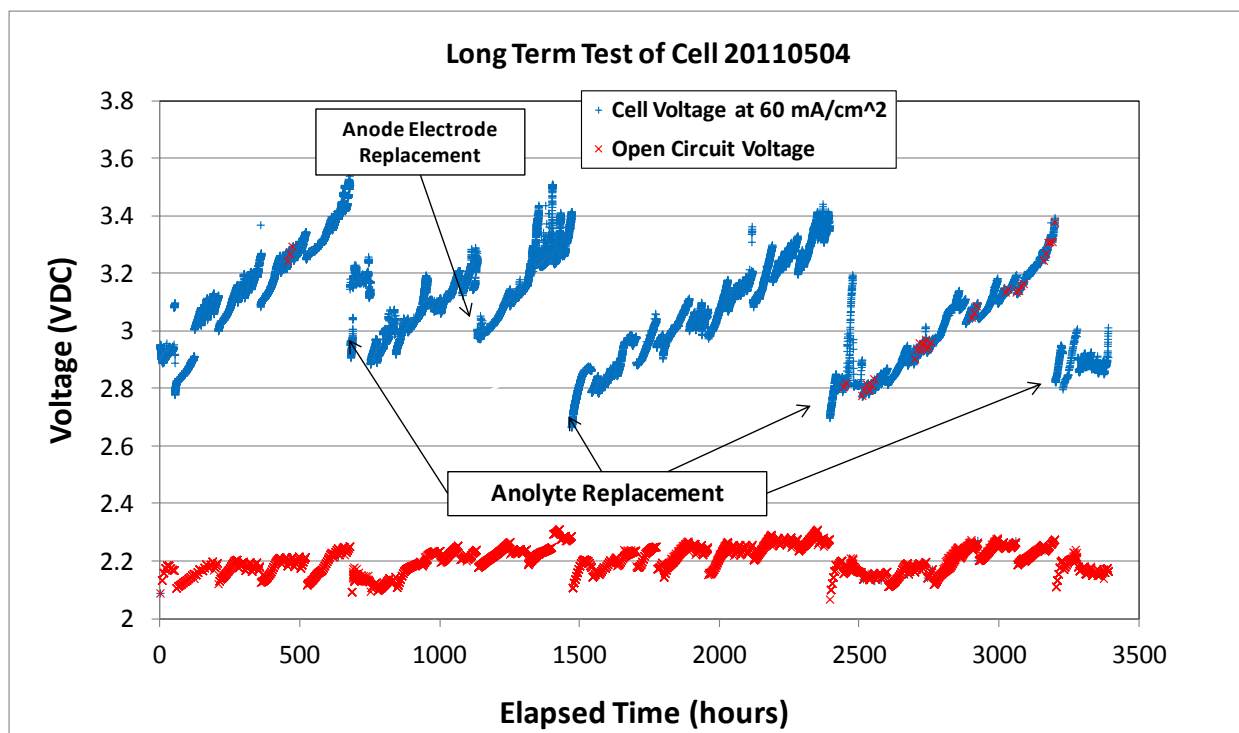


Figure 5. Cell voltage at 60 mA/cm² and Open Circuit Voltage (OCV) versus run time for sodium recovery cell *Na_molten_20110504*. Run time includes time periods for OCV measurements (no current).

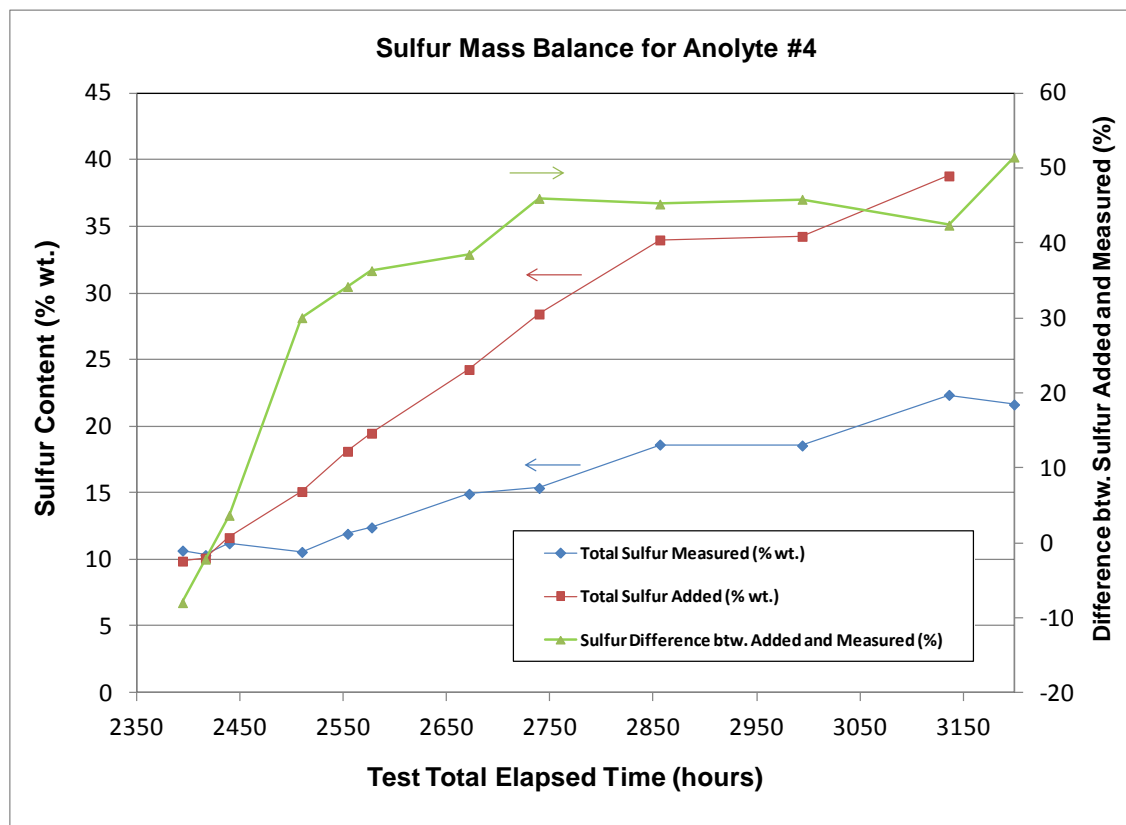


Figure 6. Comparison between total sulfur added and measured for Anolyte #4 during long term test for cell *Na Recovery Cell 20110504*

Sodium recovery test cells results using solids from processed oil samples:

The sodium salts solids were separated after the upgrading of Canadian Cold Lake bitumen and San Joaquin heavy oil. The upgrading process of all these runs was done using hydrogen gas with sodium metal at a temperature range of 375-425°C. The separation of the solid fraction is a multi-step process, which involves separation from the upgraded oil liquid fraction by centrifugation, followed by solvent extraction of the non-polar components with hexane. Finally, the polar fraction is dissolved in the preferred electrolyte solvent. Table 6 lists the conditions of each of the nine oil upgrading runs (seven from bitumen and two from heavy oil), whose solids fractions were separated and used to recover sodium metal by electrolysis. The table also summarizes the specific solids separation schedule followed and the C, H, N, S composition of the solids after the hexane extraction step. The solids from some of the runs reacted with the electrolyte solvent, which is an indication of the presence of unreacted sodium metal in the solids.

In all, five sodium recovery cells have been assembled and tested using the solids recovered. Table 7 displays the properties of construction of these cells. Four cells were assembled using the solids from only one oil upgrading run, while solids from four different oil runs were added to one cell over the testing period. Both cell runs using the San Joaquin heavy oil solids resulted in a very quick cell deactivation due to the formation and deposit of insoluble solid material on the anode electrode surface. Figure 7 shows the current density of cell *Molten Na_SJ_DL07166_20110630* versus run time at a constant controlled voltage of 3.5V. The cell current density initially reached 60 mA/cm², but quickly decreased to less than 10 mA/cm². After approximately 37 hours of run time, the cell appeared to be completely deactivated. Similar results were obtained with the second San Joaquin cell *Molten Na_SJ_DL07174_20110721*. The Ti electrode of this cell was completely covered on a black oily substance after the test (Figure 8A). In addition, the NaSICON membrane was heavily stained and covered on the same material (Figure 8B). We are not certain whether the material is formed as a result of the oxidation reaction in the cell's anode or whether it is an oil residue that precipitated out of solution during the test.

On the other hand, the results of the electrolysis runs, using the solids from the bitumen samples, are much more encouraging. Figure 9 shows the current density at constant voltage of 3 and 3.25V for the first three runs with cell *Na_Bitumen_20110808*. In the first run, the solids from bitumen runs *DL07180 and DL07189* were initially combined. Then in runs 2 and 3, the solids from bitumen runs *DL07183 and JK03004* were respectively added to the anolyte during the test. In all the three runs, the cell remained active through the test and relatively high current densities were maintained. Since the cell is run in batch mode, the current density decreases as the sodium ions are depleted from the anolyte solution. After the addition of the solids from bitumen run *JK03004*, the cell was able to reach 60 mA/cm² (at 3.25V). The cell was operated for a total of 150 hours, at an approximate average current density of 30 mA/cm². During that time, 7 grams of sodium metal were recovered (Figure 9). Figure 10 show pictures of the anode electrode (10-A) and the NaSICON membrane (10-B) after the test. The Ti electrode appears free of solids and the membrane is only slightly stained. Cell *Na_Bitumen_JK03028_20110908* was assembled using a small NaSICON tube (0.75 cm long x 2.08 cm ID), instead of a disk like in the other cells. A cylindrical Titanium expanded mesh was used as anode electrode. The test results were also very positive, demonstrating for the first time commercial current density targets using a tubular membrane. The cell was run in constant current mode at 60 mA/cm² for 10 hours and at 30 mA/cm² for 8.5 hours. The cell voltage started under 3V at the beginning of the test and ended up around 3.5V at the end of the run (Figure 11). 3.3 grams of sodium metal were recovered during the test (Figure 13). A post-run picture of the NaSICON tube (Figure 14-B) shows a clean electrode and a lightly stained membrane. The membrane staining was just superficial and it was easily removed by light sanding with a 200 grit diamond stone. Unfortunately, the test results for cell *Molten Na_Bitumen_JK03010_20110826* were very different from the other five runs using solids separated from bitumen oil samples. Similarly to the San Joaquin heavy oil cells, the cell deactivated very quickly and large amount of solids were found on the electrode and membrane. In fact, as Figure 10-A shows, the solids completely filled the electrode-membrane gap and large

amounts also collected along the alumina tube. At this point, we have not been able to find a discrepancy in the solids composition, separation process or the cell construction to explain this difference in performance with the other bitumen cells.

So in summary and excluding cell *Na_Bitumen_JK03010_20110826*, all the cells tested with the Canadian bitumen solids performed significantly better than the cells with the San Joaquin heavy oil solids. A look at the carbon content of the solids from both oil runs reveals that the heavy oil solids have in general higher carbon content than the bitumen solids. In some cases, up to 50% higher. If the oil upgrading process is able to remove the sulfur contained in the oil by converting it into inorganic sodium sulfides, then one would expect the solids to be carbon free. However, this is not the case for any of the samples, and even the lowest carbon containing solids (*DL07189*) are still 20% carbon. So, it is possible that the sulfides formed are organic in nature instead, and therefore contain carbon in their molecular structure. Moreover, it is also possible that the solids still have oil residues that could not be removed during the washing step with hexane. For instance, if asphaltenes were present originally in the oil, this fraction would not dissolve in hexane and hence would still remain mixed with the solids. To prove this hypothesis in future runs, a toluene extraction will be conducted after the hexane extraction since asphaltenes are known to dissolve in toluene.

Table 6: Summary of processed oil run conditions and properties of separated solids

Oil Upgrading Run#	Oil Type	Cell ID#	Solids Separation Process	CHNS Analysis of Processed Solids C (%), H(%), N(%), S(%)	Added Na (% stoichiometric)	Apparent Reaction with MF?
DL07166	San Joaquin heavy oil	SJ_DL07166_20110630	1. Centrifuged from upgraded oil 2. Dissolved in MF	50.9, 6.7, 1.4, 4.3	100%	No
DL07174	San Joaquin heavy oil	SJ_DL07174_20110721	1. Centrifuged from upgraded oil 2. Washed with hexane 3. Centrifuged from hexane 4. Dried at room temp 5. Dissolved in MF	40.1, 5.1, 1.2, 11.7	100%	No
DL07180	Cold Lake Bitumen	Bitumen_DL07180-189_20110808	1. Centrifuged from upgraded oil 2. Washed with hexane 3. Centrifuged from hexane 4. Dried at 50C 5. Dissolved in MF	22.2, 2.9, 0, 18.2	60.50%	No
DL07189	Cold Lake Bitumen	Bitumen_DL07180-189_20110808	1. Centrifuged from upgraded oil 2. Washed with hexane 3. Centrifuged from hexane 4. Dried at 50C 5. Dissolved in MF	19.4, 3.8, 1.1, 12.2	80%	No
DL07183	Cold Lake Bitumen	Bitumen_DL07180-189-183_20110808	1. Centrifuged from upgraded oil 2. Washed with hexane 3. Centrifuged from hexane 4. Dried at 50C 5. Dissolved in MF	34.6, 3.1, 0.6, 19.7	62%	No
JK03004	Cold Lake Bitumen	Bitumen_DL07180-189-183+JK03004_20110808	1. Centrifuged from upgraded oil 2. Washed with hexane 3. Centrifuged from hexane 4. Dried at 50C 5. Dissolved in MF	32.9, 2.9, 3.5, 18.8	83%	No
JK03016	Cold Lake Bitumen	Bitumen_DL07180-189-183+JK03004+JK03016_20110808	1. Centrifuged from upgraded oil 2. Washed with hexane 3. Centrifuged from hexane 4. Dried at 80C 5. Dissolved in MF	32.6, 3.7, 0.5, 9.9	118%	Yes
JK03010	Cold Lake Bitumen	Bitumen_JK03010_20110826	1. Centrifuged from upgraded oil 2. Washed with hexane 3. Centrifuged from hexane 4. Dried at 80C 5. Dissolved in MF	31.2, 2.76, 0.6, 21.8	94%	No
JK03028	Cold Lake Bitumen	Bitumen_JK03028_20110908	1. Centrifuged from upgraded oil 2. Washed with hexane 3. Centrifuged from hexane 4. Dried at 80C 5. Dissolved in MF	34.5, 3.3, 0, 18.1	90%	Yes

Table 7: Sodium recovery test cells, using dissolved solids from processed oil samples, assembled and tested during the reporting period

Cell ID#	Anolyte	Anode Electrode	Membrane	Catholyte	Cathode Electrode	Cell Operating Conditions
Molten Na_SJ_DL07166_20110630	250 g of 17% wt. salts in MF solution	Graphite (1.1" diam.) 3 mm from membrane	NaSICON G, Pressed Disk (1 mm thick, 0.8" diam.) Active area=1.5 cm ²	Molten Na	Molten Na, Ti rod current collector	Temperature=130C Cte Voltage=3.5 V
Molten Na_SJ_DL07174_20110721	254 g of 3.1% wt. salts in MF solution	Platinized Ti mesh (1.1" diam.) 3 mm from membrane	NaSICON GY, Pressed Disk (1 mm thick, 0.8" diam.) Active area=1.43 cm ²	Molten Na	Molten Na, Ti rod current collector	Temperature=130C Cte Voltage=3.25-3.5 V
Molten Na_Bitumen_DL07180-189_20110808_Run 1	262.5 g of 6.37% wt. solids in MF solution. 8.0 g solids from DL07180 and 8.7 g solids from DL07189.	Platinized Ti mesh (1.1" diam.) 3 mm from membrane	NaSICON GY, Pressed Disk (1 mm thick, 0.8" diam.) Active area=1.84 cm ²	Molten Na	Molten Na, Ti rod current collector	Temperature=130C Cte Voltage=3.0 V
Molten Na_Bitumen_DL07180-189-183_20110808_Run 2	Added 85 gr of solution with DL07183 solids to anolyte of cell <i>Molten Na_Bitumen_DL07180-189_20110808</i>	Platinized Ti mesh (1.1" diam.) 3 mm from membrane	NaSICON GY, Pressed Disk (1 mm thick, 0.8" diam.) Active area=1.84 cm ²	Molten Na	Molten Na, Ti rod current collector	Temperature=130C Cte Voltage=3.0-3.25 V
Molten Na_Bitumen_DL07180-189-183+JK03004_20110808_Run 3	Added a fraction of JK03004 solids dissolved in MF to anolyte of cell <i>Molten Na_Bitumen_DL07180-189-183_20110808</i>	Platinized Ti mesh (1.1" diam.) 3 mm from membrane	NaSICON GY, Pressed Disk (1 mm thick, 0.8" diam.) Active area=1.84 cm ²	Molten Na	Molten Na, Ti rod current collector	Temperature=130C Cte Voltage=3.0-3.5 V
Molten Na_Bitumen_DL07180-189-183+JK03004-03016_20110808_Run 4	Added a fraction of JK03004 solids dissolved in MF to anolyte of cell <i>Molten Na_Bitumen_DL07180-189-183 +JK03004_20110808</i>	Platinized Ti mesh 3 mm from membrane (1.1" diam.)	NaSICON GY, Pressed Disk (1 mm thick, 0.8" diam.) Active area=1.84 cm ²	Molten Na	Molten Na, Ti rod current collector	Temperature=130C Cte Voltage=3.0-3.25 V
Molten Na_Bitumen_JK03010_20110826	290 g of 7.12% wt. solids in MF solution. 20.6 g of actual dissolved solids in MF.	Platinized Ti mesh (1.1" diam.) 3 mm from membrane	NaSICON GY, Pressed Disk (1 mm thick, 0.8" diam.) Active area=1.84 cm ²	Molten Na	Molten Na, Ti rod current collector	Temperature=130C Cte Voltage=2.75-3.0 V
Molten Na_Bitumen_JK03028_20110908	222 g of 9.42% wt. solids in MF solution	Cylindrical Ti mesh with perforated holes 3 mm from membrane	NaSICON GY Tube (1.25 mm thick, Tube OD=22.8 mm, Tube ID=20.8 mm) Active area=4.9 cm ² (based on inner area)	Molten Na	Molten Na, Ti rod current collector	Temperature=130C Cte Current=30 and 60 mA/cm ²

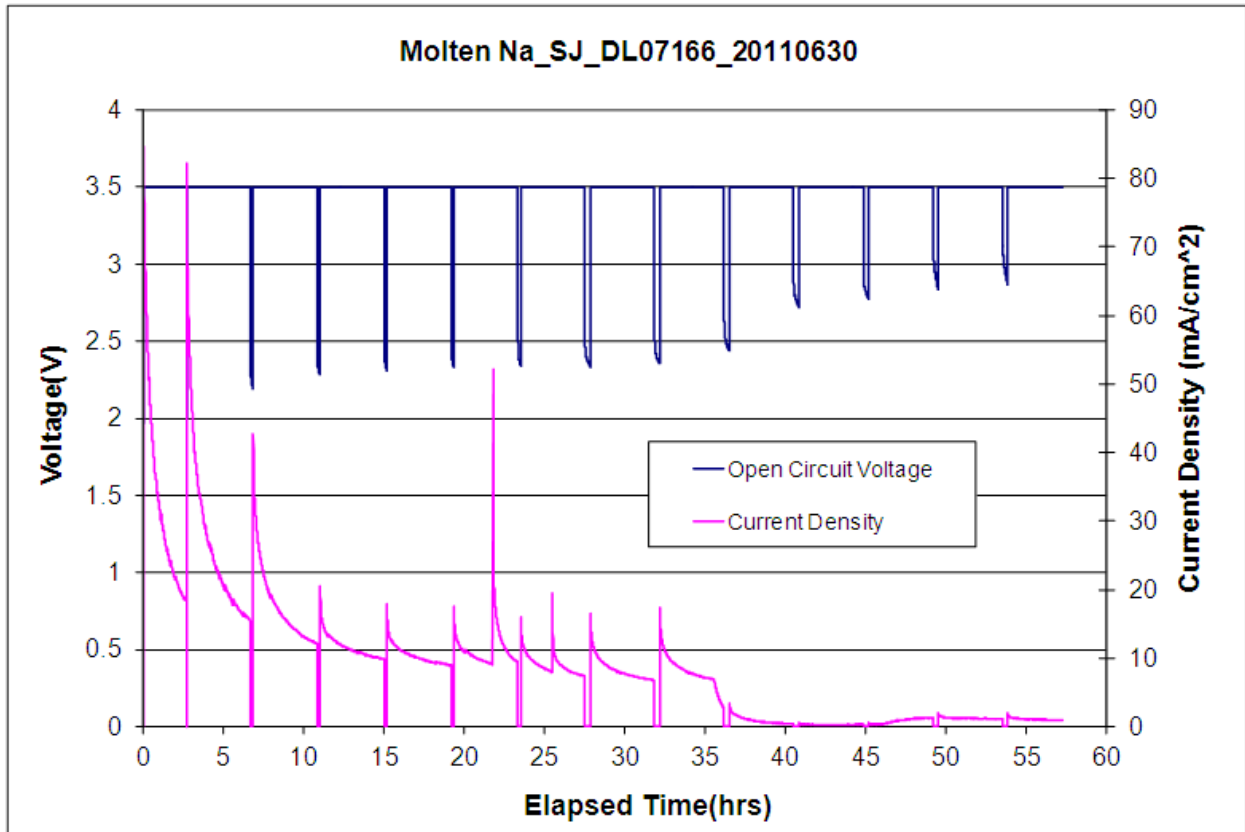


Figure 7. Cell voltage and current density versus test elapsed time for sodium recovery Test Cell *Molten Na_SJ_DL07166_20110630*

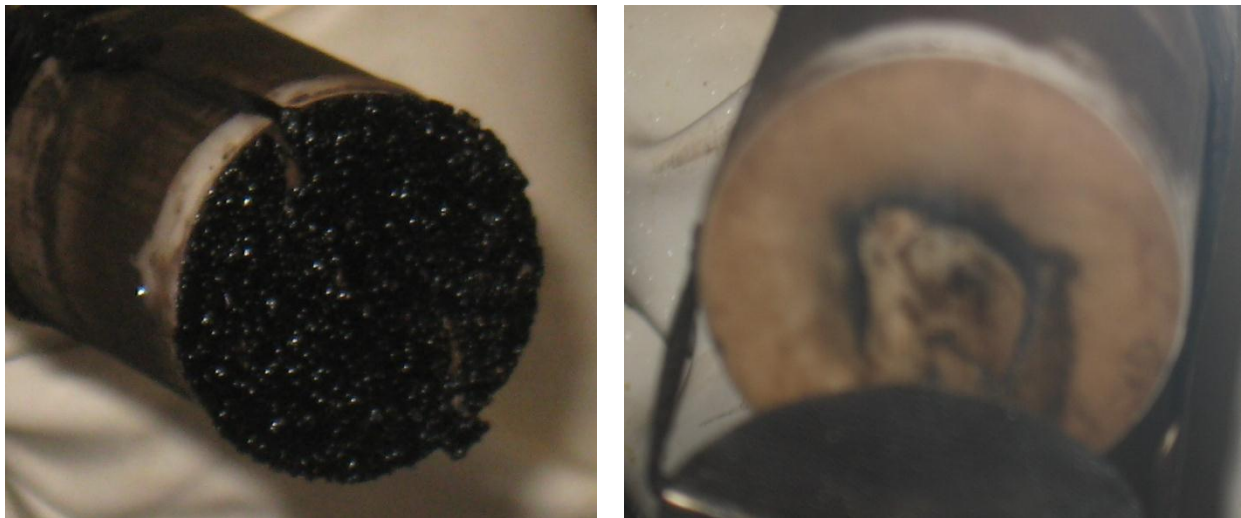


Figure 8. Platinized Ti electrode [A] and anode side surface of NaSICON-GY membrane [B] of Test Cell *Molten Na_SJ_DL07174_20110721* after the test

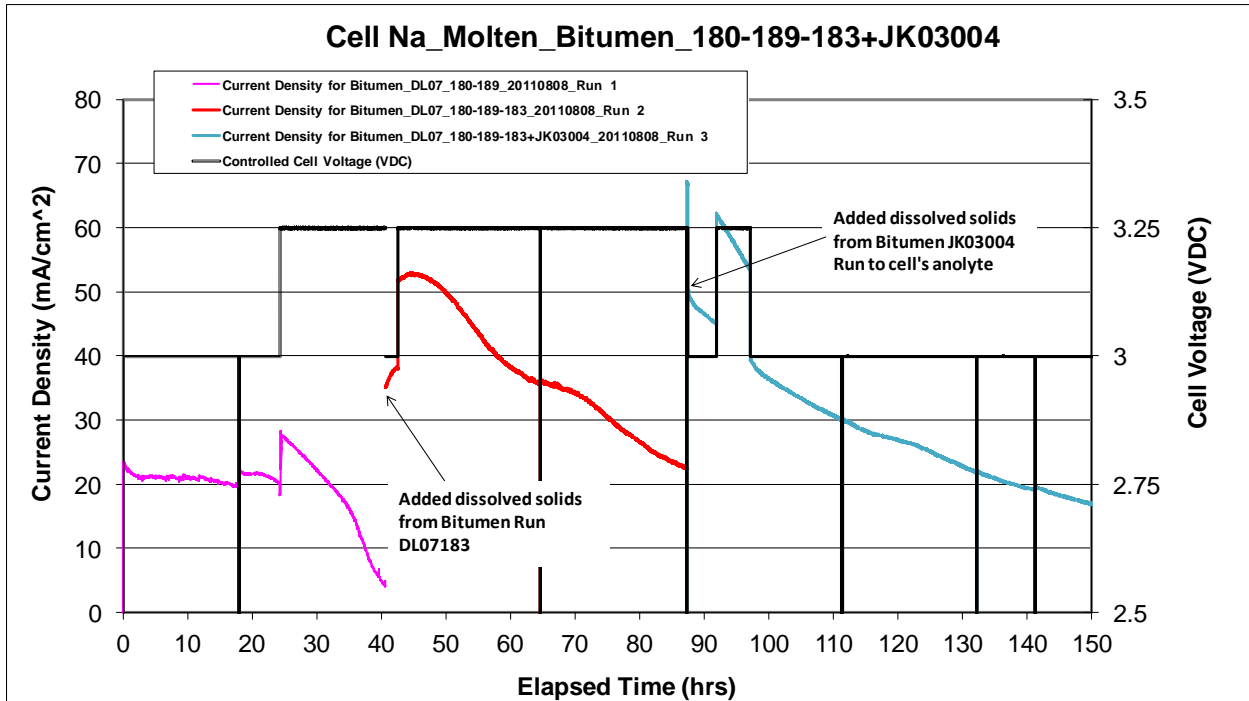


Figure 9. Cell voltage and current density versus total elapsed time for sodium recovery Test Cell *Molten Na_Bitumen_DL07_180-189-183+JK03004_20110808*

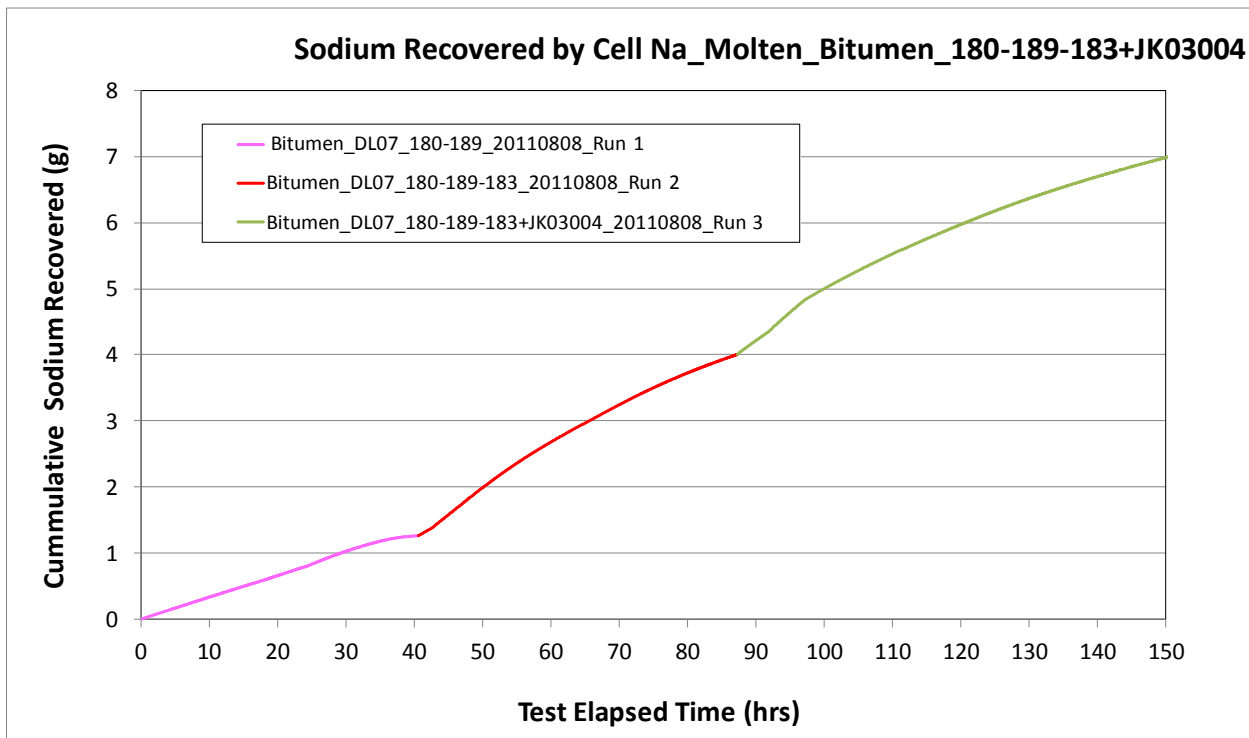


Figure 10. Total sodium recovered during operation of Test Cell *Molten Na_Bitumen_DL07_180-189-183+JK03004_20110808*



Figure 11. Platinized Ti electrode [A] and anode side surface of NaSICON-GY membrane [B] of Test Cell *Molten Na_Bitumen_DL07_180-189-183+JK03004_20110808* after the test

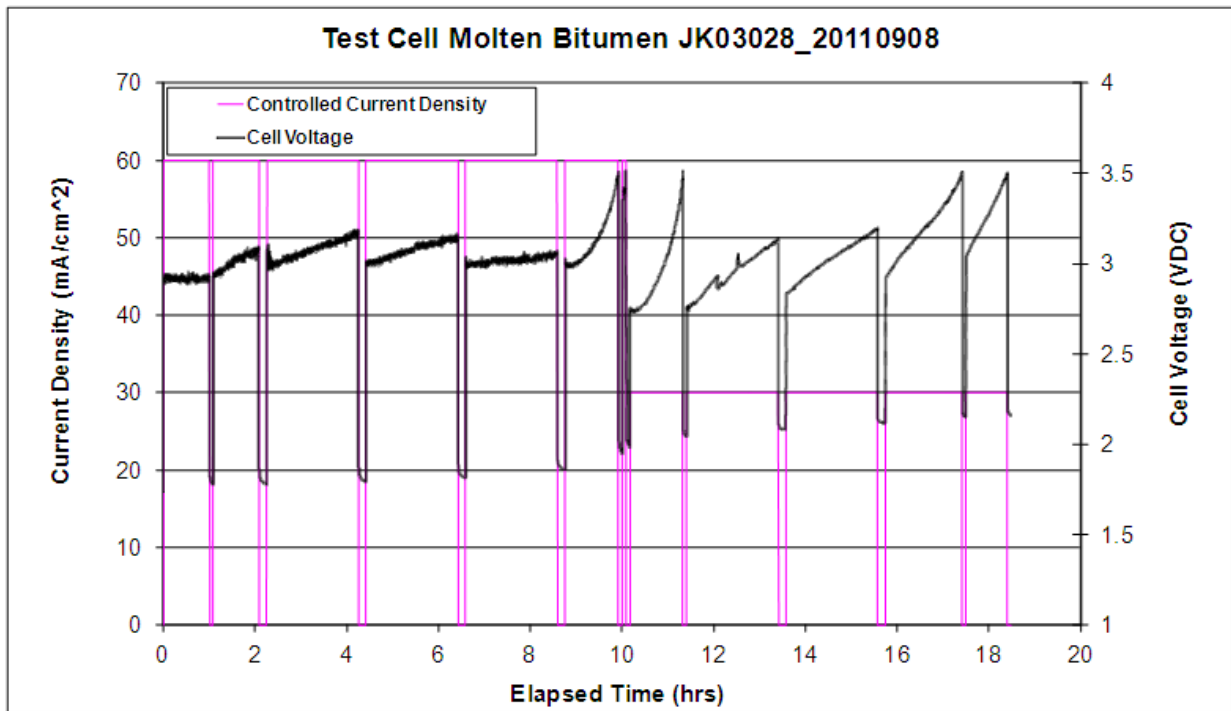


Figure 12. Cell voltage and current density versus total elapsed time for sodium recovery Test Cell *Molten Na_Bitumen_JK03028_20110908*

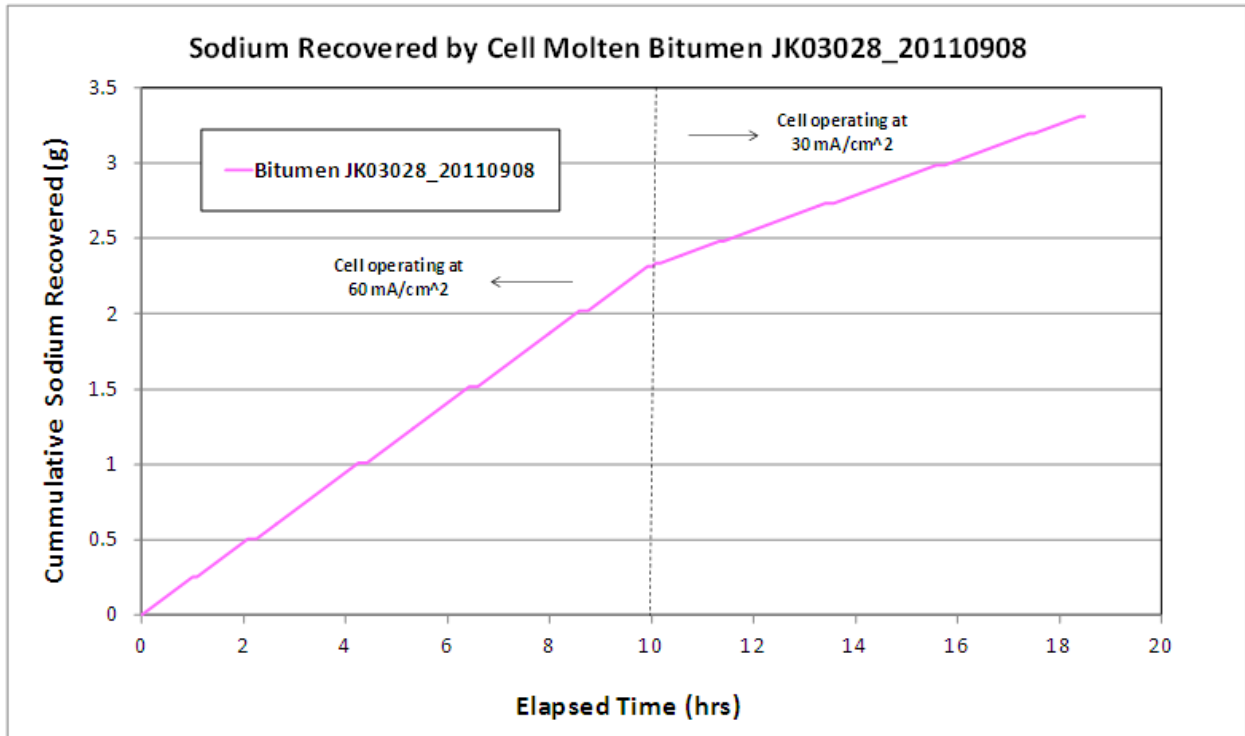


Figure 13. Total sodium recovered during operation of Test Cell *Molten-Na_Bitumen_JK03028_20110908*

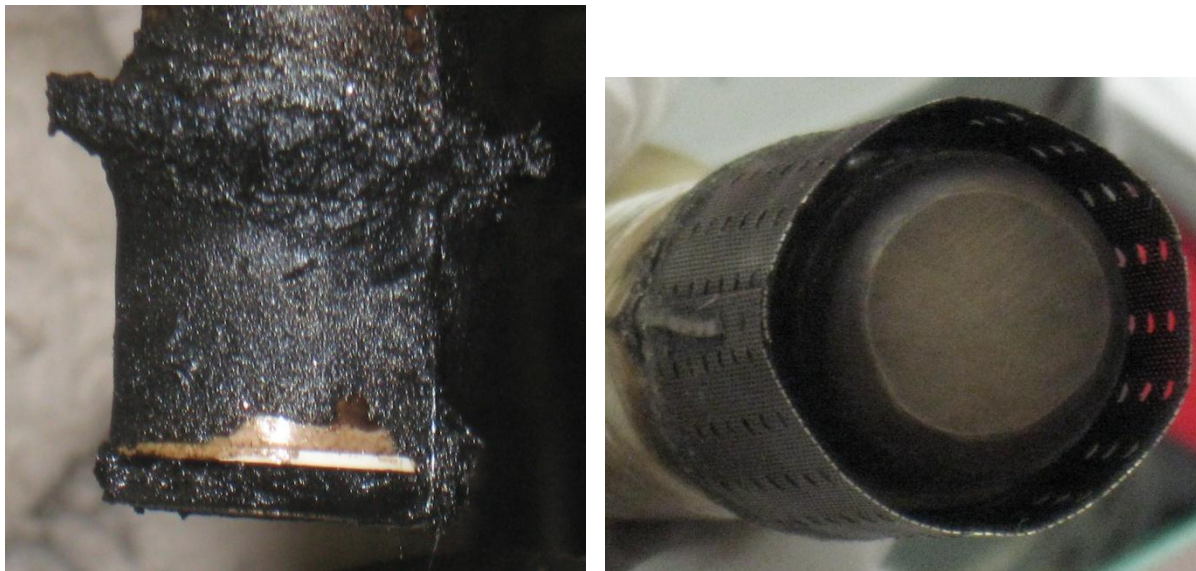


Figure 14. Test Cell *Molten Na_Bitumen_JK03010_20110826* [A] and Test Cell *Molten Na_Bitumen_JK03028_20110908* [B] after their respective tests

Task 7.0 – Analysis

Subtask 7.1 – 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.

The model from Task 4.0 will be updated in the future.

Subtask 7.2 – 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.

Sodium was selected because of higher efficiency of removing sulfur and lower cell voltage in electrolysis compared to Lithium.

2.8 Task 8.0 – Modeling and Economic Analysis

2.8.1 Subtask 8.1 – Model Upgrading process

The Recipient shall model the upgrading process constructed in Budget Period 1. The design model of separation scheme of Task 3 shall be added to the overall model of upgrading process. The process model shall also take into account the performance comparison with current commercial hydrotreating processes.

No work on this sub-task this quarter.

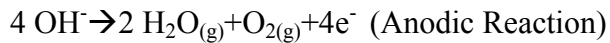
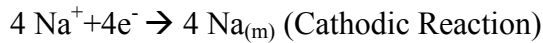
2.8.2 Subtask 8.2 – Model Electrolysis process

The Recipient shall analyze data from Task 7.0 above and the exiting Budget Period 1 performance model shall be updated and improved. The inputs of the model shall be coupled with the outputs of the upgrading process model to quickly analyze the effect of changes in the value of upstream variables. The model shall contain enough detail to be able to provide accurate cell's performance predictions that shall be used for future optimization and scale-up activities.

Make-up Sodium Production Process

A process model for the production of sodium metal from sodium hydroxide through a low temperature electrolysis process has been proposed. This sodium production process can be implemented as an alternative to directly purchasing sodium to make up for the metal losses expe-

rienced in the sodium recovery process. Figure shows a schematic of the overall process. Anhydrous sodium hydroxide is fed into a stirred tank, where it is mixed with recycled anolyte coming from the electrolysis cells. The anolyte solution is then preheated to the electrolysis cell temperature conditions using the Joule heating from the cells as heat source. The preheated anolyte solution enters the electrolysis cell, where the following oxidation/reduction reactions occur.



Sodium ions selectively diffuse through the NaSICON membrane and are reduced to sodium metal within the molten sodium cathode. Simultaneously, the hydroxyl anions are oxidized to oxygen gas and water vapor within the anode chamber. At atmospheric pressure and cell temperature conditions (~120-140°C), the estimated cell Nernst Potential is equal to -3.3V. The produced molten sodium is continuously pumped to a storage tank and the depleted anolyte is recycled back to the mixing tank. A stream consisting of oxygen and water vapor flows out of the anode compartment as oxidation products.

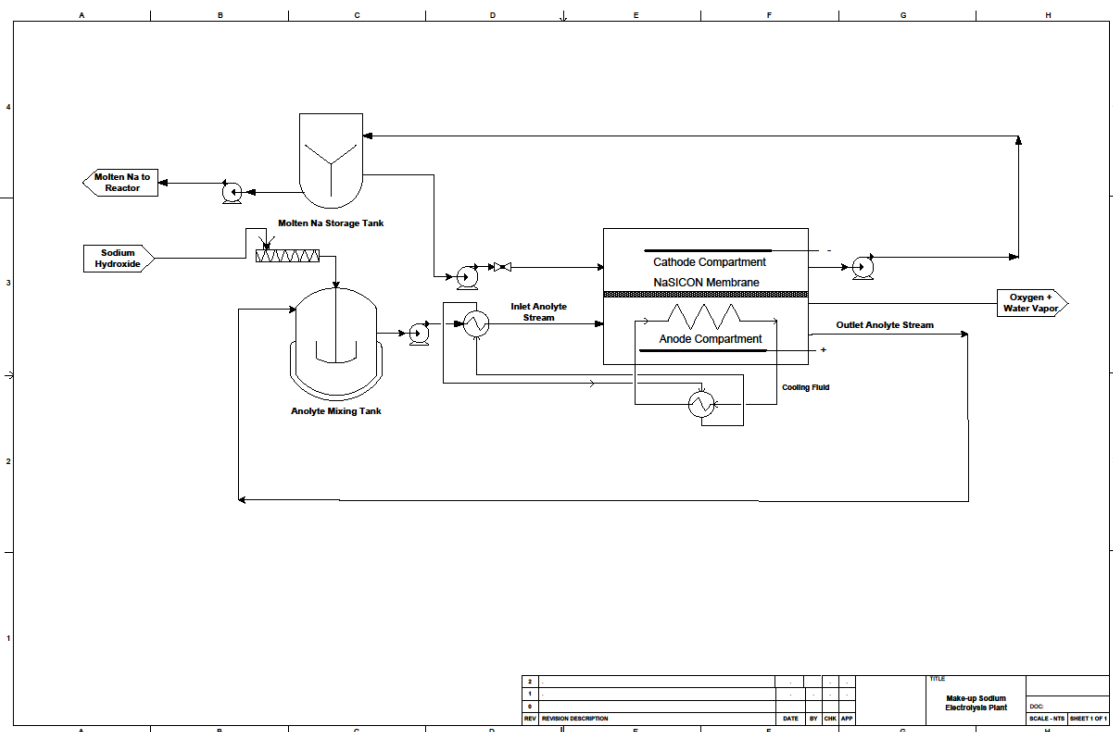


Figure 15: Schematic of the proposed make-up sodium electrolytic process

Overall mass and energy balances have been done for the proposed process. As calculation basis, we have assumed 5% sodium losses within the sodium recovery process for a 25,000 barrel per day oil upgrading facility using three different oil stocks. Other assumptions followed are listed below:

- The inlet and outlet sodium hydroxide concentrations in the anolyte solvent are equal to 12% and 2% wt., respectively.
- The purity of the anhydrous sodium hydroxide is 99.6% wt.
- 100% current efficiency or 100% selectivity towards the desired redox reactions.

- The electrolysis cells are maintained in isothermal conditions.
- The recycled anolyte and the sodium hydroxide streams are introduced into the anolyte mixing tank at ambient temperature conditions.
- Anolyte, molten sodium and gas streams exit at the temperature of the cell.
- The anolyte solution is preheated to the cell's temperature using some of the Joule heating released within the cell. The remaining heat can be exported to another process.

Table 8 displays the process streams mass flow rates for the three different type of oil feedstocks. From the process energy balance, it has been estimated that approximately only 33% of the energy released within the electrolysis cell, due to Joule heating, is needed to preheat the anolyte solution. The remaining 66% could be exported to the reaction step of the oil upgrading process to heat-up the oil in the main reactor.

Table 8: Mass balance for the electrolytic sodium make-up production process

Type of Oil	Make-up Na Produced	NaOH Consumed	Inlet Anolyte Stream	Recycled Anolyte Stream	Oxygen	Water
	ton/day	ton/day	ton/day	ton/day	ton/day	ton/day
Shale Oil 1	12.90	22.44	219.92	197.47	4.49	5.05
Shale Oil 2	5.88	10.22	100.20	89.98	2.04	2.30
Heavy Oil 1	11.77	20.47	200.61	180.14	4.09	4.61

2.8.3 Subtask 8.3 – Preliminary cost analysis

The Recipient shall incorporate the cost models for equipment procurement and installation from Subtasks 8.1 and 8.2 into an updated preliminary cost model.

Preliminary Cost Analysis for the Make-up Sodium Production Process

a. Process Operating Costs

An operating and capital cost estimation study for an electrolytic process to produce sodium metal from sodium hydroxide has been conducted. These cost estimates were conducted based on 25,000 barrels of oil per day upgrading plant, assuming that 5% of the sodium needed cannot be recovered and need to be replaced. An optimum current density of 50 mA/cm², to operate the electrolysis cells, has been found by minimizing the sum of the cost of electrical power and the cost of the NaSICON material.

To estimate the process operating costs, we have identified and focused on the largest cost contributors. These include cost of raw materials (sodium hydroxide), electrical power, membrane replacement, and labor costs. The electrolysis electrical power costs have been subdivided into cell and non-cell costs. The non-cell items include the electrical costs associated with electrolyte and sodium metal pumping, and anolyte mixing in the anolyte stirred tank. An electricity cost of 6.59 cents per kw-h has been used in the calculation of the electrolysis cost. It has been assumed that the energy needed to preheat the anolyte solution, before it enters the cells, is recovered from the heat released within the cells. We have assumed that the expected life of the ionic conductive membranes (e.g. tubes) in the cells is 18 months. Membrane replacement in-

cludes raw materials and fabrication costs, but not the removal of the old and installation of the new membranes. In the raw material losses group we have included the loss of anolyte solvent at a rate of 20% loss per year based on the total anolyte inventory. Labor costs have been calculated as a 15% flat rate of the total operating costs. Table 9 shows the contribution from each of the categories and the total operating costs of the sodium production process. The percent cost distribution is shown in a pie chart (Figure 16). We have not included other costs that might quantitatively contribute to the overall costs such as non-membrane maintenance and repairs, general plant utilities, equipment depreciation, taxes, etc. The cost of raw materials (sodium hydroxide) accounts for 67.8% of the total cost, whereas total electrical power accounts for 15.2%. Therefore, sodium production costs are ultimately dominated by the cost of anhydrous sodium hydroxide and not so much by the cost of electrical power or the cost of the NaSICON membranes.

Table 9: Operating costs (in dollars per kg of sodium) for an electrolytic sodium production process, where the cells are operated at the optimum current density and temperature conditions

Cell Power	Non-Cell Power	Raw Material Losses	Tubes Replacement	Labor	Total
\$/kg Na	\$/kg Na	\$/kg Na	\$/kg Na	\$/kg Na	\$/kg Na
0.300	0.000	1.341	0.039	0.296	1.977

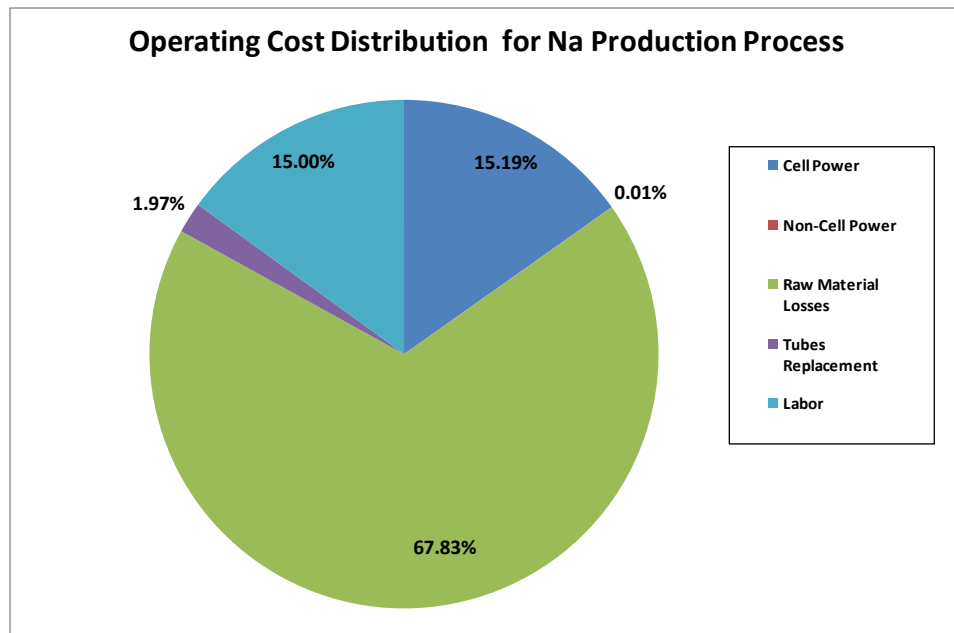


Figure 16: Operating costs distribution for the sodium production process

b. Capital Estimation Costs

The estimation of the capital costs of an electrolytic sodium metal production plant, operating at the optimum conditions, has been conducted. This estimation covered the cost of the main pieces of equipment, raw materials, equipment installation, installed piping and fittings, instrumentation and controls, basic plant facilities, and the cost of electrical installations. Indirect costs such as engineering and supervision, construction expenses, contractor fees, or contingencies were not considered at this time. Equipment sizing was based on a sodium metal production rate equivalent to 5% of the sodium requirements (loses) for a 25,000 barrels per day oil upgrading facility. Costing of standard pieces equipment such storage and mixing tanks, heat exchangers, filters, pumps, and others was done based on general engineering rules of thumb and order of magnitude scaling factors.

The electrolysis cells were priced based on the cost of their materials of construction after a basic design was proposed. Raw materials included fresh anolyte solvent and enough sodium to prime the electrolysis cells. The costs of equipment installation, instrumentation+controls, installed piping+fittings, electrical installations, and service facilities were calculated as percentages of the total capital of purchased equipment. The percentages used are approximations based on ordinary chemical processing plants. Table 10 shows the total plant capital cost for the three different types of oils considered. The columns showing the total cost in terms of dollars per kilo of sodium produced and in dollars per barrel of oil upgraded reflect the total capital investment of the plant divided by an expected plant life of 15 years. Figure 17 displays the capital cost distribution among the different categories as a percentage of the total cost for Shale Oil #1.

Similarly to the sodium recovery plant costs, reported in the January-March Quarterly Report, the two priciest pieces of equipment in the plant are the electrolysis cells and electrical transformers-rectifiers. It should be kept in mind that this cost estimation is very preliminary and a large error (>50%) is expected.

Table 101: Total capital costs for an electrolytic sodium production facility sized to produce 5% of the total sodium metal requirements of a 25,000 barrel per day oil upgrading plant

Type of Oil	Total Capital Costs		
	MM\$	\$/kg Na	\$/bbl oil
Shale Oil 1	5.755	0.081	0.042
Shale Oil 2	4.831	0.150	0.035
Heavy Oil 1	5.611	0.087	0.041

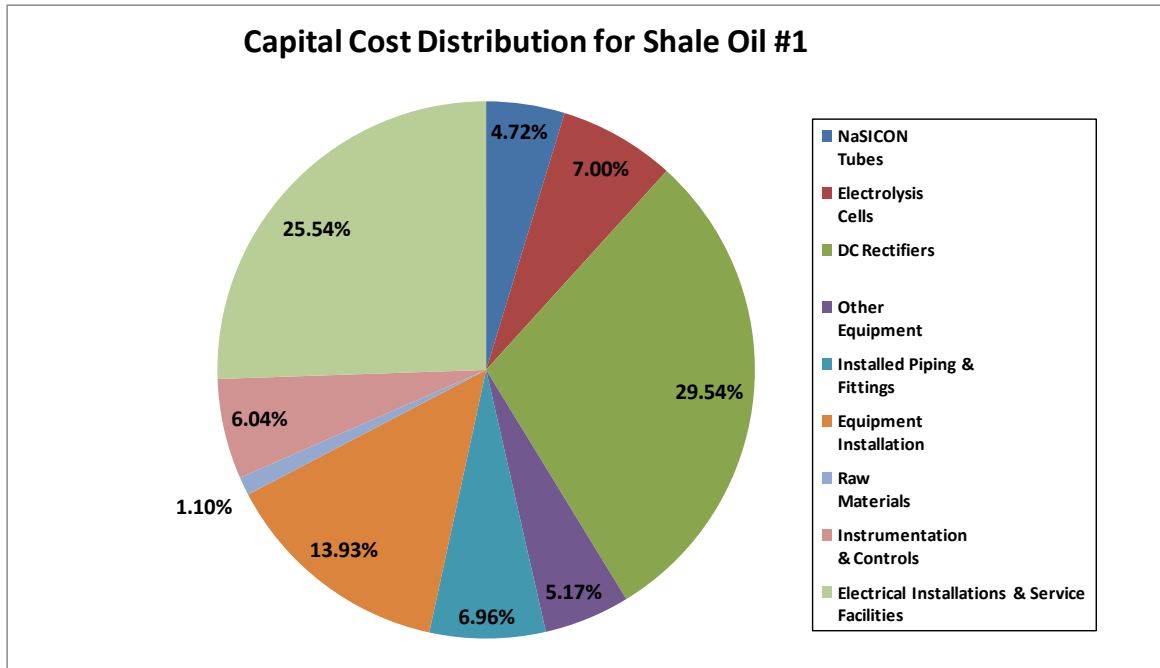


Figure 171: Capital costs distribution for an electrolytic sodium production facility sized to produce 5% of the total sodium metal requirements of a 25,000 barrel per day oil upgrading plant

2.8.4 Subtask 8.4 – Pilot plant cost estimate

The Recipient shall estimate the costs for equipment procurement and installation based on knowledge obtained in earlier tasks. This task is underway.

3. CONCLUSION

Our conclusion at this point is that high levels of both sulfur and metals can be removed from shale oil, heavy oil or bitumen with the process tested. Nitrogen removal has been less successful. In most cases, both methane and hydrogen are effective in removal of sulfur, nitrogen, heavy metals, and increasing API gravity

4. COST STATUS

The corrected monthly costs of the 7th quarter are shown in Table 11, along with the projected costs stated in the Project Management Plan and the monthly costs of the 8th quarter are shown in Table 12, along with the projected costs stated in the Project Management Plan.

Table 11: Project revised costing profile for the 7th Quarter

		Jan-11		Feb-11		Mar-11		Q6	
		Projected	Actual	Projected	Actual	Projected	Actual	Projected	Actual
Direct Labor			25,511.93		19,790.29		25,991.27		71,293.49
Benefits	32%		8,163.82		6,332.89		8,317.21		22,813.92
Overhead	41%		10,459.89		8,114.02		10,656.42		29,230.33
Total Burdened Labor			44,135.64		34,237.20		44,964.90		123,337.74
Direct Materials / Spec Test			31,202.93		26,913.53		38,574.26		96,690.72
Equipment					59,498.10				59,498.10
Travel							-		-
Subtotal			75,338.57		120,648.83		83,539.16		279,526.56
G&A	29%		21,848.19		34,988.16		24,226.36		81,062.71
Total monthly		67,115.12	97,186.76	60,237.08	155,636.99	70,063.18	107,765.52	197,415.39	360,589.27

Table 12: Project costing profile for the 8th Quarter

		Apr-11		May-11		Jun-11		Q7	
		Projected	Actual	Projected	Actual	Projected	Actual	Projected	Actual
Direct Labor			25,179.91		29,743.90		27,035.16		81,958.97
Benefits	32%		8,057.57		9,518.05		8,651.25		26,226.87
Overhead	41%		10,323.76		12,195.00		11,084.42		33,603.18
Total Burdened Labor			43,561.24		51,456.95		46,770.83		141,789.02
Direct Materials / Spec Test			26,116.28		27,626.47		29,029.52		82,772.27
Equipment			31,637.50						31,637.50
Travel			1,240.50		893.83		3,419.61		5,553.94
Subtotal			102,555.52		79,977.25		79,219.96		261,752.73
G&A	29%		29,741.10		23,193.40		22,973.79		75,908.29
Total monthly		291,122.91	132,296.62	-	103,170.65	-	102,193.75	291,122.91	337,661.02

In April 2011 an equipment charge was erroneous which was caught and corrected in Aug 2011.

Figure 18 shows a plot of the total monthly costs and the initially projected costs versus time and Figure 19 shows the cumulative monthly costs versus time. Also shown in the figure is the fraction of actual over planned cumulative expenses.

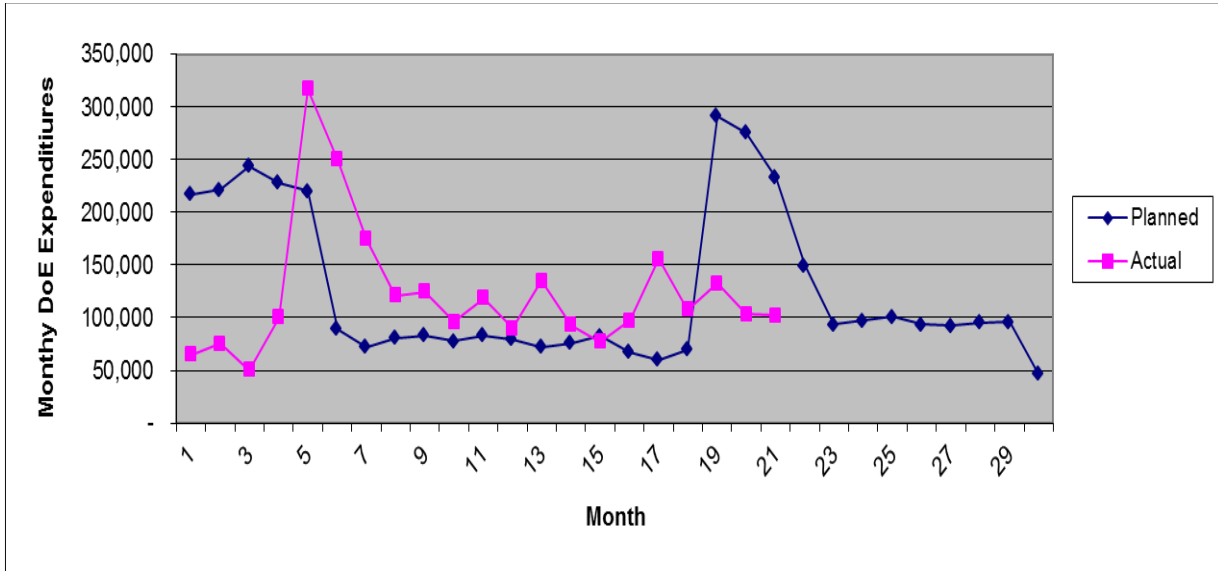


Figure 18: Projected and actual monthly costs over time

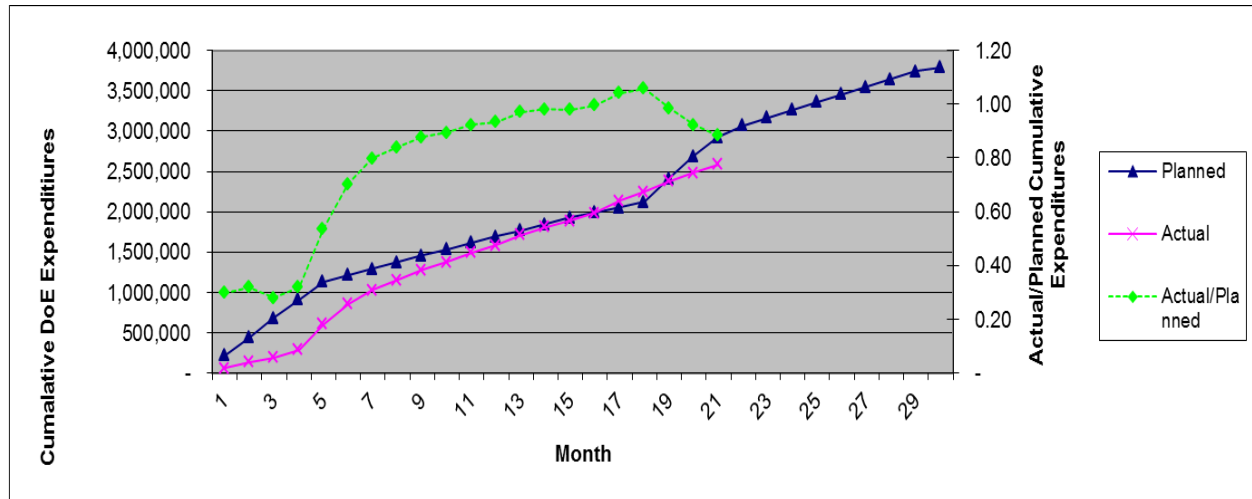


Figure 19: Projected and actual cumulative costs over time

5. MILESTONE STATUS

New milestones need to be set for the current Budget Period.

Table 13: Milestone log for 6th 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	3/26/10	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	3/26/10	3/31/11	Process runs underway
5	3.1.1	Complete membranes for Phase 1	9/29/09	7/5/10	9/29/09	9/20/10	Membrane fabrication has exceeded demand for fabrication. Mechanical characterization was complete on September 20, 2010.
6	3.3	Cells ready for operation	4/13/10	2/28/11	4/13/10	3/31/11	Cells were ready for operation on time. Initial cells testing began running 4/26/10 when sufficient sodium polysulfide was synthesized.
7	4.3	Preliminary cost model complete	2/8/11	3/14/11	1/4/11	3/18/11	A preliminary cost model was completed and reviewed internally. Adjustments were recommended by the reviewers and additional cases suggested for updated cost models.

6. ACCOMPLISHMENTS

- Electrolysis of sodium sulfide at temperatures of molten sodium have continued and are showing very encouraging results.
- Salts from reaction with bitumen were dissolved and electrolyzed to produce sodium.
- Reactor tests bitumen have begun with results similar to heavy oil.
- Separation procedure was modified and head space analysis was instituted to work toward a mass balance.
- The API model is a predictor for bitumen as well as heavy oil.
- Electrolysis of Na₂S₄ has run nearly 3400 hours at the target current density and temperature on a single membrane with no deterioration in performance.

7. PROBLEMS OR DELAYS

We are still working on improving the separation processes of the salts after reaction. In some cases the salts electrolyze very well, in other cases the anolyte polarizes the cell. We need to determine why some runs provide better results than others.

8. PRODUCTS

No products to report at this time.

9. LIST OF APPENDICES

None

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