Causticizing for Black Liquor Gasifiers

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# ABSTRACT

The cost-benefit outlook of black liquor gasification (BLG) could be greatly improved if the smelt causticization step could be achieved *in situ* during the gasification step. Or, at a minimum, the increase in causticizing load associated with BLG could be mitigated. A number of chemistries have been proven successful during black liquor combustion. In this project, three in situ causticizing processes (titanate, manganate, and borate) were evaluated under conditions suitable for high temperature entrained flow BLG, and low temperature steam reforming of black liquor. The evaluation included both thermodynamic modeling and lab experimentation. Titanate and manganate were tested for complete direct causticizing (to thus eliminate the lime cycle), and borates were evaluated for partial causticizing (to mitigate the load increase associated with BLG). Criteria included high carbonate conversion, corresponding hydroxide recovery upon hydrolysis, non process element (NPE) removal, and economics. Of the six cases (three chemistries at two BLG conditions), only two were found to be industrially viable: titanates for complete causticizing during high temperature BLG, and borates for partial causticizing during high temperature BLG. These two cases were evaluated for integration into a gasification-based recovery island. The Larsen [28] BLG cost-benefit study was used as a reference case for economic forecasting (i.e. a 1500 tpd pulp mill using BLG and upgrading the lime cycle). By comparison, using the titanate direct causticizing process yielded a net present value (NPV) of \$25M over the NPV of BLG with conventional lime cycle. Using the existing lime cycle plus borate autocausticizing for extra capacity yielded a NPV of \$16M.

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# **INTRODUCTION**

In order for both the low and high temperature black liquor gasification (LTBLG, HTBLG) technologies to become economically viable alternatives to the conventional recovery cycle, the issues relating to causticization and dregs purge must be addressed. LTBLG (i.e. the MTCI process) is carried out with steam, in a fluidized bed, at 600°C, near atmospheric pressure, and requires over 50 hours residence time for organic carbon conversion. 600°C is well below the melting point of the inorganic products, producing a solid inorganic phase which is then dissolved to make green liquor. HTBLG (i.e. the Chemrec process) is carried out with air or oxygen, using an entrained flow reactor, at approximately 950°C, and requires about 5 seconds residence time. It can be accomplished at either atmospheric or pressurized conditions, and it produces a molten inorganic phase, which is then quenched into an aqueous solution. Causticization refers to the overall conversion of Na<sub>2</sub>CO<sub>3</sub> to NaOH and CO<sub>2</sub>. In a conventional recovery boiler the reducing conditions in the char bed region produce partial causticization of the smelt prior to exiting the boiler. Additionally, a portion of the sodium in the smelt is bound up as Na<sub>2</sub>S, thereby reducing the amount of sodium available to form Na<sub>2</sub>CO<sub>3</sub>. Causticization of the remaining  $Na_2CO_3$  is then completed by the lime cycle. In the case of LTBLG, the bulk of the sulfur ends up in the gas phase, and the solid product is predominantly Na<sub>2</sub>CO<sub>3</sub>, creating an even greater causticizing load than for conventional recovery. If scrubbing is used to remove H<sub>2</sub>S from the gas, then some CO<sub>2</sub> will be coabsorbed; this CO<sub>2</sub> must also be causticized. The inherent separation of sulfur and sodium creates opportunities for high yield pulping but the additional causticizing load must be addressed. The situation is only slightly better for HTBLG. The sulfur is split between the gas and solid phases so a smaller portion of the sulfur is available to bind up sodium as Na2S as compared to conventional recovery. Additionally, in the Chemrec HTBLG system, the water quenching of the smelt results in co-absorption of CO<sub>2</sub>, which must be subsequently causticized. So, although the reasons are different for each case, increased causticizing load will be a problem for both HTBLG and LTBLG processes. Direct and auto causticizing processes offer a solution to this problem. These in situ processes involve adding some chemical agent to either the black liquor or the product smelt that reacts preferentially with the sodium to form a salt and thus allow the carbon to be released as CO<sub>2</sub>. At the minimum, partial in situ causticization would mitigate the *increase* in causticizing load compared to conventional recovery; thus allowing existing lime cycle equipment to be used in conjunction with a gasifier. However if a sufficiently high yield of in situ causticization can be obtained, it would eliminate the need for the lime cycle resulting in significant energy and capital savings.

Currently there are three promising processes that are worthy of testing and evaluation, at realistic gasifier conditions, for feasibility of partial and complete in situ causticization during BLG. Methods of purging dregs will be explored for the feasible processes. Finally, economic and mill integration studies will be performed for the viable candidates. The three processes are:

# Direct Causticization using Titanates.

In this system sodium trititanate is added to the liquor to bind up the sodium as pentatitanate and allow the carbon to be released as CO or  $CO_2$ . The main reactions involved are considered to be:

$$Na_2CO_3 + 3 TiO_2 (s) \iff Na_2O'3TiO_2 (s) + CO_2 (g)$$
 (1)

$$7 \operatorname{Na_2CO_3} + 5 (\operatorname{Na_2O'3TiO_2})(s) \iff 3 (4\operatorname{Na_2O'5TiO_2})(s) + 7 \operatorname{CO_2}(g)$$
 (2)

$$Na2O \cdot 6TiO2(s) + Na2CO3(s) \leftrightarrow 2(Na2O \cdot 3TiO2)(s) + CO2(g)$$
(3)

[Abbreviated NT3, N4T5, NT6]

Reaction (1) is how make-up titanate is introduced to the system. Reactions (2) and (3) are repeated cyclically in the gasifier. The sodium pentatitanate formed in the gasifier is leached with water, forming solid sodium trititanate and sodium hydroxide (white liquor) via reaction (4):

$$3 (4Na_2O 5TiO_2) (s) + 7 H_2O \leftrightarrow 14 NaOH (aq) + 5 (Na_2O 3TiO_2) (s)$$
 (4)

$$2(\text{Na2O}\cdot3\text{TiO2})(\text{s}) + \text{H2O} \leftrightarrow 2\text{NaOH}(\text{aq}) + \text{Na2O}\cdot6\text{TiO2}(\text{s})$$
(5)

Recent work at IPST has shown that NT3 can be further leached to NT6 via reaction (5), which has additional causticizing potential than NT3 via reaction (3). The leached NT3 and NT6 solids are separated from the caustic (white liquor) and recycled to the gasifier/reactor where reactions (2) and (3) repeat. For HTBLG the remaining solution is sulfur-lean white liquor since some Na<sub>2</sub>S is present. For LTBLG the remaining solution is non-sulfur white liquor since virtually no Na<sub>2</sub>S is present in the solid phase. The H<sub>2</sub>S

is separated from the gasification gas and can be used to produce an aqueous sulfur-rich stream. Consequently, white liquors of varying sulfidity can be obtained as shown in Figure 1 below.

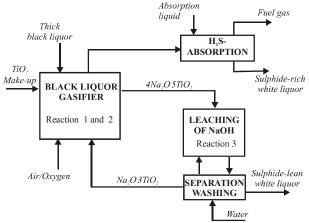


Figure 1. Black liquor gasification process with titanate direct causticization. The process would be analogous for manganates.

The kinetics of these reactions has been shown to be fast enough to occur within a HTBLG system [2&3]. Nearly complete conversion was obtained at 900-1000°C under  $CO_2$  gasification conditions. It was also found that the causticization reactions took place faster during simultaneous black liquor gasification than for mixtures of titanate and carbonate with no black liquor. This is strong evidence that complete causticization could be obtained in a gasifier. The chemistry must be tested under pressurized, water vapor/O2 blown gasification conditions representative of those found in a Chemrec-type gasifier. Also, the means to purge dregs must be addressed.

A number of studies [11]-[15] have shown that titanates will causticize sodium carbonate under conditions relevant to LTBLG. However, minimal work has been done during actual BLG [15], and even that was done under gasification with  $CO_2$ . To date, no published BLG work has been done with titanates in water vapor at or near 600°C.

# Direct Causticization using Manganates.

In this system  $Mn_3O_4$  is added to bind up the sodium and allow carbon to be released as CO or CO<sub>2</sub>. For gasification, the process schematic would be analogous to that shown in Figure 1. A Canadian patent [29] describes a direct causticizing process using  $MnO_2$ , but there was no experimental work supporting the claims. Eames and Empie [4&5] have determined the causticization reaction to be:

$$Na_2CO_3 + Mn_3O_4 \Longrightarrow 2NaMnO_2 + MnO + CO_2$$
(6)

Over 98% conversion was obtained in under 24 hours for both the solid (650-850°C), and liquid (850-950°C) phase regimes chosen for this work. Mn3O4 is recovered and hydroxide is formed upon hydrolysis:

$$2NaMnO_2 + MnO + H_2O \Longrightarrow 2NaOH(aq) + Mn_3O_4(s)$$
(7)

The Mn<sub>3</sub>O<sub>4</sub> precipitate would then be separated from the solution and added to the black liquor entering the gasifier. A major consideration is whether manganate will interfere

with sulfur chemistry. When  $Na_2S$  was added to reaction (6), it was oxidized to  $Na_2SO_4$  as shown in reaction (8); however the metallic sulfide (MnS) was not found in either the product smelt or the precipitate following hydrolysis [4&5].

$$Na_2S + 4Mn_3O_4 => Na_2SO_4 + 12MnO$$
 (8)

So, in a system where significant amounts of sulfur partition into the smelt phase (HTBLG, and conventional recovery boilers), this creates a problem in that a major pulping chemical is oxidized and must then be reduced in a separate process. For this reason we feel it is fruitless to pursue this process under HTBLG conditions. However, in LTBLG virtually all of the sulfur leaves with the gas as H2S. It has yet to be determined experimentally if H2S released during LTBLG will react to form MnS. It has been determined [4] that the required residence time for causticization via reaction (6) is much less than the 50 hours of residence time required by the MTCI LTBLG process, and is therefore worthy of further investigation under LTBLG conditions.

### Autocausticization using Borates.

In this process the sodium would be bound up by borate in the gasifier as follows:

$$NaBO_2 + Na_2CO_3 \iff Na_3BO_3 + CO_2$$
(9)

The caustic is recovered upon hydrolysis:

$$Na_{3}BO_{3} + H_{2}O \Longrightarrow 2NaOH(aq) + NaBO_{2} (aq)$$
(10)

Note here that autocausticization differs from direct causticization in that the agent is soluble in water and thus circulates through the pulping cycle. The dregs would be the only precipitates, resulting in a convenient removal mechanism. The drawback is that the circulating borates are essentially dead load with respect to the pulping operation, somewhat limiting the throughput capacity. The use of borates for partial autocausticizing (as incremental capacity) in kraft mills is well documented, and mill trials have been successful [6]-[8]. Partial borate autocausticization has been obtained with black liquor under CO<sub>2</sub> gasification conditions at 5 bar in the IPST pressurized gasifier (PEFR) at 950°C [9]. Additional testing is needed to determine if complete autocausticization can be obtained at HTBLG, and if the process is viable at LTBLG conditions.

# Scope of Work

In Phase I of the project the in situ causticizing technologies will be tested, both experimentally and with an equilibrium model, at realistic black liquor gasification conditions to determine if complete causticization can be achieved, or alternately if sufficient partial (approximately 40%) in situ causticization can be achieved. The high temperature borate and titanate cases will be evaluated using the pressurized entrained flow reactor at IPST. The low temperature experiments with borate, titanate, and manganate will be carried out at IPST using a semi-batch fixed bed reactor. A special autotitrator on loan from U.S. Borax will be used to analyze the borate samples. Standard analytical techniques will be used on the remaining samples. In all cases, the goal is to gasify the liquor/agent mixtures under conditions representative of the gas leaving an industrial gasifier. In Phase II the processes that pass Phase I will be developed for potential ways to purge dregs. The dregs will first be characterized. Possible purge

methods include, but are not limited to: selective dissolution, clarifiers, liquid cyclones, and agglomerating agents. Passing Phase III requires that a sound method for dregs purge be developed. The options will be assessed jointly by all collaborators after the dregs have been characterized. IPST will then conduct laboratory measurements to test the proposed methods. In Phase III the processes that pass Phase II (if any) would undergo an economic evaluation including a plan for mill/gasifier integration. This will be done by James Cantrell of Jacobs Engineering Group with the support of all collaborators as needed.

# EXPERIMENTAL

The in situ causticization reactions (Reactions 2, 6, and 9) were evaluated both experimentally and with an equilibrium computer model. The equilibrium calculations were carried out using FactSage<sup>TM</sup> 5.1, which determines the equilibrium composition of a chemical system by minimizing Gibbs free energy of the entire system. It was introduced in 2001 as a fusion of the FACT-Win<sup>TM</sup>/F\*A\*C\*T<sup>TM</sup> and ChemSage<sup>TM</sup>/SOLGASMIX<sup>TM</sup> thermochemical packages. The FactSage<sup>TM</sup> package runs on a PC operating under Microsoft Windows and consists of a series of information, database, calculation, and manipulation modules.

The composition of the base liquor used in this project is shown in Table 1. It is fairly typical North American kraft liquor. Various causticizing agents were added in the proportions shown in Table 2. The combined elemental composition was used as input to FactSage<sup>TM</sup>, and for the experiments.

Та	ible 1
Starting Black	<u>Liquor Dry Mass</u>
Com	<u>position</u>
Carbon	34.8%
Hydrogen	3.1%
Oxygen	35.6%
Sodium	19.5%
Sulfur	5.2%
Potassium	1.7%
Chlorine	0.1%

Table 2           Causticizing Agent Additions to Black Liquor			
Compound g/Kg DBLS Metal/Na mass ratio			
Titanate (100% conv)	Na <sub>2</sub> O·3TiO <sub>2</sub>	960	1.34
Borate (20% conversion)	NaBO2*2H2O	58	0.03
Manganate (100% conv)	Mn3O4	979	3.62

	Table 3
	Species Included in the FactSage Equilibrium Calculations
Gases	CH <sub>4</sub> , C <sub>2</sub> H <sub>2</sub> , C <sub>2</sub> H <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , CO, CO <sub>2</sub> , COS, CS, CS <sub>2</sub> , H, HS, H <sub>2</sub> S <sub>2</sub> , H <sub>2</sub> , H <sub>2</sub> O, H <sub>2</sub> S, O, O <sub>2</sub> , OH, N, N <sub>2</sub> , S, S <sub>2</sub> , SO, SO <sub>2</sub> , SO <sub>3</sub> , SSO, Na, Na <sub>2</sub> , NaOH, NaCN
Liquids*	$\begin{array}{llllllllllllllllllllllllllllllllllll$
Solids*	$\begin{array}{llllllllllllllllllllllllllllllllllll$
	* Two key compounds, Na3BO3 and NaMnO2, were not found in the FactSage database. Data could not be found in the literature for these compounds. See text for explanation.

Table 3 shows the relevant chemical species included in the modeling. For species not included in the FactSage thermodynamic database, the required information can be added, assuming it is available. One key borate compound is not included in the database and data for that compound could not be found in the literature. However, some conclusions can still be drawn for the borate system and the rationale for doing so is explained in the results section. For the manganate system, the database did not include any sodium-manganese compound, nor could the required data be found in the literature. The manganate system therefore could not be modeled.

The experimental portion of the work was performed in specialized reactors that mimic the conditions of temperature, pressure, and gas composition found in full scale gasifiers. They are described in detail below. The black liquor fuels were prepared by doping the liquor shown in Table 1 with causticizing agents as shown in Table 2, drying in a laboratory oven at 110C, grinding in a ball mill, and finally sieving to obtain particles of size 63-90 microns.

# Laminar Entrained Flow Reactors

Laminar entrained-flow reactors have been used extensively to investigate coal, biomass, and black liquor combustion and gasification. The advantages of using a laminar entrained-flow reactor for gasification studies are the rapid heating and cooling rates which allow for experiments at nearly isothermal conditions for controlled amounts of time, and the possibility to make experiments in controlled and well-defined gas atmospheres. The atmospheric-pressure entrained-flow reactor (LEFR) located at IPST

(schematic shown in Figure 2) has been successfully utilized for numerous studies of black liquor pyrolysis, combustion and gasification. A larger pressurized entrained flow reactor (PEFR) has been used successfully in three studies involving various aspects of gasification of black liquor [9, 18, 19].

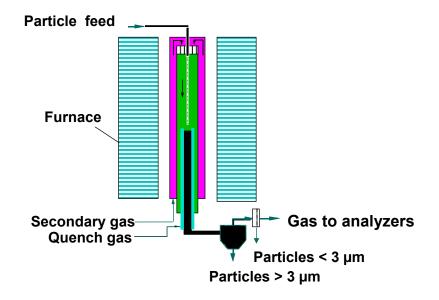


Figure 2. Diagram of an entrained flow reactor

In these reactors, solid particles of the material to be gasified are entrained in the primary gas stream and fed into the reactor via a water-cooled injection tube. A secondary gas stream, which constitutes the main part of the reaction gas is preheated to the desired reaction temperature and then enters the reactor concentric to the particles and primary gas stream. The solid particles and the primary gas are rapidly heated (particle heating rates of  $10^4 - 10^5$  °C/s) by radiation from the hot reactor walls and convection from the hot secondary gas. The flow pattern through the reactor is laminar to prevent deposition of particles on the reactor walls. The gas and particles exit via a water-cooled probe. They are rapidly cooled by a quench gas that is introduced at the upper tip of the collector. The particles are separated from the sample gas and collected, and the gas is sent to gas analyzers. Placing such a reactor inside a pressure vessel allows for variable pressure. Photos of the PEFR and LEFR are shown in Figure 3.



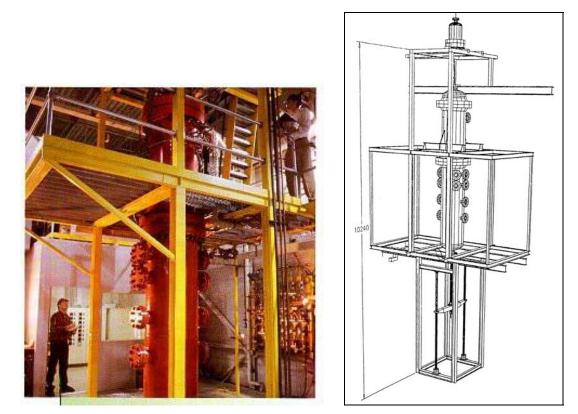


Figure 3. IPST's LEFR (top) shown with furnace open. Total height is 11 feet. Lower left is IPST's PEFR. Lower right is a CAD drawing of the PEFR. Total height is 35 feet.

An LEFR also has the flexibility of functioning as a semi-batch reactor. Rather than feeding fuel continuously, a sample container (supported by the collector probe) is placed inside the reactor. The reactor is purged with an inert gas and heated to the test temperature. The reaction gases are then fed through the reactor for a fixed amount of time, and then the reactor is cooled down and the sample removed. The heating and cooling time should be small compared to the total exposure time for good results. For the LTBLG experiments described above, the total residence time (50 hours) is large compared to the heat-up time (1 hour). The feed gas composition can be chosen to approximate the product gas composition from an industrial gasifier. In this way, a batch of solid fuel is exposed to the same conditions as if it was in a flow reactor or fluidized bed. A fixed bed reactor can be used to obtain gas-solid reaction conversion data, which can then be corrected to fluid bed conditions [20]. In this way, the difficulties of operating a lab-scale black liquor fluid bed reactor are avoided (i.e. agglomeration, carryover, temperature variations, etc).

The experimental conditions are summarized in Table 4. The causticizing agents were added to black liquor in the ratios shown in Table 2, mixed, and then spray-dried. The mixture ratios (doping levels) reflect amount calculated from the stoichiometry above to achieve specified conversions shown in the table. The solids were sieved to 63-90 microns for use in the entrained flow reactors.

Table 4. Experimental conditions			
	Low Temp	Pressurized High Temp	High Temp at 1 bar (for borates only)
Reactor	LEFR (semi-batch)	PEFR	LEFR (flow)
Temperature C	600	950	950
Pressure, bar	1	5 & 15	1
Feed gas	50%H2O in N2, with and w/o 5% and 10% CO2	5% &10% CO2 in N2, with and w/o 3% H2O	2% & 5% CO2 in N2
Residence time	50 hours	5 seconds	2 seconds

After reacting the doped liquors in the respective reactors, the residual solid material (char) was collected and analyzed by Coulometry for total carbon and carbonate carbon, and by Inductively Coupled Plasma emission spectroscopy for Na, K, Mn, Ti, and B. These tests each required about 1 gram of sample. If a sufficient mass of char was recovered on the borate experiments (additional 2 grams per test), then it was dissolved in water and titrated using a special dual titration technique. In this technique, developed by U.S. Borax, the sample is split into two parts to be titrated simultaneously by hydrochloric acid, and by silver nitrate. The combined results of the two titrations yields the concentration of carbonate, bicarbonate, hydroxide, borate, and sulfide ions. The test assumes that no other titratable ions are present in solution.

# Char Leaching Procedure

For the titanate and manganate cases, the char must be leached in accordance with reactions (3) and (9) to obtain aqueous hydroxide and the insoluble starting agent (which would be recycled to the gasifier with fresh black liquor in the real world process). The leachate (solution) can then be titrated for determination of carbonate and hydroxide concentrations.

The analytical leaching of the char samples was carried out in a 500 ml 3-necked flask (Figure 4) equipped with a water-cooled condenser, a thermometer and a Pasteur pipette through which  $N_2$  gas was bubbling through in order to eliminate air ( $O_2$  and  $CO_2$ ). While provided constant stirring with magnetic stirrers, the flask was heated via an oil bath in order to bring the water to boil. Evaporated water was condensed on the condenser and fell back down into the flask. When the distilled and deionized water reached its boiling point, 1.000 g of the recycled sample was added to the boiling water. The leaching time was 90 minutes in order to ensure complete reaction. Some of the samples were leached multiple times as explained in later sections.

After the leaching time had elapsed, the flask with the contents was removed from the oil bath and allowed to cool to room temperature. When cooled, the solution was quantitatively transferred to a previously weighed 60 ml 4-5.5  $\mu$ m fine glass filter Büchner funnel set up on a 1-liter Erlenmeyer flask and suction filtered by using an aspirator. The filtrate was thereafter transferred to a 250 ml volumetric flask and diluted with distilled and deionized water and put aside for further analysis. The filter cake was dried in an oven overnight (105 °C), and then weighed and stored for further analysis. Finally, the filtrate's caustic concentration was determined by acidimetric titration in a 751 GPD Titrino from Metrohm.

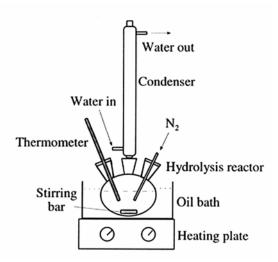


Figure 4. The leaching apparatus.

A 25 ml sample volume of the Na-Ti leachate was pipetted into a beaker. Barium chloride, 10 wt%, was added to the sample to bind any anions, such as carbonate, that would interfere with the titration of OH<sup>-</sup>. After adding phenolphthalein (PP) indicator, the

mixture was titrated to the PP end point 8.67 with a 0.1 M HCl solution. The volume of added HCl was noted and the NaOH concentration was calculated (see Appendix B).

To account for sulfide a formaldehyde solution (HCHO, 40% in water) was added to convert  $Na_2S$  to NaOH. If there were any sulfide ions present, the pink color should return. If the pink color of PP returned, the mixture was titrated again to the PP end point.

# Other Analysis

The titanate and manganate chars were also examined by X-ray diffraction (XRD), which can distinguish [qualitatively] between the reacted (e.g. N4T5) and unreacted (e.g. NT3) forms.

For the Phase II work on dregs purge, the leached solids were characterized by scanning electron microscopy (SEM) to determine how the non-process elements (NPE's or "dregs") were distributed; as discrete particles or bound to the titanate or manganate solids. This information was used to narrow the options for separating the NPE's from the leached solids prior to mixing the solids with fresh black liquor.

For the phase III work, the Larson study [28] was used as reference case for the economics of straight BLG. The incremental NPV and IRR of adding each in situ causticization case was then evaluated. For the mill integration study, the experimental results were used to build a WinGems<sup>™</sup> model of a gasification based recovery island with in situ Causticization using the processes found viable in Phases I and II.

# **RESULTS and DISCUSSION**

# **Equilibrium Modeling Results**

# Borate Modeling

For the equilibrium modeling the FactSage database contains data for several Na/B compounds (NaBO2, NaB3O5, NaB5O8, NaB9O14, Na2B4O7, Na2B8O13, Na4B2O5), but not Na<sub>3</sub>BO<sub>3</sub>. No thermodynamic data could be found in the literature. Only the existence of Na<sub>3</sub>BO<sub>3</sub> is mentioned in a 1939 patent. This does not however completely prevent us from making some reasonable predictions about sodium borates and BLG. Consider the phase diagram in Figure 5 for oxides of sodium and boron. For the case of Reaction 1 (above), the reactant is Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> and the desired product is 3Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>. On a phase diagram, starting with Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> and increasing the ratio of Na/B, the species 3Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> (equivalent to Na<sub>4</sub>B<sub>2</sub>O<sub>5</sub>) would be formed. Adding Na would eventually give 3Na2O-B2O3 (equivalent to Na3BO3). When viewed in this manor it is easy to see that if the thermodynamics do not favor the formation of Na4B2O5, then it is unlikely that Na<sub>3</sub>BO<sub>3</sub> would be favored either. Therefore the FactSage prediction that no Na4B2O5 forms during the gasification reaction also indicates that Na3BO3 should However that is not to say that if Na4B2O5 does form then Na3BO3 not form either. would also.

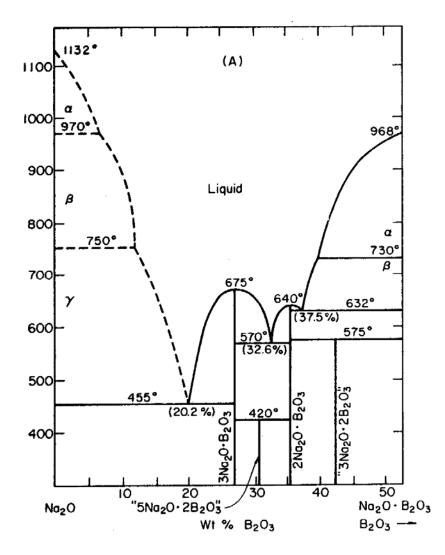


Figure 5. System Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>. Dashed lines refer to metastable equilibrium [21].

Figure 6 shows the FactSage equilibrium results for causticization of sodium carbonate in air as a function of temperature. In this simulation a large amount of air was used; therefore the hindering effects of CO<sub>2</sub> were not modeled. The reaction is favored above 800C. This is consistent with the experimental results of Tran, et.al. [6]

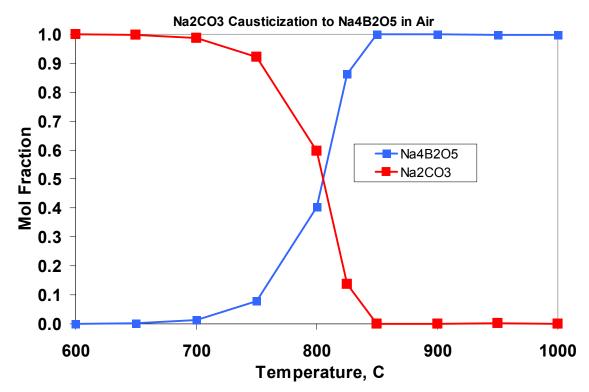


Figure 6. FactSage equilibrium model of sodium carbonate, sodium borate, at 100 mols air per mol solid (i.e. excess air to dilute CO<sub>2</sub>).

**Final Report** 

Figure 7 shows the FactSage prediction of the products of borate autocaust during  $O_2$ blown BLG. The  $O_2$ /fuel ratio is reasonable for industrial conditions. The autocaust (blue diamonds indicating  $Na_4B_2O_5$ ) reaction is favored only at very low pressures; in this simulation below about 1.2 bar. Above 1.2 bar the reaction does not proceed due to the partial pressure of  $CO_2$  in the product gas.  $CO_2$  hinders reaction (9). This is not encouraging for potential  $O_2$ -blown BLG envisioned to operate at 20-30 bar.

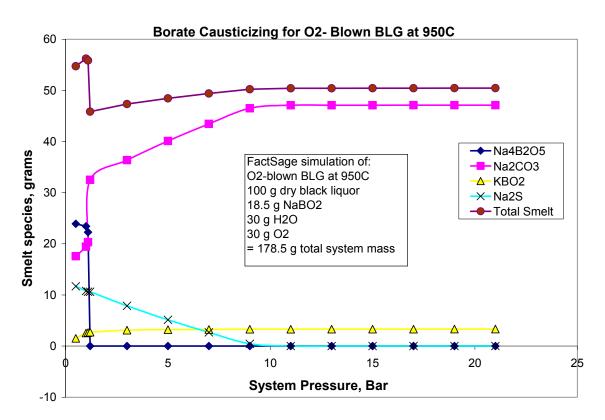


Figure 7. FactSage model of O2-blown BLG at an industrial gas/solid ratio

The impact of temperature on borate autocaust is shown in Figure 8 for the air-blown case BLG case. The result is dramatic. At 900C there is no conversion of NaBO<sub>2</sub> to Na<sub>4</sub>B<sub>2</sub>O<sub>5</sub>. Between 950C and 975C the reaction kicks in and carbonate is causticized. Note that the NaBO<sub>2</sub> concentration drop s zero but there is still carbonate present. The doping level modeled is appropriate for complete conversion to Na<sub>3</sub>BO<sub>3</sub>. Since Na<sub>3</sub>BO<sub>3</sub> is not in the FactSage database, the reaction can only proceed part way to Na<sub>2</sub>B<sub>2</sub>O<sub>5</sub>. Thus some carbonate remains. While this is not proof that Na<sub>3</sub>BO<sub>3</sub> would form, it is encouraging evidence. However the temperature of 950-975C for conversion is just about the value we expect to run.

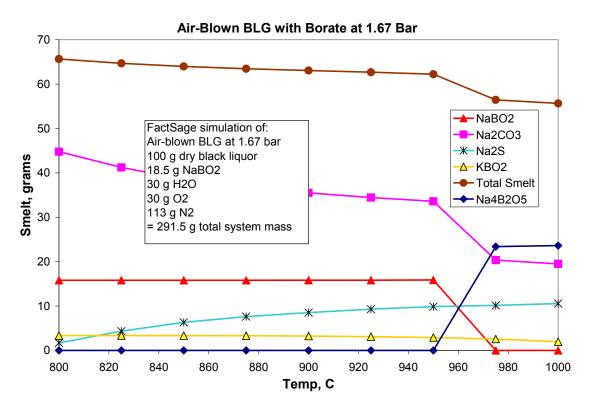


Figure 8. FactSage model of Air-blown BLG with borate at reasonable conditions for an industrial booster gasifier.

Figure 9 shows the FactSage predictions for borate autocaust during steam reforming at 600C. The results are similar to the air-blown case. The reaction (i.e. Rxn 9) begins to take place above 950C. However steam reforming of black liquor is carried out at 600C. In order for the bubbling bed steam reformer to work, the temperature must be kept below the melting point (in fact below the sticky temperature) of the solids. Therefore the FactSage model does not predict borate autocaust to work for black liquor steam reforming.

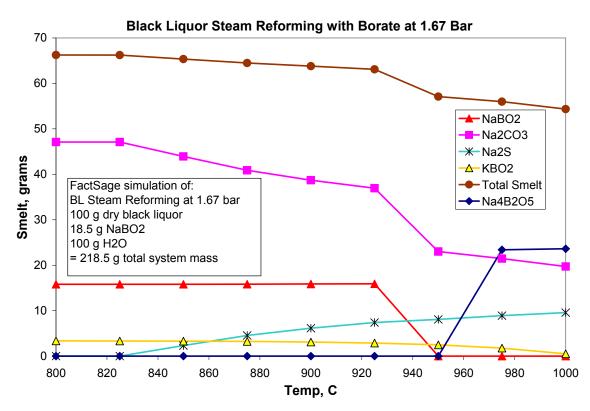


Figure 9. FactSage model of BLG with borate using steam over a range of temperatures.

### Equilibrium Modeling of BLG and Titanates

The FactSage simulation of BLG with titanate at air-blown atmospheric pressure conditions is shown in Table 10. The model predicts that causticizing conversion will take place above 600-650C. The conversion remains nearly complete until 800C, where the last remaining NT3 forms N4T5. It is interesting to note the presence of the NT species at 600C, so some causticizing is taking place even at 600C. Based on these results we would expect complete causticizing for BLG above 800C.

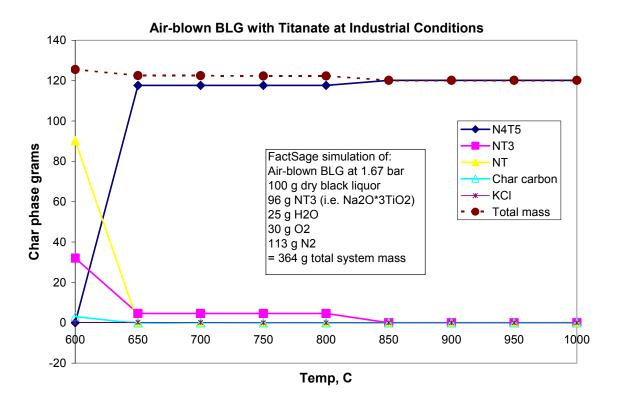


Figure 10. FactSage simulation of temperature dependence on air-blown BLG at 1.67 bar (10 psig) with titanate added for complete causticization.

In Figure 11, we see the results of the pressure dependence on oxygen-blown BLG with titanate at 950C, which is the specified temperature for the HTBLG process. Causticizing is complete at pressures to 10 bar and only drops off a bit between 10 and 20 bar. Based on this simulation, we would expect titanates to work fine for both atmospheric and pressurized HTBLG.

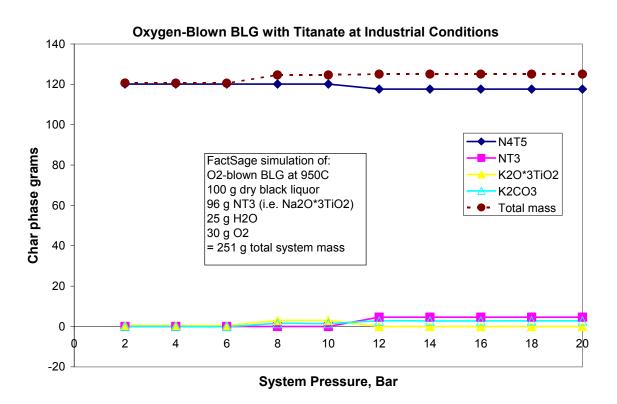


Figure 11. FactSage simulation of pressure dependence on oxygen-blown BLG at 950C with titanate added for complete causticization.

In Figure 12 on the following page the FactSage simulation for BL steam reforming with titanate causticizing is shown. The specified temperature for the industrial-scale process is 600C. The model predicts that the causticizing reactions progress at between 625 and 650C. Therefore we would not expect titanates to work for the BL steam reforming process.

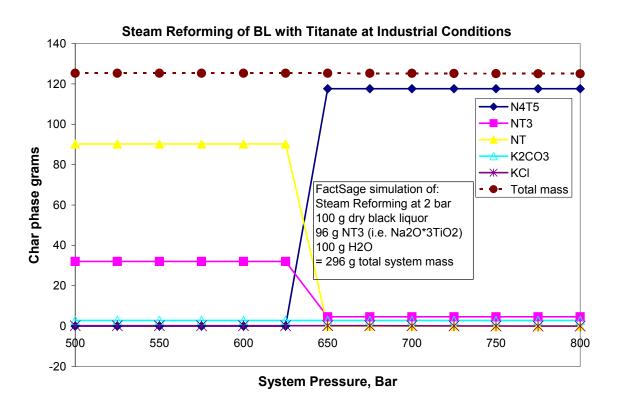


Figure 12. FactSage simulation of temperature dependence on steam reforming of BL at 2 bar, with titanate added for complete causticization.

# Equilibrium Modeling of BLG and Manganates

It was not possible to model the manganate/BLG system since thermodynamic data for one key compound ( $NaMnO_2$ ) was not in the FactSage database nor could it be found in the literature. Experimentation will have to suffice.

# **Experimental Results and Discussion**

A Table of raw data from the experiments is included in Appendix 1. Some discussion of how the data were analyzed is in order. The objective of this work is to reduce the amount of carbonate in gasification smelt via Reactions (2), (6), and (9). However, even if the reactions do not take place (i.e. conversion = 0) there will be a significant reduction in smelt carbonate due to the diluting effect of the causticizing agent. This must be

accounted for in the interpretation of the data. This is done by applying some assumptions and simple stoichiometry to the liquor composition shown in Table 1. The assumptions are as follows for the un-doped liquor:

- 1. Sodium forms chloride, sulfide, and carbonate
- 2. Potassium forms carbonate
- 3. The sulfur partitioned to the char phase in the high temperature case was measured for each experiment and the conversion back calculated based on the carbonate measured in the char. For the LT case, 100% of the sulfur portioned to the gas phase.
- 4. Complete gasification of fixed carbon is assumed

From these assumptions the composition of the smelt resulting from gasification of the black liquor is easily calculated. The result is the theoretical reference smelt and is shown in Table 5. The mass fraction of carbonate is the key quantity.

Table 5		
	Theoretical Reference Smelt C	Composition
Species	HT case (example 60% of S	LT case (no S in smelt)
1	to smelt) Mass %	Mass %
Na	43.1%	40.7%
K	3.8%	3.5%
CO <sub>3</sub>	46%	55.6%
S	6.9%	-
Cl	0.2%	0.2%

Once the reference smelt composition has been calculated, the causticizing agents are then included in the composition. Using stoichiometry again, the smelt composition is then calculated as a function of the conversion of the causticizing reactions. Specifically the theoretical carbonate concentration is calculated as a function of reaction conversion. This is done for each of the agents at each doping level. This is combined with the carbonate concentration in the reference smelt to obtain the percentage decrease in carbonate as a function of reaction conversion (shown in Figure 13). These relationships can be used to estimate the reaction conversion given the measured carbonate content in the smelt from the experiments. For example, 0% conversion would lead to a reduction in carbonate from the reference smelt due to dilution only. 50% conversion would yield a greater reduction in carbonate compared to the reference smelt (i.e. due to dilution and the causticizing reaction). By comparing experimental results from the doped liquors to experimental results from the un-doped liquor the net effect of the doping agent is measured. Then, the sulfur split must be taken into account as Na2S will offset Na2CO3 formation sans any causticizing taking place. This is most accurately done by measuring the sulfur in the smelt (char) phase and adjusting the reference smelt to match. Table 5 assumes a sulfur split of 60% but it will likely vary for each experiment. This technique results in lines like those in Figure 13 for each data point. This is the method that was used to back calculate causticizing conversion from smelt carbonate data.

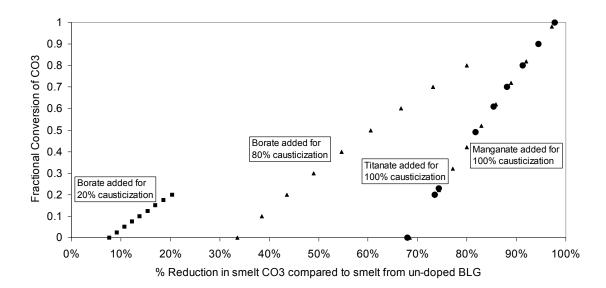


Figure 13. Predicted causticization reaction conversion as a function of the percent decrease in carbonate concentration compared to the reference (un-doped) case. These relationships are used to account for the diluting effects of the causticizing agent and translate the experimental smelt carbonate concentrations into the degree of reaction conversion.

#### **Titanate Experimental Results**

The results for the titanates at high temperature are shown in Figure 14. As expected from the stoichiometry and L'Chatlier's principal, CO2 inhibits all of the desired reactions. In order to utilize the results, we estimate the CO2 concentration in the syngas leaving a full scale gasifier over a range of conditions (Figure 15). These results are then superimposed on the experimentally derived conversion levels to estimate if the process in question would work in the real gasifier. The ranges of CO2 concentration are shown in Figure 14 to estimate the conditions for which titanates would be effective at high temperature. We estimate that from 1 to 5 bars total reactor pressure, the CO2 levels during BLG would be low enough to allow titanate direct causticizing (Task 1.1.2) to work to high conversion levels. This would correspond to a low pressure air or O2-blown booster gasifier such at the one at Weyerhaeuser, New Bern. However, at 20 bars the conversion drops to zero. In order to be effective at 20 bars the process would have to be modified to lower the CO2 partial pressure in the product gas.

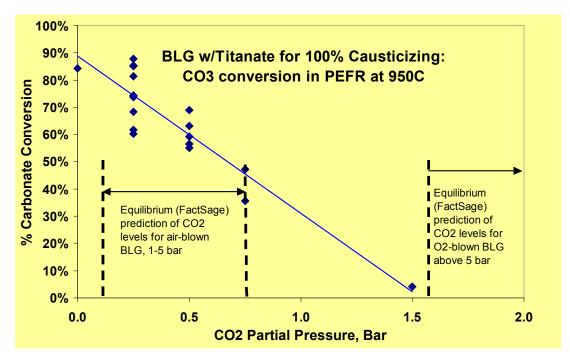


Figure 14. Titanate direct causticizing conversion at high temperature entrained flow as a function of CO2 partial pressure.

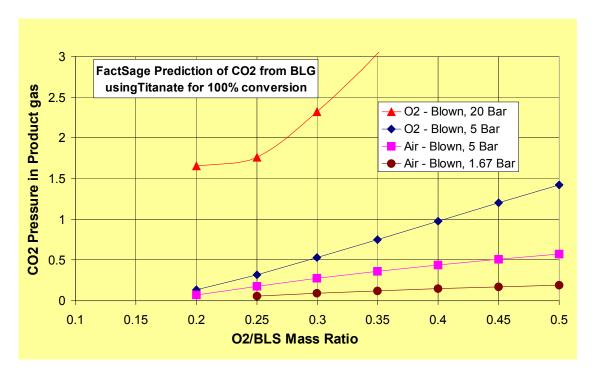


Figure 15. Equilibrium calculations of CO2 levels from black liquor gasification over a range of oxygen to fuel ratios. Realistic values are around 0.3

The results for titanate direct causticizing during steam reforming (task 1.1.3) are shown in Figure 16. With no CO2 present, high conversions were achieved. However when 10% CO2 was added, the conversion dropped to zero. Thus the titanate chemistry will not work for steam reforming in its current configuration. FactSage modeling suggests however that at 650C the reaction would reach high conversion. Given that titanates would also raise the smelting temperature of the char, the steam reformer temperature might well be raised to 650C without problems with bed sintering. For the present, no further work will be done with titanates for steam reforming.

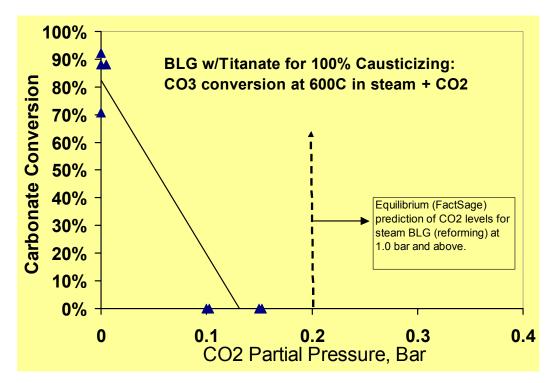


Figure 16. Titanate direct causticizing during steam reforming at 1 bar.

#### Borate Experimental Results

The experimental results for the borates (task 1.3.1) are shown in Figures 17 and 18 for partial (20%) conversion. This would be appropriate for either a booster or full scale gasifier when the existing lime kiln will be used to handle the bulk of the causticizing load. At high temperature and low pressures, the chemistry reaches high conversion due to low CO2 partial pressure. The borates will be tested for complete causticization at 950C and low pressure as well. However, as before, at 20 bars total pressure, the CO2 would be sufficiently high to inhibit the conversion of this reaction as well.

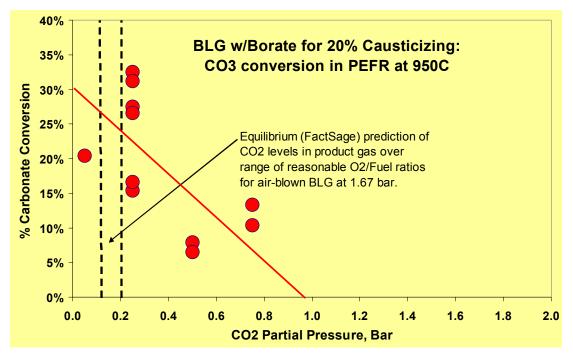


Figure 17. Borate autocausticization at high temperature

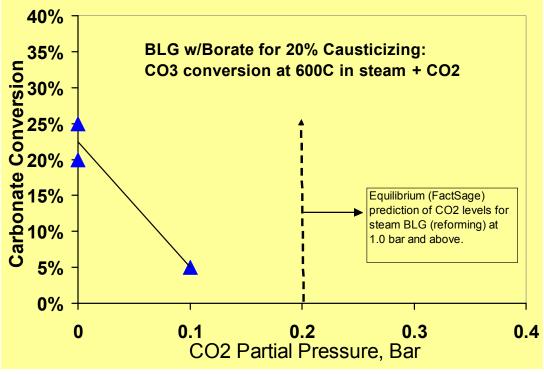


Figure 18. Borate autocausticization during steam reforming

The steam reforming case for the borates at 20% conversion is shown in Figure 18. Again, the CO2 levels would be too high in the real gasifier to achieve any conversion. FactSage modeling suggests that the temperature would have to reach 925C before the causticizing reactions move forward in this case. Borates for steam reforming will not be considered further.

# Manganate Experimental Results

The experimental results for gasification of manganate-doped black liquor are shown in Tables 6 and 7 (a graph is not in order for this case). For the high temperature case, zero conversion was achieved. Manganates for high temperature gasification will not be considered further.

Table 6. Manganate conversion during high temperature gasification			
Gas Conditions	Stoichiometric maximum conversion based on Mn added	Fixed (i.e. char) carbon in smelt	Experimental causticizing conversion
5%CO2	100%	0.6%	0%
5%CO2	100%	0.1%	0%
10%CO2	100%	0.5%	0%
10%CO2	100%	1.7%	0%

For the steam reforming case (Task 1.2.2), manganates gave complete conversion in almost all cases, with and without CO2 present. Experiments with manganates will continue into the non-process element removal stage of the project.

Table 7. Manganate conversion during steam reforming		
Gas Conditions		Experimental causticizing
Ous Conditions	(i.e. char) carbon in smelt	conversion
50%H2O	0.00%	100%
50%H2O	0.05%	100%
50%H2O	0.01%	100%
50%H2O+10%CO2	0.03%	95%
50%H2O+10%CO2	0.02%	100%

The results for all of the cases are summarized in Table 8 below. Three of the six combinations will be retained for non-process element removal, and caustic recovery experiments. Chars from the successful causticizing processes above were hydrolyzed (leached) and titrated to measure the hydroxide recovered for comparison to the carbonate causticized.

Table 8.           Summary Results of Causticizing Experiments		
	600C, 50hrs Steam reforming	950C, 5sec using CO2 and H2O
	No; CO2 is too high in product gas	Works below 4-5 bar total pressure. Good leaching recovery
Borates for 20% conv	No; CO2 is too high in product gas	Works below 2-3 bar total pressure. Good leaching recovery
Manganates for 100% conv	No; achieved 100% caust'n but fails to reform Mn3O4 during leaching.	No; zero causticizing

# Char Leaching

Once the causticization conversion has been confirmed, the chars must be hydrolyzed (leached) to recover the hydroxide for pulping and return the agent back to a form where it can be returned to the gasifier and again causticize more carbonate. The overall process is shown in Figure 19. The amount of hydroxide formed during leaching must be compared to the carbonate consumed to verify material balance closure. Also the leached solids and leachate must be characterized to determine the fate of the non-process elements.

Three of the six variants considered thus far did not yield sufficient causticizing and were eliminated. The remaining three, shown in Table 9, were tested for caustic recovery to see if the OH formed matches the CO3 removed during gasification. This gives an indication that the causticizing agent returns to its initial state during hydrolysis and is ready for another cycle through the gasifier. The titanates yielded fairly good hydroxide recovery in most tests. Some low yields were observed however and remain unexplained. The borates yielded good recovery. The manganates consistently returned only 40% of the expected hydroxide.

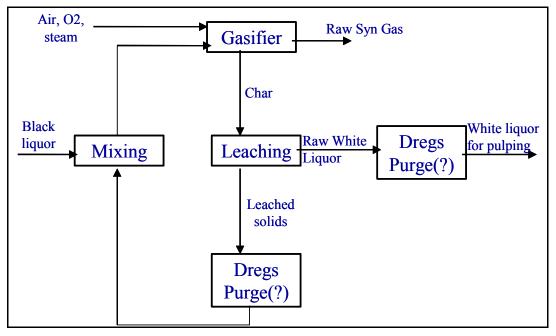


Figure 19. Hydroxide recovery and non-process element removal schematic

Table 9. Caustic Recovery Upon Char Hydrolysis			
# of runs     Average %OH recovered as % of maximum possible     Range of %			Range of %
Titanates for 100% conversion at HTBLG	15	54%	32-88%
Borates for 20% conversion at HTBLG	5	18%	16-20%
Manganates for 100% conversion at LTBLG	5	39%	38-40%

The apparent reason for the low hydroxide yield from the manganates is that some of the sodium and virtually all of the potassium are retained in the solid phase with the manganate despite two successive leachings for 90 minutes at 90°C (Table 10). The desired product should be pure Mn3O4 as shown in reaction (5) to obtain cyclic chemistry. If a significant portion of the causticizing agent is rendered inert in one cycle then cyclic chemistry cannot be maintained and the process is not viable. Manganates were therefore eliminated from further consideration, leaving no causticizing option for LTBLG.

Table 10 Analysis of Mn3O4 solids after 2 leachings		
Element % of element in char found in 2nd leached solid		
Mn	98%	
Na	29%	
К	94%	

Hydroxide recovery (in a single leaching step) for the titanate system varied from 32-88% (avg 55%) of that expected. To improve recovery, multiple leachings were attempted. An example is shown in Table 11. While not all cases resulted in 98% OH closure, factors such as particle agglomeration or sintering could be resolved with additional work.

Table 11. Staged leaching results		
Experiment	D02/24/04	
OH recovered on 1st leaching	86.1%	
OH recovered on 2nd leaching	8.9%	
OH recovered on 3rd leaching	3.6%	
Total of 3 stages	98.6% (of the OH expt'd)	

# **XRD Analysis for Titanate Chars**

As an independent check to confirm the leaching is restoring the titanate to the forms expected in reactions (4) and (5), the char and subsequent leached solids were analyzed by X-ray Diffraction (XRD). Figure 20 shows the XRD spectra of titanate-doped black liquor gasified in CO2 at 950C. The spectral signature of both the NT3 (same as Na2Ti3O7) reactant form, and the N4T5 (shown as Na16Ti10O28) causticization product are both prominent. This suggests there was either incomplete causticization or an excess of NT3 in the system. Either way, reaction (2) is confirmed to occur. Additional XRD scans are included in the Appendix.

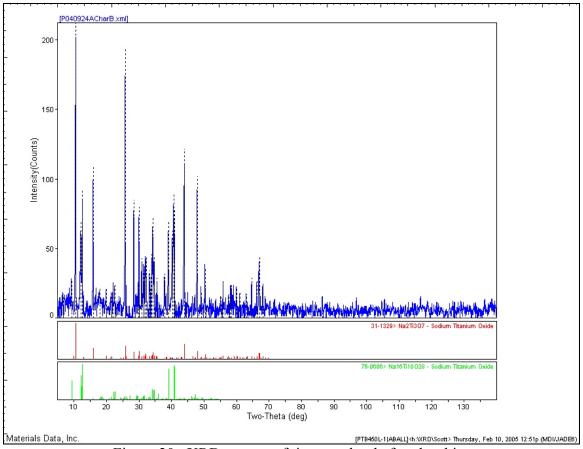


Figure 20. XRD spectra of titanate char before leaching

Figure 21 shows the XRD spectra of the same char from Figure 20 but after leaching. Note that N4T5 is not present but NT3 and a species with formula Na0.57Ti2O4 (equivalent to NT7, which is even better) are detected. From reaction (5), the form should be NT6 but the trend is the same in that the leaching step reduces the ratio of Na/Ti, while the causticizing step increases it.

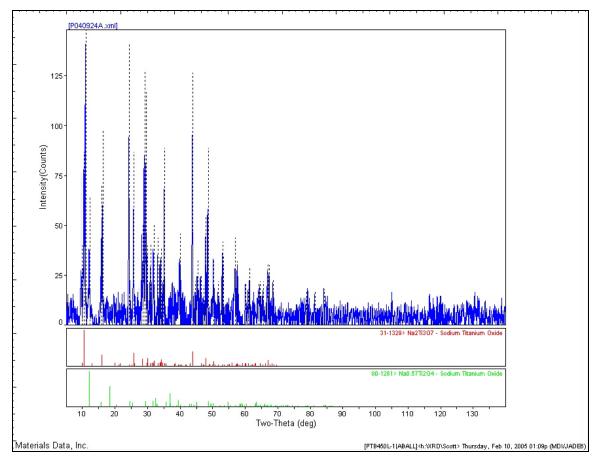


Figure 21. XRD of leached solids formed from leaching of char in Figure 20.

XRD data for the manganate case is irrelevant since manganates were eliminated. For the borate case, the char is soluble so there is no leached solid to examine. Confirmation of the borate chemistry is limited to disappearance of carbonate and appearance of hydroxide.

# NPE Removal

For the borate case, since the borates are soluble the NPE's can be removed as grits from the white liquor. Soluble NPE's such as potassium and chloride can be purged by purging a small amount of white liquor.

For the titanate case, the char, leached solids, and leachate (i.e. white liquor) were all analyzed by ICP to try and close the material balance on the NPE's. For major system species such as Na, K, Ti, and S, the material balance closed to within a few percent. For the trace metals of interest, such as Fe, Al, Si, Ca, Mg, Ba, etc., the closure was not good enough to draw conclusions. An example is shown in Table 12. The poor closure may have been due to small sample sizes not representative of the bulk solids or incomplete acid digestion prior to analysis.

Table 12. Elemental balance between char, leachate and solids for two successive						
leachings (in ppm)						
ICP	Char	Leached	% to solid	1st leachate	2nd leachate	Mat'l bal
element	ppm	Solid ppm	phase	ppm	ppm	%error
AI	397	121	31%	1177	30	-234%
В	48	13	28%	2495	509	-6217%
Са	530	683	129%	114	74	-64%
Cr	77	7	9%	62	2	9%
Cu	30	23	76%	5	8	-17%
Fe	572	613	107%	15	10	-11%
К	15500	2353	15%	13433	215	-3%
Mg	11	141	1322%	15	10	-1456%
Mn	131	150	115%	1	0	-15%
Мо	7	7	89%	11	7	-223%
Na	266000	61587	23%	197457	8787	-1%
S	23200	155	1%	23180	155	-1%
Sb	213	21	10%	34	21	65%
Si	1210	247	20%	22877	2558	-2022%
Ti	282000	291692	103%	4	7	-3%
V	203	3	2%	31	1	83%

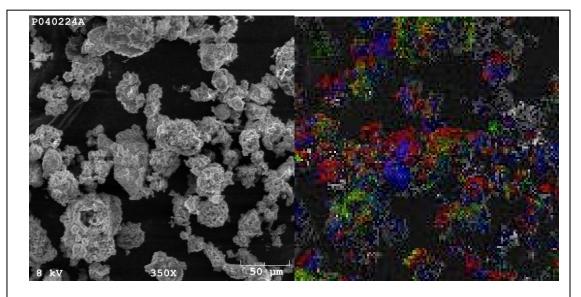
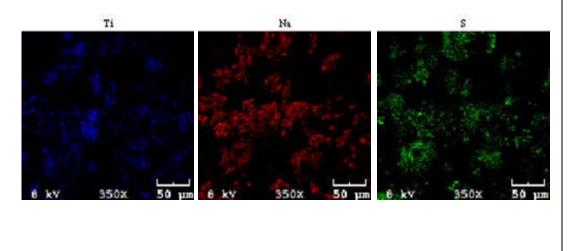
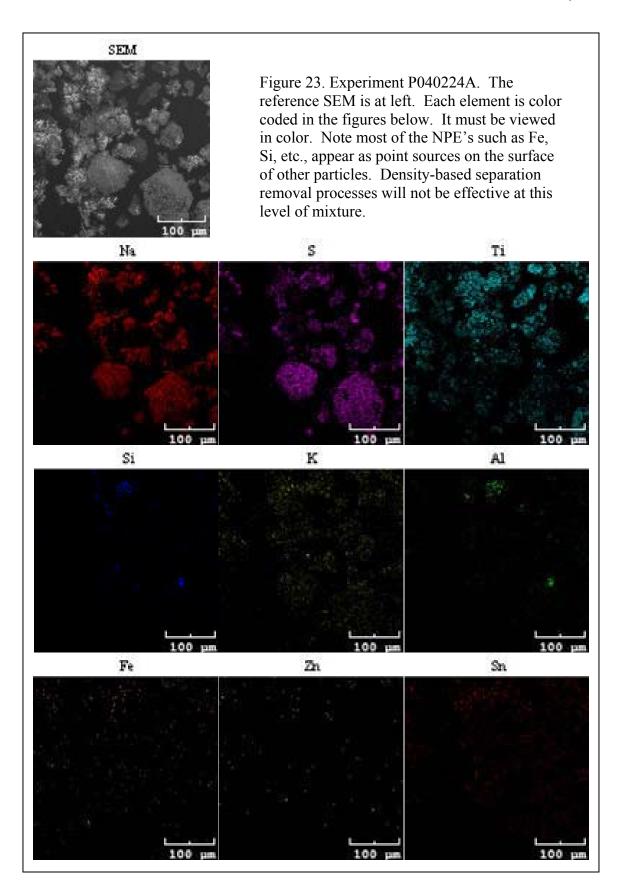


Figure 22. Above left is the SEM-EDS micrograph (titanate leached solids from run P040224A) with 50 micron size reference bar shown. On the left is the same image with major surface species concentrations shown in colors. Below are the same regions shown for each species. Note that while sulfur appears to be abundant, only 0.7% of the sulfur in the char remained with the solids after leaching.





In any case, there must be an NPE purge mechanism. There are two approaches: 1) chemical separation (acid treatment, or metal complexing), or 2) size or density based techniques as used in the mining industry.

To try and narrow the options, SEM EDS was carried out on samples of leached Ti solids (Figures 22 and 23). In this analysis several SEM images are taken of the same area, as shown in Figures 22 and 23, with each photo color-coded to show only one element (e.g. Fe, Si, etc.). They require a color medium to interpret results so they are not shown here. What they reveal is that while species such as Na, K, and S are uniformly distributed over each particle, some of the NPE's are concentrated on a few particles, and others appear as points appearing on nearly every particle.

We conclude from the SEM-EDS that the NPE's are intimately bound to the particles, and thus any size or density based separation technique is not likely to work. This leaves us with chemical techniques. The simplest option in the case of Ti solids is to titrate with an acid. Ti remains solid down to very low pH; lower than the NPE's we wish to remove, as shown in Table 13.

Table 13. pH precipitati	on points
Metal	pН
Ca <sup>++</sup> , Mg <sup>++</sup>	10-11
Mn	8-9
Fe	7
Zn, Cu	6
Al	4-5
Fe	2-3
Ti	2

FactSage 5.4 was used to simulate the titration prior to lab testing. HCl, HNO<sub>3</sub>, and  $H_2SO_4$  were considered (Table 14). The latter two failed to dissolve BaSO<sub>4</sub>. Only HCl produced clean NT3 in the simulation. Lab testing confirmed that all NPE's were removed by HCl titration.

Table 14.	FactSage Simulation of Titration of Leached
	Solids for NPE removal
Acid	Results
H2SO4	TiO2, CaSO4, BaSO4 remained
П2504	in solid phase
HNO3	TiO2, Fe2O3, BaSO4 remained
ninO3	in solid phase
HC1	TiO2 is the only solid

## Mill Integration and Economic Evaluation

The final phase of the project was a mill integration study to develop the most likely process configuration for the borate and titanate options based on the reference mill design basis, perform capital cost estimates for the options, and then to perform economic evaluations for the options as compared to the base case. The base case is pressurized HTBLG with a conventional causticizing operation that has been upgraded with oxygen enriched fuel oil firing in the lime kiln. The reference mill basis used for this study is the same as that used by Larson et al. [28]. The study by Larson et al. was quite thorough and provides an excellent benchmark to assess just the in situ causticizing option of a BLG based mill. The Larson mill is an integrated pulp and paper mill producing uncoated freesheet paper from a 65/35 mix of hardwood and softwood. The mill produces about 5.4 MM lbs/day of black liquor solids (BLS). The HTBLG case data from the Larson Study is used for the base case in this study. Detailed mill data and assumptions can be found in the report by Larson et al. [28].

#### The Base Case

The base case process is based on HTBLG followed by conventional calcium oxide causticizing. Since HTBLG will increase smelt sodium carbonate, the lime requirement for slaking increases by a like amount. Larson et al. [28] assumes a conservative increase of 16%, although this number will vary with gasification conditions, sulfur split, and sulfur recovery technique. This puts an increase load on the lime kiln. Considering that many mills are kiln limited and the hypothetical mill is at its kiln design limit, Larson et al [28] includes oxygen enrichment, a new kiln burner system, and new refractory brick to increase the kiln capacity.

#### Borate Autocausticization Case

Borate autocausticizing is a partial causticization process (20% of lime is replaced with borate). This means that the conventional lime caustic plant continues to run but at a reduced rate. Borate in the form of sodium tetraborate pentahydrate (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·5H<sub>2</sub>O) is added to the liquor system to achieve the desired level of lime substitution. Once this level is achieved, borate can be made up to the liquor system in small amounts to account for natural system losses [7]. The borate is fed to a small mix tank from a supersack/screw feeder. A side stream of clarified green liquor is sent to the mix tank to dissolve and absorb the borate. This green liquor/borate stream then flows to the slaker by gravity. A spreadsheet balance was used to develop the chemical flows and borate makeup. Borate makeup is based on lime substitution, lime availability, white liquor causticity, borate loss rate, and borate reaction efficiency

## Titanate Direct Causticizing Case

Titanate direct causticizing is for full 100% substitution of lime, hence, the conventional caustic plant is shut down. The envisioned overall process is shown in Figure 24. For the economical use of titanate, it must be recovered and recycled back to the black liquor prior to gasification. Following smelt dissolving, titanate remains in the green liquor as a suspended solid. By assuming physical properties of the titanate being similar to lime mud, we can extrapolate to a mill-scale process utilizing three staged leaching tanks for

reaction residence time with each stage followed by disc filtration. The green liquor/titanate slurry goes to a first stage leaching tank. The leaching tank is agitated to keep the solids in suspension. Each tank is sized for 60 minutes of residence time to allow adequate mass transfer and leaching of the sodium hydroxide. From the first stage leaching tank, the slurry is pumped to a disc filter. Solids discharge from the filter at 85% solids. The filtrate from the first stage filtrate tank is essentially white liquor that is transferred to the digester area. The first stage filter discharge solids are diluted and gravity fed to the second stage leaching tank. The second and third leaching stages are configured the same as the first stage. Note that only a single leaching stage is shown in Figure 4 but more could be added as needed. Filtrate moves countercurrent to the solids flow through the system. Hot water or evaporator condensate is added to the third stage filter showers. Titanate solids off the third stage filter are conveyed to a black liquor mix tank prior to the gasifier. Note that two leaching stages are very likely sufficient but three were used for a conservative analysis.

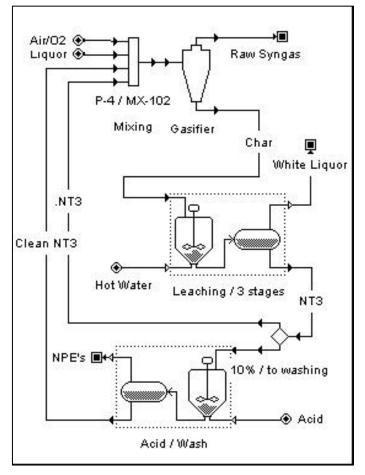


Figure 24. BLG with Ti-direct causticizing and acid treatment to purge NPE's. Circles are feed streams; squares are product.

A portion of the titanate solids stream (10%) is transferred to an acid slurry mix tank. The purpose of the acid slurry tank is to mix hydrochloric acid with the titanate solids. The acid leaches out the NPE's from the titanate. The acid slurry is transferred to a disc filter. Filtrate from the NPE purge filter flows by gravity to the NPE purge filtrate tank. Caustic is added to neutralize the acid. The neutralized filtrate then flows to the sewer. Solids from the NPE purge filter are conveyed to a new black liquor mix tank. Titanium dioxide makeup is added to the black liquor mix tank as well via the screw conveyor. It is assumed that the mill already has available hydrochloric acid and caustic make-down and delivery systems.

Potassium remains in the system either as potassium titanate or potassium hydroxide and carbonate. Potassium lowers the melting point of recovery boiler ash and is a primary cause of boiler tube pluggage in Tomlison recovery boilers. In a HTBLG system, the potassium poses no problem.

A new agitated heavy (50%) black liquor mix tank is required to recycle the titanate prior to the black liquor concentrator. This allows the 85% solids titanate recycle stream to be uniformly mixed prior to concentrating the black liquor to 80% solids for gasification. The titanate suspended solids flow is substantial, adding about 40% to the overall mass flow of the black liquor. The black liquor volume flow increases about 20%. Although no increase to the evaporation capacity of the black liquor concentrator is required, modifications are required to increase the hydraulic capacity. Primarily pump and motor upgrades are required. An allowance is included in the capital estimate to cover concentrator upgrades for the increased liquor flow. The additional suspended solids should enhance the crystallization process and reduce fouling for 80% solids liquor production by providing sites for crystallization to take place rather than on heat transfer surface areas.

A material and energy balance was performed to calculate material flows and temperatures for the titanate recovery and NPE purge process (Table 15). The balance is

TABLE 15. TITANATE BALANCE BASIS A	AND ASSUMPTIONS
Smelt	(w/o potassium)
Na <sub>2</sub> CO <sub>3</sub> , mt/hr	4.76
NaOH, mt/hr	0.79
Na <sub>2</sub> S, mt/hr	4.73
HCI, mt/hr	0
NPE's (Dissolved), mt/hr	3.15
Inerts (Suspended), mt/hr	1.46
Black Liquor Sodium Carbonate Converted, %	88.0
1st Leaching Stage Caustic Recovery, %	86.1
2nd Leaching Stage Caustic Recovery, %	8.9
3rd Leaching Stage Caustic Recovery, %	3.6
Titanate Split to NPE Purge, %	10
HCI ratio to Treated Solids, kg/kg	0.1

based on HTBLG smelt chemical flow data from the Larson et al. [28] and stoichiometric titanate requirements for causticization. In addition, results from IPST experimental data were also used for the balance around the caustic leaching stages and the NPE acid

leaching stage. Table IV shows the basis and assumptions for executing the material and energy balance for the Titanate case.

The Titanate split to acid treatment for NPE purge was varied to observe the effect on the steady-state level of NPE's in the recycled titanate. Figure 25 shows the effect on NPE levels at different purge fractions. At 5% fraction to acid treatment, the NPE's level in the recycled titanate is 23%. A higher level of NPE's in the system means a higher dead-load through the process. This causes higher loads on the causticizing equipment and higher hydraulic/pumping loads on the black liquor concentrator system. Of course the acid and caustic costs decrease, but there is still more operational risk with the higher dead-load through the process. At 10% fraction to acid treatment, the NPE's level decreases to 15%. Further increases in acid treatment fractions yield lower decreases in the NPE's level. It appears that 10% fraction to acid treatment is good conservative minimum for the purpose of this mill integration study. In a traditional lime based causticizing system, the amount of NPE's or inerts carried in the reburned lime is typically 10 to 15% as well.

Note also that three leaching stages were used to recover 98.6% of the hydroxide (Table IV). Conventional lime cycles are not this efficient. It is likely that two or even one leaching stage could be employed. However conservative estimates were desired for this study.

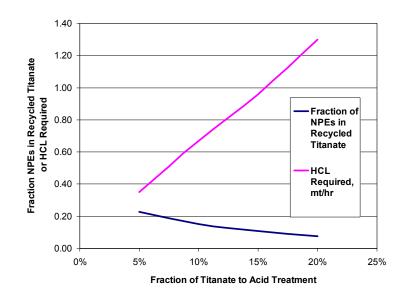


Figure 25. NPE acid treatment sensitivity analysis

#### Water Balance

Water usages for the three options are compared in Figure 26 along with a base case that uses a scrubber on the kiln flue gas instead of an electrostatic precipitator (ESP). The state of the art mill with an ESP on the lime kiln flue gas uses minimal water because the recycle lime dust is returned dry. The base case assumes a state of the art mill with a lime kiln ESP. The borate case water usage is even less due to a lower lime requirement.

The base case with a conventional kiln scrubber has the highest water usage due to evaporative losses. The titanate case water usage is an improvement upon a kiln scrubber but it does require more water than the base case with a kiln ESP.

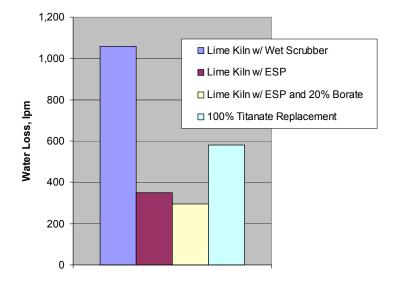


Figure 26. Causticizing process water balance.

#### Capital and Operating Cost Summary

The capital cost estimates are  $\pm 30\%$  accuracy factored total installed cost (TIC). The estimates are based on preliminary process flow diagrams, priced equipment lists, and project scope descriptions. Equipment pricing was obtained from Andritz for disc filters and leaching tank agitators. Pump pricing was obtained from ITT Goulds. All other equipment pricing was obtained from historical database of recent projects with similar equipment. Piping, structural, electrical, and controls material and equipment were factored based on the process equipment direct cost. The estimates assume an engineering, procurement, and construction management (EPC) type contract to execute the project. The estimates assume a site in the southeastern United States, non-union, and no escalation is included. The capital cost estimates are summarized in Table 16. The base case capital cost is taken from Larson et al. [28] and factored up to account for inflation from 2002 to 2006.

TABLE 16. CAPITAL CO	ST SUMMARY
Case	<b>\$MM U.S.</b>
Base	1.20
Borate	0.17
Titanate (3-stage leaching)	31.55

The operating and maintenance costs for each option are estimated from the following sources of information:

- Chemicals usages from M&E balances (Table 17)
- Lime kiln fuel oil usage for HTBLG [28]
- Electricity usage based on total connected equipment horsepower times 80% for each case (Table 18)
- Chemicals, fuel oil, and electricity costs from current market pricing (August, 2006) (Table 18)
- Annual maintenance cost equal to 5% of capital cost

TABLE 17. CHEMICALS, FUEL, AND ELECTRI	CITY COSTS (2006)
#6 Fuel Oil , \$/MMBTU	\$8.51
Electricity, \$/MWh	\$58.60
Borate, \$/mt	\$425.00
Titanium Dioxide, \$/mt	\$480.00
Hydrochloric Acid, \$/mt	\$135.00
Sodium Hydroxide, \$/mt	\$370.00
(note: mt=metric ton, MM=million, MW=megawatt)	

TABLE 18. EXI	PERIMEN	TAL CON	DITIONS
	Borate	Titanate	
Fuel Oil Savings	217,386	1,086,928	MMBTU/yr
Electricity Savings	4,310	7,038	MWhr/yr
Borate Usage	1,177		mt/yr
Titanium Dioxide		3,951	mt/yr
Hydrochloric Acid		5,559	mt/yr
Sodium Hydroxide		3,912	mt/yr

Table 19 shows the costs or savings items for each option. Avoided cost savings are treated as positive cash flow. The annual maintenance cost for the base case is based on 5% of the capital cost of a new lime kiln and caustic plant of similar capacity. The order of magnitude capital cost of a new lime kiln and caustic plant is approximately \$35,000,000. Note that if this were a greenfield comparison, the cost of a new lime cycle would make the titanate option far more attractive.

TABLE 19.	ANNUAL	0 & M CO	STS
	Base	Borate	Titanate
<b>Avoided Costs</b>			
Avoided kiln fuel		1,849,503	9,247,514
Avoided elec		252,567	412,428
Total		2,102,070	9,659,943
Direct Op Costs			
Borate		500,288	
Titanate			1,896,391
HCl			750,454
NaOH			1,447,375
Inc waste treat (.10 kW/lpm)			29,809
Op & Maint.	1,750,000	1,408,700	1,577,250
Total	1,750,000	1,908,988	5,701,279

#### Economic Analysis

Both the internal rate of return (IRR) and net present value (NPV) analyses were performed on each case and also performed relative to the base case. The key inputs to the analyses are the capital costs and the annualized operating and maintenance costs. Table 20 shows the economic assumptions used for the analyses.

TABLE 20. ECONOMIC ASS	UMPTIONS
Financial Parameters	
Annual Inflation Rate	4.0%
Debt Fraction of Capital	50%
Equity Fraction of Capital	50%
Interest Rate on Debt	8.0%
Return on Equity	15%
Resulting Discount Rate used for NPV calculations	9.9% (after tax)
Income Tax Rate (combined Federal & State)	40%
Economic Life (years)	25
Depreciation Method	20-year MACRS rate schedule <sup>1</sup>
Construction Time	1 yr
Mill Assumptions	
Annual Operating Hours	8,330
Annual O&M Costs, % of Capital Cost	5%
Start-up Assumptions	
Year 1 of Operation	100%
(1 - Modified Accelerated Cost Recovery System (M	ACRS) per IRS Tax Code)

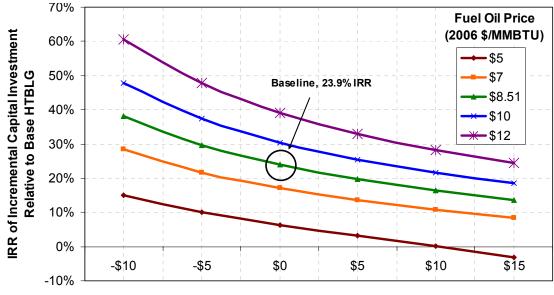
The IRR and NPV cash flow analyses were performed for each case and for relative comparison to the HTBLG base case. Total net cash flows are shown in Table 21. The stand-alone base case is taken directly from Larson et.al. [28]. The numbers for the stand-alone borate and titanate cases are incremental beyond the base.

TABLE 21	. TOTA	L NET CA	ASH FL	OW
	Stand	-Alone	Relativ	e to Base
	IRR	NPV	IRR	NPV
	(%) (\$ MM) (%) (\$ MM)			
Base - HTBLG	16%	72.8	N/A	0
Borate	135%	1.4	N/A	16.1
Titanate				
	15.9%	10.6	23.9%	25.2
(3-stage leach)				

Considering the stand-alone NPVs over the total project life of 25 years, the titanate option clearly has the best NPV of \$10.6MM primarily from the substantial fuel savings over the base case. The borate option has a high stand-alone IRR of 135% due to the minimal capital investment required. The borate option still achieves 20% of the fuel savings of the titanate option. Relative to the base case the titanate option is more economically attractive with an NPV of \$25.2MM and an IRR of 23.9%.

The titanate carries some technical risks though because it is a new technology. The performance of titanate as a direct causticizing agent and the subsequent acid purging of NPE's was proven successful on the lab scale. Some basic assumptions are made about the titanate char physical properties in order to configure the process presented in this report. The actual performance of the process must be determined through pilot plant trials to refine the process configuration and minimize risk (e.g. two leaching stages will likely suffice). Hence, the capital cost could vary depending on the final process scope from pilot plant work. Borate, on the other hand, has been proven effective in conventional Tomlinson based recovery cycles but only for partial auto-causticization.

Figure 27 shows IRR sensitivity to titanate capital cost variance at varying fuel oil prices. Fuel oil price variance has a significant effect on the IRR. If fuel oil price rises to \$10 per MMBTU, then the IRR will increase from 23.9% to 31%.



**Capital Cost Variance (\$ million)** 

Figure 27. Fuel oil and capital cost sensitivity analysis.

On the other hand a significant drop in fuel oil price will severely negate the economics of titanate as well. Therefore, fuel price trends must be carefully analyzed to predict economic performance for future projects.

#### CONCLUSIONS

The borate and titanate options are both effective auto and direct causticizing agents, respectively, within the pressure and temperature limits found in this study. Borate carries minimal capital investment and provides attractive payback and economics by alleviating the additional burden on the lime cycle that HTBLG causes and by saving some kiln fuel oil cost.

Titanate can replace up to 100% of the lime cycle and provide equal white liquor quality. This has been demonstrated on the lab scale. By assuming physical properties of the titanate being similar to lime mud we can extrapolate to a mill-scale process utilizing three staged agitated leaching tanks for reaction residence time followed by disc filtration. Acid leaching of a final titanate side stream achieves the required NPE purge of metals. Potassium remains in the system either as potassium titanate or potassium hydroxide and carbonate. This poses no problem without a Tomlinson recovery boiler in the system.

An additional hydraulic burden is put on the black liquor concentrator system due to the high flow rate of suspended titanate solids to 50% black liquor. The fact that most of the sulfur portioned to the smelt phase means that less NT3 would be required in the real system compared to what was allowed for in the study. It is not known exactly what the performance and maintenance impact will be with this additional 40% mass flow load

increase. The additional suspended solids could enhance the crystallization process and reduce fouling for 80% solids liquor production by providing sites for crystallization to take place rather than on heat transfer surface areas. On the other hand, the added abrasiveness of the concentrated black liquor may pose a maintenance risk to the process equipment.

Titanate bears no advantage to the mill water balance except when compared to a conventional lime kiln wet scrubber system. In this case there is a 40 to 50% reduction in water lost to the sewer or atmosphere with the titanate option.

The titanate option economics are very favorable. The titanate recovery system is estimated at about \$32MM with an NPV and IRR, relative to the base case, of \$25.2MM and 23.9%. The situation would improve by using only two leaching stages: NPV increases to approximately \$35MM and IRR to approximately 35%. The main issue as of this writing is scale-up from lab results. Pilot plant testing is required to firm up the process scope and capital cost estimate.

The borate case is also attractive, with NPV of \$16MM and very low initial capital cost. The chemistry has also been demonstrated at the mill scale in Tomlinson boilers, and thus is a lower risk. The existence of a functioning caustic plant would favor the borate option.

Using the Larson study as a reference, it was commensurately assumed that a working lime cycle is already in place and the decision to use BLG is being weighed against a new recovery boiler. A cost of a caustic plant is approximately \$35MM, which was not included in the economics. Thus if a greenfield mill or forest products biorefinery is being planned, or if both the boiler and caustic plant are in need of refit at an existing mill, then the titanate option is the better choice.

It should be noted that the reference case selected from the Larson [2] study was based on HTBLG at 35 bar pressure. Our findings indicate that pressures below 5 bar were required to limit the  $CO_2$  partial pressure and thus allow the causticizing reactions to proceed. This is simply a technology gap that must be overcome if the planned process requires pressurized syngas (e.g. combine cycle power generation, or Fischer-Tropsh diesel). There are other processes to gasify kraft black liquor, all of which will require some form of causticizing to produce suitable pulping liquors. This study focused only on gasification conditions found in two actively marketed processes of current industry interest. The favorable economics provide incentive to resolve the pressure limitation.

# **FUTURE WORK**

A number of key questions arose during this project which were either beyond the scope of the project, or for which resource limitations prevented further investigation. Additional work in the area of in situ causticization for BLG should address one or more of these points:

- The manganates showed great promise by achieving complete conversion of carbonate to hydroxide for the LTBLG case. Manganates failed during the leaching step when they could not be leached back to Mn<sub>3</sub>O<sub>4</sub>. The potassium remained with the solid phase and thus contaminated the manganate. Further work could be done to identify the exact reason for this and possibly modify or add to the leaching procedure to restore the Mn<sub>3</sub>O<sub>4</sub> for subsequent cycles through the process.
- The titanate solids recovered from leaching of the char should be mixed with black liquor and gasified a second time to determine if the same conversion is achieved as in the first cycle. The complete operational cycle should be verified to confirm that the titanates are not altered in some way that was not characterized in this study.
- The borates should be run at higher doping levels to determine of complete (at least 85%) causticization can be achieved for the HTBLG case.
- The pressure limitation on the titanates would rule out their use in pressured BLG. This is due to the high partial pressure of CO<sub>2</sub> inhibiting the causticizing reaction at high gasifier pressures. It is worth investigating the possibility of using some sort of multi-stage reactor or arrangement of reactors (e.g. circulating fluid beds) that would achieve the carbon gasification while keeping the CO<sub>2</sub> concentration low enough to allow the causticizing reactions to proceed.

# ACKNOWLEDGEMENTS

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## **ABBREVIATIONS**

PEFR: Pressurized laminar Entrained Flow Reactor

LEFR: Laminar Entrained Flow Reactor

BLG: Black Liquor Gasification

HTBLG: High Temperature BLG

LTBLG: Low Temperature BLG

BLGCC: Black Liquor Gasification with Combined Cycle power generation

BL: Black Liquor

XRD: X-Ray Diffraction

SEM: Scanning Electron Microscopy

# END OF MAIN BODY OF REPORT APPENDIX A FOLLOWS

# Project DE-FC26-02NT41492

# **APPENDIX A**

# **EXPERIMENTAL DATA**

Sample ID	P030514A	P030514B	P030516A	P030520	P030521A	P030522	P030604	P030605	P030611	P030619
Feeding Materials	Ti / BL	Ti / BL	Ti / BL	Ti / BL	0.03B / BL	0.03B / BL	0.03B / BL	0.03B / BL	0.03B / BL	Ti / BL
Gas (balance N2)	5%CO2	5%CO2	5%CO2	5%CO2	10%CO2	5%CO2	5%CO2	5%CO2	10%CO2	10%CO2
Pressure, Bar	5	5	5	5	5	5	5	5	5	5
Analysis Results						31.62				
From Analytic lab										
Coulometer CO3(wt%)	4.89	3.920	4.615	5.7	34.63	28.9	30.05	28.5	36.0	8.7
Total C (wt %)	3.49	66'0	1.88	1.30	7.18	6.91	8.02	2.03	8.37	2.00
Leachate CO3 (ppm)			317	544						623
S (mg/kg)	23000	28400	24100	22700	64300	58400	55800	52300	61400	10600
Na(mg/kg)	201000	201000	192000	168000	266000	236000	249000	226000	308000	166000
K(mg/kg)	8320	8370	8330	8000	21200	18000	21300	18900	26000	7650
B(mg/kg)					8040	6730	7200	0889	8200	
Mn(mg/kg)										
Ti(mg/kg)	328500	317000	300000	333000						346000
From Duo Titration										
BO2 as Na2O (%w/w)					0.59	0.21	0.23	96.0	2.32	
OH as Na2O (%w/w)					0.63	1.10	3.41	2.50	2.06	
CO3 as Na2O (%w/w)					40.25	39.42	34.58	36.35	39.98	
S as Na2O (%w/w)					8.92	7.66	3.17	7.23	6.95	
Causiticity (%)					1.26	2.29	8.29	5.10	4.20	
NaOH(mol/gBRS)			3.85E-03	7.42E-03	0.00020287	0.00035557	0.00110138	0.00080793	0.00066435	7.60E-03
NaOH(mol/gChar)										
Calculations										
C (fixed) %	2.512	0.204	0.957	0.16	0.254	1.13	2.01	1.33	1.17	0.26
Metal/Na mass ratio	1.634	1.577	1.563	1.982	0:030	0.029	0.029	0.030	0.027	2.084
Avg CO3 for ref runs	41.350	41.350	41.350	41.350	42.950	41.350	41.350	41.350	42.950	41.350
% reduc'n from ref ()	88.17%	90.52%	88.84%	86.22%	19.37%	30.11%	27.33%	31.08%	16.18%	78.96%
S/Metal in char	0.070	0.090	0.080	0.068	7.998	8.678	7.750	7.602	7.488	0.031
%S went to char	61.6%	78.5%	70.7%	60.0%	95.5%	103.7%	92.6%	90.8%	89.5%	26.9%
S/Metal in starting liquor	0.1137	0.1137	0.1137	0.1137	8.3700	8.3700	8.3700	8.3700	8.3700	0.1137
-										
Caust'n conv from stoich	73.8%	81.4%	74.4%	68.3%	2.9%	26.9%	26.6%	32.5%	6.5%	55.0%
Exp'd OH(mol/gChar)			5.09E-03	4.95E-03	9.10E-04	2.32E-03	3.27E-03	4.10E-03	7.70E-04	4.67E-03
Exp1 OH % accd for					22.3%	15.3%	33.7%	19.7%	86.3%	

Sample ID	P030627	P030630	P030710a	P030710b	P030715	P030716	P030721a	P030721b	P030725a	P030725b
Feeding Materials	Ti /BL	Ti / BL	1.0Mn/BL	1.0Mn/BL	1.0Ti/BL	1.0Ti/BL	0.4Mn/BL	0.4Mn/BL	BL	BL
Gas (balance N2)	5%CO2	5%CO2	5%CO2	10%CO2	5%CO2	10%CO2	5%CO2	10%CO2	5%CO2	10%CO2
Pressure, Bar	5 bar	5	5 bar	5 bar	5 bar	5 bar				
Analysis Results										
From Analytic lab	101	10 1	10 17	10.01		10 0		10.00	11 00	10.01
Coulometer CO3(wt%)	1.35	4.95	15.65	16.65	1.25	6.25	25.4	26.05	39.75	42.95
Total C (wt %)	3.69	1.18	3.71	3.81	1.64	1.46	5.22	6.96	7.99	9.95
Leachate CO3 (ppm)		685	237	569	569	600	961	626		
S (mg/kg)	12800	22350	30600	30500	17600	24900	56700	53700	89300	75400
Na(mg/kg)	181000	168500	121000	124000	183000	195000	216000	216000	363000	353000
K(mg/kg)	8560	<u> 2608</u>	10500	11100	8320	9830	14700	14900	24100	23400
B(mg/kg)										
Mn(mg/kg)			444000	458000			266000	270000		
Ti(mg/kg)	329000	344000			337000	331500				
From Duo Titration										
BO2 as Na2O (%w/w)										
OH as Na2O (%w/w)										
CO3 as Na2O (%w/w)										
S as Na2O (%w/w)										
Causiticity (%)										
NaOH(mol/gBRS)		7.82E-03								
NaOH(mol/gChar)										
Calculations										
C (fixed) %	2.22	0.185	0.58	0.48	0.19	0.21	0.14	1.75	0.04	1.36
Metal/Na mass ratio	1.818	2.042	3.669	3.694	1.842	1.700	1.231	1.250	0.000	0.000
Avg CO3 for ref runs	41.350	41.350	39.750	42.950	39.750	42.950	39.750	42.950	41.350	41.350
% reduc'n from ref ()	82.22%	88.03%	60.63%	61.23%	81.76%	85.45%	36.10%	39.35%	×	×
							Average CO:	Average CO3 for ref runs	-	41.35
S/Metal in char	0.039	0.065	0.069	0.067	0.052	0.075	0.213	0.199	0.246	0.214
%S went to char	34.2%	57.1%	93.5%	90.4%	45.9%	66.1%			92.3%	80.1%
S/Metal in starting liquor	0.1137	0.1137	0.0737	0.0737	0.1137	0.1137			0.2667	0.2667
-	200 10		200	0.00/	20000					
Caustn convitrom stoich	61.8%	74.2%	0.0%	0.0%	60.2%	63.3%				
Exp'd OH(mol/gChar)	4.99E-03	5.33E-03			4.72E-03	4.58E-03				
EXPI UH % acc d for										

Sample ID	P030731a	P030731b	P030805	P040220A	P040220B	P040224A	P040224B	P040224C	P040819A	P040819B
Feeding Materials	BL	BL	1.0Ti/BL	BL	BL	Ti / BL	Ti / BL	Ti / BL	Ti / BL	Ti / BL
Gas (balance N2)	5%CO2	10%CO2	5%CO2	Py	5%CO2	N2	5%CO2	10%CO2	5%CO2	10%CO2
Pressure, Bar	15 bar	15 bar	15 bar	2	5	2	5	2	9	5
Analysis Results										
From Analytic lab										
Coulometer CO3(wt%)	40.75	46.45	10.55	26.75	44.45	3.05	8.30	9.55	3.1	6.4
Total C (wt %)	9.46	10.26	2.28	6.57	9.29	2.48	2.23	5.41	2.91	1.97
Leachate CO3 (ppm)			578			737	723	719		
S (mg/kg)	51250	38600	18500	99800	79000	33900	31100	26700	28200	29100
Na(mg/kg)	328500	338000	184000	269000	335000	204000	214000	195000	218000	213000
K(mg/kg)	22250	23700		17300	23400	9280	10800	10600	11200	11200
B(mg/kg)										
Mn(mg/kg)										
Ti(mg/kg)			316000			325000	311000	293000	333000	321000
From Duo Titration										
BO2 as Na2O (%w/w)										
OH as Na2O (%w/w)										
CO3 as Na2O (%w/w)										
S as Na2O (%w/w)										
Causiticity (%)										
NaOH(mol/gBRS)						8.49E-03	7.90E-03	7.67E-03	7.61E-03	7.42E-03
NaOH(mol/gChar)						0.00402	0	0	0.00176	0
Calculations		10.0				1		1		
C (fixed) %	1.31	0.97	0.17	4.22	0.4	1.87	0.57	3.5	2.29	0.69
Metal/Na mass ratio	0.000	0.000	1.717	0.000	0.000	1.593	1.453	1.503	1.528	1.507
Avg CO3 for ref runs	43.600	43.600	40.750			39.75	39.75	43	39.75	42.95
% reduc'n from ref ()	×	×	74.11%			92.33%	79.12%	77.79%	92.20%	85.10%
		43.6								
S/Metal in char	0.156	0.114	0.059	0.371	0.236	0.104	0.100	0.091	0.085	0.091
%S went to char	58.5%	42.8%	51.5%			91.7%	88.0%	80.1%	74.5%	79.7%
S/Metal in starting liquor	0.2667	0.2667	0.1137	0.2670	0.2670	0.1137	0.1137	0.1137	0.1137	0.1137
Cartet'n convition stoich			3E 70/2			700 707	11 102	70 V 22	RE 10/	EQ 20/
			2011/02			5 1 E E O O	2 22E 02	c		1 175 03
			3.28E-U3			0.10E-U3	0.20E-U0	Z.30E-U3	31 6%	4.17E-03
						10.1/0			01.0/0	

Sample ID	P040924A	P040924B	P040827A	P040827B	P040929	P041006
Feeding Materials	Ti / BL	Ti / BL	Ti / BL	Ti / BL	Ti / BL w/par	Ti / BL w/par
Gas (balance N2)	5%CO2	10%CO2	5%CO2	10%CO2	5%CO2	10%CO2
Pressure, Bar	5	5	5	5	15	15
Analysis Results						
From Analytic lab					1	
Coulometer CO3(wt%)	2.8	5.35	3.1	6.8	7.9	14.05
Total C (wt %)	1.96	1.39	1.19	1.98	3.28	4.40
Leachate CO3 (ppm)						
S (mg/kg)	27700	26500	30300	27800	29400	21500
Na(mg/kg)	223000	196000	224000	208000	215000	215000
K(mg/kg)	12000	10500	11900	10900	12700	13600
B(mg/kg)						
Mn(mg/kg)						
Ti(mg/kg)	352000	328000	342000	314000	320000	299000
From Duo Titration						
BO2 as Na2O (%w/w)						
OH as Na2O (%w/w)						
CO3 as Na2O (%w/w)						
S as Na2O (%w/w)						
Causiticity (%)						
NaOH(mol/gBRS)	8.52E-03	7.35E-03	8.12E-03	7.36E-03	8.25E-03	7.42E-03
NaOH(mol/gChar)	0.00329	0.00288	0.00186	0.00178	0.000821	0
Calculations						
C (fixed) %	1.4	0.32	0.57	0.62	1.7	1.59
Metal/Na mass ratio	1.578	1.673	1.527	1.510	1.488	1.391
Avg CO3 for ref runs	39.75	42.95	39.75	42.95	41	43.6
% reduc'n from ref ()	92.96%	87.54%	92.20%	84.17%	80.73%	67.78%
S/Metal in char	0.079	0.081	0.089	0.089	0.092	0.072
%S went to char	69.2%	71.1%	77.9%	77.9%	80.8%	63.2%
S/Metal in starting liquor	0.1137	0.1137	0.1137	0.1137	0.1137	0.1137
Caust'n conv from stoich	87.8%	69.0%	85.2%	56.5%	47.2%	
Exp'd OH(mol/gChar)	5.83E-03	4.80E-03	5.49E-03	4.07E-03	3.59E-03	1.66E-03
Exp'I OH % acc'd for	56.4%	60.0%	33.9%	43.8%	22.9%	

Sample ID	08/08/03c(1)	08/08/03c(1) 08/08/03d(11)	08/08/03e(2)	08/08/03f(22)		08/08/03q(3) 08/08/03h(33)
Feed Materials	BL	BL	BL/0.11B	BL/0.11B	BL/0.03B	BL/0.03B
Temp, C	950	950	950	950	950	950
CO2 (%)	2	2	2	2	2	2
N2 (%)	98	98	98	98	98	98
Prim ml/min	110	110	110	110	110	110
Sec. L/min	10	10	10	10	10	10
Q I/min	12	12	12	12	12	12
Feeding BL(g)	0.6994	0.4300	0.7652	0.6303	0.882	1.3731
Feeding Time(min)	14	12	11	12	12	14
Feeding Rate (g/min)						
Filter (g)	0.7705	0.7650	0.7724	0.7677	0.7638	0.7636
Filter + Fume(g)	0.8649	0.8298	0.8409	0.8305	0.8516	0.9049
Fume (g)	0.0944	0.0648	0.0685	0.0628	0.0878	0.1413
Char(g)	0.1152	0.1179	0.1414	0.0788	0.0743	0.2978
Notes	T3=850	T3=850	T3=850	T3=850	T3=850	T3=850
Analysis Results						
CHAR						
Coulometer CO3 (wt%)	29.25	29.05	21.55	20.05	24.35	28.65
Total C (wt %)	16.77	19.75	10.81	10.74	15.07	13.09
S (mg/kg)	49100	53300	38500	33300	45400	53650
B(mg/kg)	309	213	25700	24300	10600	10430
Na(mg/kg)	220000	220000	238000	218000	234000	262500
K(mg/kg)	19600	18500	16900	16500	20200	22900
Analysis Results						
FUME						
Coulometer CO3 (wt%)	37.85	39.95	34.1	25.9	32.5	38
Total C (wt %)	9.23	9.02	7.27	6.7	7.17	7.96
S (mg/kg)	35700	36200	18900	22700	30000	27600
B(mg/kg)	24000	44200	35100	60700	32100	18000
Na(mg/kg)	230000	298000	225000	296000	285000	248000
K(mg/kg)	36100	53200	40300	61500	53600	42300
Char Calculations						
C (fixed) %	10.92	13.94	6.5	6.73	10.2	7.36
Metal/Na mass ratio	0.001	0.001	0.108	0.111	0.045	0.040
Avg CO3 for ref runs	29.15	29.15	29.15	29.15	29.15	29.15
% reduc'n from ref ()	-0.34%	0.34%	26.07%	31.22%	16.47%	1.72%

Sample ID	08/12/03a(1)	08/12/03b(2)	08/12/03b(2) 08/12/03c(22)	08/12/03d(3)	08/12/03d(3) 08/12/03e(33)08/12/03f(333	08/12/03f(333)
Feed Materials	BL	BL/0.03B	BL/0.03B	BL/0.11B	BL/0.11B	BL/0.11B
Temp, C	950	950	950	950	950	950
CO2 (%)	5	5	5	5	5	5
N2 (%)	96	96	36	95	36	96
Prim ml/min	110	110	110	110	110	110
Sec. L/min	10	10	10	10	10	10
Q l/min	12	12	12	12	12	12
Feeding BL(g)	0.4867	0.7584	0.7345	0.4382	1.1220	1.583
Feeding Time(min)	8	8	8	10	12	14
Feeding Rate (g/min)						
Filter (g)	0.763	0.7600	0.7700	0.7733	0.7592	0.7686
Filter + Fume(g)	0.8207	0.8267	0.8307	0.8295	0.8561	0.8951
Fume (g)	0.0577	0.0667	0.0607	0.0562	0.0969	0.1265
Char(g)	0.0735	0.1663	0.1287	0.5878	0.3096	0.4538
Notes	T3=790	T3=790	T3=790	T3=790	T3=790	T3=790
Analysis Results						
CHAR						
Coulometer CO3 (wt%)	31.65	26.35	29.35	32.25	23.7	24.95
Total C (wt %)	16.72	14.4	10.66	7.46	5.59	7.09
S (mg/kg)	51300	20000	50700	54600	48400	42300
B(mg/kg)	546	7350	0068	16150	29900	28800
Na(mg/kg)	241000	257000	268000	273000	295000	268000
K(mg/kg)	21400	25100	26000	16400	20000	19000
Analysis Results						
FUME						
Coulometer CO3 (wt%)	24.9	28.75	29.65	22.4	31.4	30.15
Total C (wt %)	7.33	7.47	6.95	5.7	6.71	7.48
S (mg/kg)	75100	48500	38200	33400	19800	20000
B(mg/kg)	86900	68100	52500	66300	42100	47100
Na(mg/kg)	360000	410000	349000	315000	261000	307000
K(mg/kg)	113000	87200	73500	68100	49300	57000
Char Calculations						
C (fixed) %	10.39	9.13	4.79	1.01	0.85	2.1
Metal/Na mass ratio	0.002	0.029	0.033	0.059	0.101	0.107
Avg CO3 for ref runs	29.15	29.15	29.15	29.15	29.15	29.15
% reduc'n from ref ()		9.61%	-0.69%	-10.63%	18.70%	14.41%

Sample ID	D02/19/03	)6/17/03 (Red	D02/18/04	D02/24/04	D03/01/04	D03/16/04	D05/11/04	D05/17/04	D05/25/04	D06/02/04
Feeding Materials	Ti / BL	Ti / BL	Straight BL	BL with Ti						
Particle Size (um)	<53	<53	<53	<53	<53	<53	<53	<53	<53	<53
Feeding Amount(g)	80.19	49.65	23.13	26.28	28.34	27.35	28.59	28.50	30.25	28.23
Char Amount(g)	50.19	32.12	8.51	15.7	16.99	17.00	20.03	20.06	21.76	20.46
Char Yeild(%)	62.59	64.69	36.79	59.74	59.95	62.16	70.06	70.39	71.93	72.48
React Temp (oC)	009	009	600	600	600	600	600	009	600	600
N2 (L/min)	2.00	2.00	2.00	2.00	2.00	2.00	35%	35%	40%	40%
Steam(%)	20	50	50	50	50	50	50%	20%	50%	50%
CO2 (%)		0		0	0.005	0	15%	15%	10%	10%
Quench (L/min)	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
React Time (hr)	50	50	50	50	50	50	50	50	50	50
Analysis Results										
From Analytic lab										
Char Coulometer CO3(wt%)	8.98	4.5	48.8	2.70	2.45	1.85	17.45	14.95	14.0	13.45
Char leachate CO3 (ppm)	405.93			858	892	697				
Char Total C (wt %)	1.605	0.91	10.39	0.96	0.52	0.41	3.08	2.885	2.725	2.635
S (mg/kg)		39500	21200	24000	27000	44300	37600	17800	37700	23800
Ti(mg/kg)	146000	272000		283000	221000	259000	237000		258000	262000
Na(mg/kg)	232000	245000	371000	267000	275000	269000	236000	248000	217000	224000
Char leachate Na (mg/L)	815									
K(mg/kg)		16000	17900	13900	17200	16400	18200	11300	14200	11600
From Titration										
NaOH(mol/gChar) no BaCl2	0.006899	0.004974		0.007167	0.006200	0.006128	0.004178	0.004162	0.003940	0.003877
NaOH(mol/gChar) w/BaCl2				0.005667	0.001590	0.000814	0.000000	0.000228	0.000000	0.000206
Calculations										
C (fixed) %	-0.2	0.0	0.6	0.4	0.0	0.0	-0.4	-0.1	-0.1	-0.1
Metal/Na mass ratio	0.63	1.11	0.00	1.06	0.80	0.96	1.00	0.94	1.19	1.17
Avg CO3 for ref runs	48.8	48.8	48.8	48.8	48.8	48.8	48.8	48.8	48.8	48.8
% reduc'n from ref ()	81.61%	90.78%	0.00%	94.47%	94.98%	96.21%	64.24%	69.36%	71.31%	72.44%
			S/K							
S/Ti ratio		0.14522	1.18436	0.08481	0.12217	0.17104	0.15865	0.07607	0.14612	0.09084
S/Ti in starting liquor	0.114	0.114	3.059	0.114	0.114	0.114	0.114	0.114	0.114	0.114
% of S went to char		127.39%	38.72%	74.39%	107.17%	150.04%	139.17%	66.73%	128.18%	79.68%
% CO3 conversion		70.80%		88%	88.20%	92.30%	%0	%0	%0	%0
exp'd OH mol/g smelt		0.004389		0.005754	0.005155	0.00534	0.001488	0.001488	0.001488	0.001488
expt1 % OH from titr		113.32%		98.49%	120.27%	114.76%	280.75%	2/9.68%	264.76%	260.53%

Sample ID	D03/03/03	05/27/03 (Redd	D07/08/03	06/22/04	07/06/04	07/13/04	07/19/04	07/26/04
Feeding Materials	BL with Mn	BL with Mn	BL with 0.4Mn	BL with Mn	BL with Mn	BL with Mn	BL with Mn	BL with Mn
Particle Size (um)	<53	<53	<53	<53	<53	<53	<53	<53
Feeding Amount(g)	52.77	58.56	45.01	29.98	29.5	28.88	28.98	30.79
Char Amount(g)	38.05	41.13		21.35	18.53		18.3	18.66
Char Yeild(%)	72.11	70.24	00.0	71.21	62.81	****	63.15	60.60
React Temp (oC)	009	009	009	600	600	009	009	600
N2 (L/min)	2.00	2.00	2.00	2.00	2.00	40%	40%	40%
Steam(%)	50	50	50	50	50	20%	20%	50%
CO2 (%)						10%	10%	10%
Quench (L/min)	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
React Time (hr)	50	50	50	50	50	50	50	50
Analysis Results								
Coulometer CO3 (wt%)	11.65	0.0540	6.7	0.65	1.50		1.70	0.35
Char leachate CO3(ppm)	443.55							
Total C (wt %)	2.51	0.005	1.66	0.175	0.31		0.37	0.085
S (mg/kg)		29000	48300	22200	31800		29500	30100
Mn(mg/kg)	377000	425000	270000	388000	394000		395000	386000
Na(mg/kg)	103000	125000		120000	134000		127000	128000
Char leachate Na(mg/L)	541							
K(mg/kg)		11600	14500	8680	11000		10500	10700
From Titration								
NaOH(mol/gChar) no BaCl2	2.36E-03	1.29E-03		1.69E-03	1.61E-03		1.67E-03	1.76E-03
NaOH(mol/gChar) w/BaCl2			0.0				9.00E-04	
Calculations								
C (fixed) %	0.18	-0.01	0.08	0.05	0.01		0.03	0.02
Metal/Na mass ratio	3.66	3.40	1.23	3.23	2.94		3.11	3.02
Avg CO3 for ref runs	50	50	20	50	50		50	50
% reduc'n from ref ()	76.70%	<u>99.89%</u>	84.20%	98.70%	<u>97.00%</u>		<u>96.60%</u>	<u>99.30%</u>
			017000	0.05700	0 00071		0.07460	007700
S/IVITI FALLO ILI CITAL		0.00024	0.17009	77 / CN'N	0.00071		0.0/400	0.01/190
% of S in char				77.63%	109.51%		101.33%	105.81%
S/Mn ratio in BL	0.0737	0.0737		0.0737	0.0737		0.0737	0.0737
% CO3 conversion		100%		100%	100%		95%	100%
exp'd OH mol/g smelt		0.004196		0.004196	0.004196		0.003787	0.004196
expt'l % OH from titr		30.8%		40.2%	38.4%		44.2%	42.0%

## DE-FC26-02NT41492

Sample ID	D11/25/02	D11/30/02	D12/04/02	D02/27/03	07/01/03(red	D03/30/05	D04/02/05	D01/08/03	06/23/03(Red
Feeding Materials	BL	BL	L w/ 0.11 B:N	L w/ 0.03 B:N	L w/ 0.11 B:N	3L with 0.03 🛱	L with 0.03 E	BL with 25% B	3L with 25% E
Particle Size (um)	<53	<53	<53	<53	<53	53 - 90 um	53 - 90 um	<53	<53
Feeding Amount(g)	40.2183	42.62	63.95	47.22	48.82	39.78	43.87	56.78	41.4
Char Amount(g)	19.89	21.10	33.30	24.9	25.66	18.40	21.31	29.38	19.64
Char Yeild(%)	49.46	49.51	52.07	52.73	52.56	46.25	48.58	51.74	47.44
React Temp (oC)	009	600	600	600	600	600	600	009	600
N2 (L/min)	2.00	2.00	2.00	2.00	2.00	2.00	40 (%)	2.00	2.00
Steam(%)	20	50	50	50	50	50	50 (%)	20	50
CO2 (%)				0		0	10.00%		
Quench (L/min)	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
React Time (hr)	20	50	50	50	50	50	50	50	50
Analysis Results									
From Analytic lab									
Doulometer CO3-C(wt%	49.86	50.63	36.22	33.33	25.35	39.85	45.4	8.65	6.6
Total C (wt %)	26.6	10.13	7.24	6.37	5.14	7.97	9.17	1.96	1.34
S (mg/kg)	14750	13400	7710		43600				23000
B(mg/kg)	193	197	33200	7970	28200			71550	74800
Na(mg/kg)	348000	343000	335000	301000	290000			259000	262000
K(mg/kg)	27100	26400	26700		22000				18700
From Titration									
BO2 as Na2O (%w/w)	-0.2	0.3	11.4	2.42	11.5	2.5	3.7	28.1	26.8
OH as Na2O (%w/w)	-0.1	-0.1	2.6	3.1	2.4	4.3	0.0	0.0	1.65
CO3 as Na2O (%w/w)	52.8	52.4	37.3	36.95	27.45	45.2	50.0	12.5	7.215
S as Na2O (%w/w)	0.2	0.2	0.0	0.19	0.1	0.0	0.0	0.1	0.1
Causiticity (%)	-0.2	-0.2	6.6	7.7	8.0			-0.3	17.3
Calculations									
C (fixed) %	-0.002	0.004	-0.004	-0.295	0.07	0	0.09	0.23	0.02
Metal/Na mass ratio			0.09910448	0.02647841	0.09724138			0.27625483	0.28549618
Avg CO3 for ref runs	50.245	50.245	50.245	50.245	50.245	50.245	50.245	50.245	50.245
% reduc'n from ref ()			27.91%	33.67%	49.55%	20.69%	9.64%	82.78%	86.86%
CO3 conv			15%	25.00%	33.00%	20.00%	5.00%		
% S not in char	84.11%	85.35%	91.37%		43.62%				67.08%

(Ti leaching data)

Sample	Leachate Name	Leaching Time	Sample Wt.	Empty Funnel	Funnel+Residue	Residue
ID		(min)	(g)	(g)	(g)	(g)
D02/24/04	06/28/05 (1st)	1st 90 min	2.9994	60.5835		
D02/24/04	06/28/05 (2st)	2nd 90 min				
D02/24/04	06/28/05 (2st)	2nd 90 min				
D02/24/04	06/28/05 (3st)	3rd 90 min			62.3682	1.7847
D02/24/04	07/05/05 (1st)	1 st 90 min	5.9994	61.5384 (#3)		
D02/24/04	07/07/05 (2st)	2 st 90 min				
D02/24/04	07/08/05 (3st)	3rd 90 min			65.2425	3.7041
D03/01/04	07/06/05 (1st)	1 st 90 min	6.0001	61.1619 (#S4)	66.2138	5.0519
D050000	7/40/0005	1 at 00 min	5 0007	00.0740/50	05 50 40	4.0400
P050603	7/13/2005	1 st 90 min	5.9987	60.9718(F2)	65.5840	4.6122
P050603	7/13/2005(2)	1 st 90 min	6.0058	60.6015(4)	65.3008(black)	4.6993
P050621(very loose)	7/14/2005	1 st 90 min	6.0004	61.4731(#3)	283(black) split out s	2.2552 *
P050621(very loose)	7/14/2005(2)	1 st 90 min	6.0004	61.3489 (#S4)	203(DIACK) Split Out S	2.2002
1 00002 1(very 1003e)	1/14/2003(2)	1 31 30 11111	0.0000	01.0400 (#04)		
D02/19/03	7/18/2005**	1 st 90 min	6.0006	71.3095(new)	74.7854	3.4759
D02/19/03	7/18/2005(2)**	1 st 90 min	6.0005	62.1039(S4)	65.5746	304707
202/10/00	1110/2000(2)	1 01 00 11111	0.0000	02.1000(01)	00.01 10	001101
D02/19/03	7/26/2005	1 st 90 min	5.9997	61.6299(#3)		
D02/19/03	7/26/2005(2)	1 st 90 min	6.0030	60.6083(#4)		
D02/19/03	7/26/2005(3)	1 st 90 min	5.9990	60.9828(F2)		
D02/19/03	7/27/2005	1 st 90 min	5.9991	61.2333(#2)		
D06/17/03	7/27/2005(2)	1 st 90 min	6.0005	71.1018(new)		
7/27/2005	7/28/2005	2nd 90 min				
7/27/2005(2)	7/28/2005(2)	2nd 90 min				
* split a lot of solids or	ut.					
** Use vacuum pump.	. Vacuum trap is v	ery cold.				
*** Leaching solution	pink will come bac	k a little bit (0.0	58-0.094ml) afte	er it reaches to e	nd points for PEFR ru	ins.
Reference:						
D02/24/04			0.9998			
D02/19/03						
D06/17/03						
Procedure:				<u> </u>		
(1). 1st leaching: We				eaching 90min at	100C.	
	ransfer leachate to					
(2). 2nd leaching: Dry						
	dual to 3 neck bot			ning 90min at 100	JC.	
	transfer leachate t				ithe former of the	
(3). 3nd leaching: Dry						
	idual to 3 neck bo			ning 90min at 10	UC.	
	ansfer leachate to					
(4). Take 2ml leachate	e, auu tutti tu% l		WIT U. TVI HCI.	·		

(Ti leaching data)

Sample	Leachate Vol.	aliquot	[HCI] titrant	Vol. HCI	[NaOH]	[NaOH]	[NaOH]
ID	(mL)	(mL)	conc	(mL)	(mol/L)	(g/L)	(mol/g char)
D02/24/04	50	2	0.1	5.944	2.97E-01	11.89	4.95E-03
D02/24/04	50	2	0.1	0.612	3.06E-02	1.22	5.10E-04
D02/24/04		1	0.1	0.330	3.30E-02	1.32	
D02/24/04	50	2	0.1	0.248	1.24E-02	0.50	2.07E-04
D02/24/04	30	1	0.1	12.770	1.28E+00	51.08	6.39E-03
D02/24/04	30	1	0.1	0.668	6.68E-02	2.67	3.34E-04
D02/24/04	30ml H2O	1	0.1	0.162	1.62E-02	0.65	8.10E-05
D03/01/04	about 22.5ml	1	0.1	24.266	2.43E+00	97.06	
		0.5	0.1	12.540	2.51E+00	100.32	
P050603	45ml H2O	1	0.1	5.076	5.08E-01	20.30	
P050603	35ml	1	0.1	10.440	1.04E+00	41.76	
P050621(very loose)	30ml	1	0.1	9.552	9.55E-01	38.21	
P050621(very loose)	23ml						
D02/19/03	50ml H2O	1	0.1	4.628	4.63E-01	18.51	
D02/19/03	35ml	1	0.1	11.684	1.17E+00	46.74	
D02/19/03	50ml	1	0.1	5.332	5.33E-01	21.33	
D02/19/03	35ml	1	0.1	12.278	1.23E+00	49.11	
D02/19/03		1	0.1	18.764	1.88E+00	75.06	
D02/19/03		1	0.1	21.958	2.20E+00	87.83	
D06/17/03		1	0.1	24.768	2.48E+00	99.07	
7/27/2005	40ml H2O	1	0.1	4.792	4.79E-01	19.17	
7/27/2005(2)	40ml H2O	1	0.1	5.228	5.23E-01	20.91	
* split a lot of solids or							
** Use vacuum pump.							
*** Leaching solution	pink will come l	back a little	bit (0.058-0.09	94ml) after it r	eaches to er	nd points for	r PEFR runs.
Reference:							
D02/24/04	250	25	0.1	3.744	1.50E-02		
D02/19/03		25	0.1	3.946	1.58E-02	0.63	
D06/17/03		25	0.1	1.710	6.84E-03	0.27	<b> </b>
Procedure:						1000	
(1). 1st leaching: We	ignt about 3 gra	ams char ar	nd add 45ml D	DH2O, leachi	ng 90min at	100C.	
	ransfer leachate						I
(2). 2nd leaching: Dry							oven.
	dual to 3 neck				Jumin at 100	IC.	┨────┤
	transfer leachat					(h. 6	
(3). 3nd leaching: Dry							oven.
	idual to 3 neck			· •	Somin at 10	JC.	
	ansfer leachate						┨────┤
(4). Take 2ml leachate	e, add 10mi 10	70 Baulz ar	iu titrate with 0				

# (Ti leaching data)

Sample	Note	Note2
ID		
D02/24/04	Use H2O leach	Put leachate to 50ml volumetric flask.
D02/24/04	Use H2O leach	Put leachate to 50ml volumetric flask.
D02/24/04		
D02/24/04	Use H2O leach	Put leachate to 50ml volumetric flask.
D02/24/04	Use 06/28/05 (1st) sol. to leach	Got about 24.5ml leachate with a lot of CO3. Add 20ml BaCl2 to titration.
D02/24/04	Use 06/28/05 (2st) sol. to leach	Got about 25ml leachate. Add 10ml BaCl2 to titration.
D02/24/04	Use 30ml H2O.	Got about 26ml leachate.
D03/01/04	Use 07/05/05 (1st) sol. to leach	Got about 19.5ml leachate with a lot of CO3. Add 20ml BaCl2 to titration.
P050603	Use H2O to leach	Got about 38ml leachate with low Na2CO3. Add 20ml BaCL2
P050603	Use 07/13/05 (1st) sol. to leach	Got about 32ml leachate with low Na2CO3. Add 20ml BaCL2
P050621(very loose)	Use 07/13/05(2) (1st) sol. to leach	Got about 24ml leachate with extremely lot sediment. Add 20ml BaCL2
	Use 07/14/05 (1st) sol. to leach	H2O from vacuum line goes to vacuum trap.
D02/19/03	Use 50ml H2O	Got about 43ml leachate.
D02/19/03	Use 07/18/05 (1st) sol. to leach	Added 20ml BaCL2 by accidently. Got 1.7059 grams sediment.
D02/19/03	Use 50ml H2O	Got about 43ml leachate.
D02/19/03	Use 07/26/05 sol. to leach	
D02/19/03	Use 07/26/05 (2st) sol. to leach	
D02/19/03	Use 07/26/05 (3st) sol. to leach	Got about 21ml leachate. Lots of sediment.
D06/17/03		
7/27/2005		
7/27/2005(2)		
* split a lot of solids of		
	. Vacuum trap is very cold.	
*** Leaching solution	nink will come back a little bit (0.058-	I 0.094ml) after it reaches to end points for PEFR runs.
Reference:		
D02/24/04		
D02/19/03		
D06/17/03		
Procedure:		
	ight about 3 grams char and add 45m	I DDH2O, leaching 90min at 100C.
	ransfer leachate to 50ml volumetric b	
		gotten from Procedure (1) with funnel in oven.
	idual to 3 neck bottle and add 45ml D	
	transfer leachate to 50ml volumetric b	
		gotten from Procedure (2) with funnel in oven.
	sidual to 3 neck bottle and add 45ml D	
	ansfer leachate to 50ml volumetric bo	
(4). Take 2ml leachat	e, add 10ml 10% BaCl2 and titrate wi	th 0.1M HCI.

_		1					1												;n)											
C.AG-05-077-6	P 040224A	Reported	Conc.	(mg/kg)	262	52.3	263	9.26	19.0	420	25.9	269	10.2	20.4	354	8190	12.0	14.2	125	10.2	181000	4.84	30600	240	4530	26.6	2.31	277000	118	1.35
2	, –				50	-2.	00	.3	28	0	33	4	9	.7	04	00	34	135 <	00	.1	00	-2.	0	8.	0	.2 <	21	.5	6.	<u>4</u>
C.AG-05-077-5	D 04/02/05	Reported	Conc.	(mg/kg)	620	53.5	10400	12.3	0.128	1010	6.63	4.14	6.16	40.7	1970	32300	2.84	13	300	43.	365000	35.5	8810	31.8	1070	27.2	5.21	62.5	28.9	38.4
4	-		_	-	00	125 <	20	.5	25 <	939	25	> 90	325	ف	06	00	20	102	202	9.	00	с.	00	104 <	00	- 7.	35	8.	Ņ	Ņ
CAG-05-077-4	D 03/30/05	Reported	Conc.	(mg/kg)	3300	12	8320	12.5	0.125	36	3.25	4.06	32	25.6	1290	32900	2.79	10	2(	31.6	361000	48.3	14400	1(	3300	76.7	4.65	35.8	37.2	30.2
ę	, –				5	8	2	4	4	0	5	× 0	33	ŝ	1	0	6	2	3	4	0	4	0	3	8	1	6	2	S	-
CAG-05-077-3	D 03/28/05	Reported	Conc.	(ba/bm)	345	51.8	74.2	12.4	0.124	1090	2.75	4.00	2.33	21.5	162	2960	2.29	222	263	9.64	368000	12.4	24700	40.3	618	42.1	2.49	52.2	40.3	31.1
F					С	v 8	3	2	4	2	2 <	v 8	9	m	2	С	7	6	С	> 6	С	4	1	2	3	8	6	3	3	4
C.A.G-05-077-2	D 07/19/04	Reported	Conc.	(mg/kg)	440	54.8	54.3	1.77	0.484	562	39.2	4.23	106	21.8	121	13900	1.07	14.9	523000	34.9	61500	82.4	151	32.5	853	27.8	3.39	53.3	1.13	33.4
	+				3	> 0.	2	> 0	6	0	1	v 23	e.	2	4	0	4 <	3 <	2	2	0	4	5	2 2	2	۷ 0	4	0	v 6	ς.
Leached solids	D 03/01/04	Reported	Conc.	(mg/kg)	183	53.0	20.2	230	0.469	1030	2.81	5.63	10.3	34.7	924	3550	16.4	213	227	9.87	92900	31.4	235	31.5	372	27.0	8.44	440000	4.69	33.3
		L	_	_		v	_	_	-		v	-	-	-	_	_	_		_	v	_	_	V	v	-	v		_		_
			icp	element	AI	As	В	Ba	Be	Са	Cd	ပိ	с С	Cu	Fe	К	Li	Mg	Mn	Mo	Na	Ni	S	Sb	Si	Sn	Sr	Ti	~	Zn
T4503K 5/5/2005	IPST	Xiaoyan Zeng	Solids																											
Project: Receint Date:		IPST Contact:	Matrix:																											

Samples were digested and reported on an as received basis.
 Samples(CAG-05-077-6,7,8,9,10) were digested for Total Titanium using

Note:

H<sub>2</sub>SO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (per Xiaoyan's approval).

3. Samples were analyzed by Inductively Coupled Plasma Emission Spectroscopy.

## APPENDIX A EXPERIMENTAL DATA

(Ti Leach)

# (Ti Leach)

	CAG-05-077-7	CAG-05-077-8	CAG-05-077-9	CAG-05-077-10	CAG-05-077-11	P.Blank
	P 040924A	CP 040224A	CP 040924A	CD 03/01/04	CD 07/19/04	
	Reported	Reported	Reported	Reported	Reported	Reported
icp	Conc.	Conc.	Conc.	Conc.	Conc.	Conc.
element	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
AI	92.6	223	232	397	268 <	: 0.597
As	> 0.70	54.7	< 55.4 <	39.4 <	51.5	4.78
В	58.9	130	71.6	47.8	58.7	1.23
Ba	16.4	8.70	9.31	10.1 <	1.66 <	0.0913
Be	9.17	19.8	19.1	33.1	0.455 <	0.00675
Са	565	378	373	530	447	3.95
Cd	18.8	24.2	35.8	63.5	36.9 <	0.150
Co	113	257	284	453 <	3.98 <	0.219
Cr	10.1	9.67	6.86	4.77.4	93.4 <	0.141
Cu	18.3	22.2	21.1	30.3	11.4	0.0750
Fe	516	368	391	572	53.7	1.08
Х	3890	9140	10200	15500	10600	2.43
Li	13.0	12.1	10.8	13.2	2.28 <	0.0550
Mg	71.9 <	14.8	< 15.0 <	10.7 <		0.767
Mn	213	215	144	131	429000 <	0.0145
Mo	< 10.2 <	10.2	12.7 <	7.34 <	> 65.6	0.526
Na	96000	203000	193000	266000	131000 <	0.657
Ni	15.4	19.3	26.0	17.8	70.6	1.18
S	< 241	32300	27100	23200	30200 <	: 12.5
Sb	91.2	211 <	< 32.9	213 <	30.5	1.98
Si	1640	982	985	1210	537	2.78
Sn	173 <	27.8	< 28.2 <	20.0	26.2	1.55
Sr	3.86	2.42	2.45	3.14	2.28 <	: 0.00825
Ti	454000	313000	347000	282000	23.7	0.0250
V	47.3	124	121	203 <	: 1.07 <	0.0585
Zn	15.9 <	1.41 <	< 1.43 <	1.02	16.8	0.375
		CD and CP refer to Chai	to Char			

(Ti Leach)

DE-FC26-02NT41492

# (Mn Leaching data)

						г – т	
Sample	Leaching Time	Sample Wt.	Empty Funnel	Funnel+Residue	Residue	Leachate Vol.	aliquot
ID	(min)	(g)	(g)	(g)	(g)	(mL)	(mL)
03/07/05 Retitr	ate (with BaCl2)	(0)	(0)		(0)	, <i>, ,</i>	· · ·
D07/08/03	90	1.0005	60.4851	60.9750	0.4899	250	25
D06/22/04	90	1.0002	61.5305	62.3378	0.8073	250	25
D07/06/04	90	0.9997	60.5840	61.3867	0.8027	250	25
D06/22/04	90	1.0002	61.5305	62.3378	0.8073	250	25
D07/06/04	90	0.9997	60.5840	61.3867	0.8027	250	25
D07/19/04	90	1.0000	61.167	61.9869	0.8199	250	25
D07/19/04	90	1.0000	61.167	61.9869	0.8199	250	25
D07/26/04	90	1.0001	76.1245	76.9378	0.8133	250	25
03/29/05 2nd l	eaching(Use san	nple after XRD)					
D06/22/04	90	0.7982	60.5811	61.3565	0.7754	250	25
01/18/06 Leac	hing and send sa	amples to Mike					
D07/19/04	1 st 90 min	1.0052	61.0939	61.8722	0.7783	250	25
D07/19/04	2 nd 90 min	0.6346	61.4671	62.0973	0.6302	250	25

# (same table continued)

Sample         [HCI] titrant         Vol. HCI         [NaOH]         Note         Image: Construction of the structure of the								
ID         conc         (mL)         (mol/L)         (mol/g char)           03/07/05 Retitrate (with BaCl2)         pp indicator shows no color           D07/08/03         0.1         0         pp indicator shows no color           D06/22/04         0.1         0         pp indicator shows no color           D07/06/04         0.1         0         pp indicator shows no color           D06/22/04         0.1         0         pp indicator shows no color           D07/06/04         0.1         0         pp indicator shows no color           D06/22/04         0.1         0         pp indicator shows no color           D07/06/04         0.1         0         pp indicator shows no color           D07/19/04         0.1         0.924         3.70E-03         9.24E-04           D07/19/04         0.1         0.93         3.60E-03         9.00E-04           D07/26/04         0.1         0         pp indicator shows no color           D03/29/05 2nd leaching(Use sample after XRD)								
03/07/05 Retitrate (with BaCl2)         pp indicator shows no color           D07/08/03         0.1         0         pp indicator shows no color           D06/22/04         0.1         0         pp indicator shows no color           D07/06/04         0.1         0         pp indicator shows no color           D07/06/04         0.1         0         pp indicator shows no color           D06/22/04         0.1         0         pp indicator shows no color           D06/22/04         0.1         0         pp indicator shows no color           D07/06/04         0.1         0         pp indicator shows no color           D07/19/04         0.1         0.924         3.70E-03         9.24E-04	Sample	[HCI] titrant	Vol. HCI	[NaOH]	[NaOH]	Note		
D07/08/03         0.1         0         pp indicator shows no color           D06/22/04         0.1         0         pp indicator shows no color           D07/06/04         0.1         0         pp indicator shows no color           D07/06/04         0.1         0         pp indicator shows no color           D06/22/04         0.1         0         pp indicator shows no color           D06/22/04         0.1         0         pp indicator shows no color           D07/06/04         0.1         0         pp indicator shows no color           D07/19/04         0.1         0.924         3.70E-03         9.24E-04           D07/19/04         0.1         0.93         3.60E-03         9.00E-04           D07/26/04         0.1         0         pp indicator shows no color           03/29/05 2nd leaching(Use sample after XRD)         0         pp indicator shows no color           03/29/05 2nd leaching(Use sample after XRD)         0         0         0           01/18/06 Leaching and send samples to Mike         0         0         0	ID	conc	(mL)	(mol/L)	(mol/g char)	)		
D06/22/04         0.1         0         pp indicator shows no color           D07/06/04         0.1         0         pp indicator shows no color           D06/22/04         0.1         0         pp indicator shows no color           D06/22/04         0.1         0         pp indicator shows no color           D06/22/04         0.1         0         pp indicator shows no color           D07/06/04         0.1         0         pp indicator shows no color           D07/19/04         0.1         0.924         3.70E-03         9.24E-04           D07/19/04         0.1         0.99         3.60E-03         9.00E-04	03/07/05 Retitr	ate (with BaCl2	2)					
D07/06/04         0.1         0         pp indicator shows no color           D06/22/04         0.1         0         pp indicator shows no color           D07/06/04         0.1         0         pp indicator shows no color           D07/19/04         0.1         0.924         3.70E-03         9.24E-04           D07/19/04         0.1         0.99         3.60E-03         9.00E-04	D07/08/03	0.1	0			pp indicato	r shows no	color
D07/06/04         0.1         0         pp indicator shows no color           D06/22/04         0.1         0         pp indicator shows no color           D07/06/04         0.1         0         pp indicator shows no color           D07/19/04         0.1         0.924         3.70E-03         9.24E-04           D07/19/04         0.1         0.99         3.60E-03         9.00E-04								
D06/22/04         0.1         0         pp indicator shows no color           D07/06/04         0.1         0         pp indicator shows no color           D07/19/04         0.1         0.924         3.70E-03         9.24E-04	D06/22/04	0.1	0			pp indicato	r shows no	color
D07/06/04         0.1         0         pp indicator shows no color           D07/19/04         0.1         0.924         3.70E-03         9.24E-04	D07/06/04	0.1	0			pp indicato	r shows no	color
D07/06/04         0.1         0         pp indicator shows no color           D07/19/04         0.1         0.924         3.70E-03         9.24E-04								
D07/19/04       0.1       0.924       3.70E-03       9.24E-04       Image: constraint of the second s	D06/22/04	0.1	0			pp indicato	r shows no	color
D07/19/04       0.1       0.9       3.60E-03       9.00E-04       pp indicator shows no color         D07/26/04       0.1       0       pp indicator shows no color         03/29/05 2nd leaching(Use sample after XRD)       0       0       0         D06/22/04       0.1       0.276       1.10E-03       3.46E-04       There is no precipitater when I add BaC         01/18/06 Leaching and send samples to Mike       0       0       0       0	D07/06/04	0.1	0			pp indicato	r shows no	color
D07/26/04       0.1       0       pp indicator shows no color         03/29/05 2nd leaching(Use sample after XRD)       0       0         D06/22/04       0.1       0.276       1.10E-03       3.46E-04       There is no precipitater when I add BaC         01/18/06 Leaching and send samples to Mike       0       0       0       0	D07/19/04	0.1	0.924	3.70E-03	9.24E-04			
03/29/05 2nd leaching(Use sample after XRD)     Image: Constraint of the state of t	D07/19/04	0.1	0.9	3.60E-03	9.00E-04			
D06/22/04         0.1         0.276         1.10E-03         3.46E-04         There is no precipitater when I add BaC           01/18/06 Leaching and send samples to Mike         0         <	D07/26/04	0.1	0			pp indicato	r shows no	color
D06/22/04         0.1         0.276         1.10E-03         3.46E-04         There is no precipitater when I add BaC           01/18/06 Leaching and send samples to Mike         0         <								
D06/22/04         0.1         0.276         1.10E-03         3.46E-04         There is no precipitater when I add BaC           01/18/06 Leaching and send samples to Mike         0         <								
01/18/06 Leaching and send samples to Mike	03/29/05 2nd le	eaching(Use sa	ample after XF	RD)				
D07/19/04 0.1	D06/22/04	0.1	0.276	1.10E-03	3.46E-04	There is no	precipitate	r when I add BaC
D07/19/04 0.1								
D07/19/04 0.1								
	01/18/06 Leach	ning and send	samples to Mi	ke				
D07/19/04 0.1	D07/19/04	0.1						
	D07/19/04	0.1						

			Ceng	_
722K	/24/2006	ST	iaoyan Zeng	l.Liquid
: T4	: Da 1/2	à	Cont Xi	٩q
Project	Receipt	Client:	IPST Co	Matrix:

		CAG-06-009-1	CAG-06-009-2		CAG-06-009-3	e.	CAG-06-009.
		Lab DI H <sub>2</sub> O	DIW 01/20/06		D 07-19-04		D 07-19-04
					1st Leachate	e	2nd Leachat
		Reported	Reported		Reported		Reported
icp		Conc.	Conc.		Conc.		Conc.
element		(mg/L)	(mg/L)		(mg/L)		(mg/L)
A	v	0.0239 <	0.0239		0:930	v	0.0239
As	~	0.113 <	0.113 <	v	0.113	~	0.113
В	>	0.00437	0.361		4.45		7.24
Ba	>	0.00365 <	0.00365		0.00500		0.0690
Be	~	0.000270 <	0.000270 <		0.000270	v	0.000270
Са		0.184	0.305		0.422		0.478
Cd	>	0.00600 <	0.00600 <	v	0.00600	>	0.00600
Co	>	0.00874 <	0.00874 <	v	0.00874	v	0.00874
C	>	0.00562 <	0.00562		0.0290	>	0.00562
Cu	~	0.00231 <	0.00231		0.0700	v	0.00231
Fe		0.0180	0.0100		0.00800		0.00600
×	v	0.0376	0.0800		2.05		4.80
Li	~	0.00220 <	 0.00220 <		0.00220	v	0.00220
Mg		0.0470	0.0480		0.0500		0.0580
Mn		0.00100	0.00300		0.0690		0.0270
Mo		0.0240	0.0320		0.0750	v	0.0211
Na		0.590	2.67		376		52.6
Ni	v	0.0105 <	0.0105 <		0.0105	v	0.0105
S	v	0.500 <	0.500		142		0.667
Sn	v	0.0575 <	 0.0575		0.356	v	0.0575
Sr		0.00100	0.00100		0.00200		0.00100
Ti		0.00100	0.00800		0.00300		0.00100
>	v	0.00234 <	0.00234		0.0960		0.0120
Zn		0.0110	0.00500		0.439		0.00800

Note:

APPENDIX A

**EXPERIMENTAL DATA** 

			ng	
4722K	/24/2006	PST	<u> (iaoyan Z</u> eng	Solid
Project: T	Receipt Da1	Client: II	IPST Cont X	Matrix: S

70

Note:

			Solic				v	v		v	v		v	v	v				v	
	Duplicate	D 07-19-04	2nd Leaching Solic	Reported	Conc.	(mg/kg)	404 <	48.6 <	268	248 <	0.430 <	580	15.5 <	3.75	135 <	18.5	102	14300	0.945 <	
	CAG-06-009-7	D 07-19-04	2nd Leaching Solid	Reported	Conc.	(mg/kg)	377	50.7 <	227	230	0.449	575	17.1	3.92 <	132	18.0	103	14000	1.35 <	
	CAG-06-009-6	D 07-19-04	1st Leaching Solid	Reported	Conc.	(mg/kg)	384	> <mark>49.4</mark> <	73.4	1.60	0.437	568	14.0	3.82 <	135	15.7	105	13900	1.31	
			1st					v		v				v						
	CAG-06-009-5	CD 07/19/05	Char	Reported	Conc.	(mg/kg)	389	44.4	65.3	1.43 <	0.393	444	15.7	3.44 <	127	13.0	76.3	11500	1.18	
	0							v		v				v						
<b>bu</b> ð					icp	element	AI	As .	В	Ba .	Be	Ca	Cd	Co .	Cr	Cu	Fe	X	L:	
iaoyan Zeng olid												-								

2.83 0.125 0.0913

(mg/kg) 0.597

Reported

olid

Conc.

P.Blank

## (Mn Leaching)

0.150

ŝ

0.0067

APPENDIX A

**EXPERIMENTAL DATA** 

1.Samples were digested and reported on an as received basis. 2.Samples were analyzed by Inductively Coupled Plasma Emission Spectroscopy.

0.0250 0.0585 0.575

3.44 278 1.01 39.9

v

1.44

12.5

1110 < 24.7 < ٧

> **25.8** <u>3.14</u> 272 1.05 33.2

ν 25.1 <u>3.06</u> 183 1.02 <u>30.2</u>

34000 22.6 < 2.36

v

ა წ

S

ïŻ

17.7 0.920 22.0

v

1>

Zn

103C 86.

1110 82.1 55200

0.00825

0.219 0.141 0.425 0.375

2.88 0.0550 0.0250

0.526 4.00 0.475

17.6 < 56700

20.6

<u>9.62</u>

50300

65600

8.27 145000

v

Na Na Ę

73.1

86.3

515000

432000

4<u>9800</u>

Project:	T4676K
Receipt Date:	11/16/2005
Client:	IPST
IPST Contact:	Xiaoyan Zeng
Matrix:	Solids

Lab ID:	Client ID:	Τi
		(mg/kg)
CAG-05-148-27	P050603	300000
CAG-05-148-28	P050707A	299000
Duplicate	P050707A	299000
CAG-05-148-29	P050708A	286000
CAG-05-148-30	P050707B	312000
CAG-05-148-31	P050708B	304000
CAG-05-148-32	P050817A	277000

Note:

1. Samples were digested using  $H_2SO_4$  and  $(NH_4)_2SO_4.$ 

316000

P050817B

CAG-05-148-33

Samples were reported on an as received basis.
 Samples were analyzed by Inductively Coupled Plasma Emission Spectroscopy.

76K							
2/2005							
			CAG-05-148-25		CAG-05-148-26		P.Blank
yan Zeng			DI Liquid (1)		DI Liquid (2)		
-iquid			Reported		Reported		Reported
	icp		Conc.		Conc.		Conc.
	element		(mg/kg)		(mg/kg)		(mg/kg)
	AI		0.173		0.253		0.960
	В		1.21		1.73		0.280
	Ba	V	0.0144	۷	0.0142 <	v	0.0730
	Be	۷	0.00106	۷	0.00105 <	v	0.00540
	Ca		0.276		0.233		1.64
	Cd	۷	0.0236 <	۷	0.0233 <	v	0.120
	Co	۷	0.0344	۷	0.0340	v	0.175
	Cr	۷	0.0221	۷	0.0218 <	v	0.112
	Cu	۷	0.00910	۷	0.00898 <	v	0.0462
	Fe		0.130		0.117		0.980
	К	۷	0.148		0.482		2.74
						I	

Project:	T4676K			
Receipt Date:	11/22/2005			
Client:	IPST		CAG-05-148-25 C	Ű
IPST Contact:	Xiaoyan Zeng		DI Liquid (1)	
Matrix:	Aq.Liquid		Reported	R
		icp	Conc.	ŏ

APPENDIX A
EXPERIMENTAL DATA

0.614 0.0116

v

0.119

v

0.121 < 0.00229 < 1.62

v v

0.209

٧

1.82

5.40 0.0544 1.94 0.284 4.90 0.272 0.00128

10.0 1.34 3.40

v v

v

1.97 0.264 3.67 0.335 0.00130

v v V

0.0412

1.18

0.00660

v

v

v

Note:

0.540

0.0468

v

0.00909 0.0272

v

0.00922 0.0158

V

22

0.0394

0.0311

0.0200

72

Receipt Date: 11/22/2005		CAG-05-148-24	CAG-05-148-27	CAG-05-148-28	CAG-05-148-29	CAG-05-148-30
IPST		Sludge		P050707A	P050708A	P050707B
Xiaoyan Zeng		Reported	Reported	Reported	Reported	Reported
Solids	icp	Conc.	Conc.	Conc.	Conc.	Conc.
	element	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
	AI	1190		513	504	514
	В	43.3	134	258	208	334
	Ba	67.3	2.19	6.19	5.71	6.54
	Be	< 0.180	46.8	44.0	43.6	42.1
	Са	47000	438	446	401	431
	Cd	5.33	32.4	30.2	29.3	27.6
	Co	< 5.83	369	351	361	341
	Cr	12.7	10.8	21.3	22.9	19.2
	Cu	32.0	27.6	30.9	40.7	36.4
	Fe	1830	463	317	271	284
	Y	1230	12600	9280	9290	9630
	Mg	1610	32.4	39.2	32.1	43.0
	Mn	488	113	107	122	115
	Na	3630	217000	218000	212000	223000
	Ni	16.7	13.2	22.7	7.86	18.2
	S	7330	27300	26000	30800	19900
	Sb	< 44.7	< 40.3	< 46.1	< 47.9	< 31.3
	Si	1220	889	1130	1220	1090
	Sn	58.7	< 34.5	< 39.5	< 41.1 <	< 26.9
	Sr	56.7	3.00	2.75	2.86	3.27
	Ti	85.3	NA	AN	AN	NA
	۸ ا	4.00	201	190	193	190
	Zn	273	< 1.75	< 2.01	< 2.09 <	< 1.36

DE-FC26-02NT41492

# APPENDIX A EXPERIMENTAL DATA

CAG-05-148-33 P.Blank	P050817B	Reported Reported	Conc. Conc.	(mg/kg) (mg/kg)	566 0.960	315 0.280	7.00 < 0.0730	35.0 < 0.00540	449 1.64	21.0 < 0.120	282 < 0.175	25.7 < 0.112	39.1 < 0.0462	355 0.980	9500 2.74	53.6 < 0.614	111 < 0.0116	231000 1.82	24.5 < 0.209	22400 < 10.0	39.1 < 1.34	1060 3.40	33.5 1.18	2.92 < 0.00660	NA 0.0200	160 < 0.0468
3-05-148-32	050817A	orted		(mg/kg)	475	146	4.29	41.4	368	30.7	329	23.6	30.7	277	10100	34.3	104	216000	21.4	21500	47.9	1000	41.1	2.86	NA	181

		CAG-05-148-31	CAG-05-148-32	CAG-05-148-33	P.Blank
		P050708B	P050817A	P050817B	
		Reported	Reported	Reported	Reported
icp		Conc.	Conc.	Conc.	Conc.
element		(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
AI		570	475	566	0.96(
В		382	146	315	0.28(
Ba		5.56	4.29	2.00 <	0.073(
Be		43.1	41.4	35.0 <	0.0054(
Са		457	368	449	1.62
Cd		30.6	30.7	21.0 <	0.12(
Co		338	329	282 <	0.175
Cr		19.4	23.6	25.7 <	0.112
Cu		67.4	30.7	39.1 <	0.0462
Fe		297	277	355	0.98(
X		9100	10100	9500	2.74
Mg		50.7	34.3	53.6 <	0.61
Mn		112	104	111 <	0.0116
Na		226000	216000	231000	1.82
Ni		34.0	21.4	24.5 <	0.20
S		18600	21500	22400 <	10.(
Sb	v	46.6	< 47.9 <	< 39.1 <	1.34
Si		1150	1000	1060	3.4(
Sn	V	39.9	< 41.1 <	< 33.5	1.18
Sr		3.47	2.86	2.92 <	0.0066(
Ti		NA	NA	NA	0.020(
>		188	181	160 <	0.0468
Zn		91.7	< 2.09	83.4	0.54(

Project:	T4594K		-	-	-	
Receipt Date:	8/23/2005		CAG-05-121-A	CAG-05-121-B	CAG-05-121-C	P.Blank
Client:	IPST		P050816	Zeng 1 08/22/05	Zeng 2 08/22/05	
IPST Contact:	Xiaoyan Zeng		Reported	Reported	Reported	Reported
INIALLIX:	Solids	ICD olomont	CONC.	CONC. (ma/ka)	CONC. (ma/kg)	(ma/ka)
				010	150	10 20 20 20 20 20 20 20 20 20 20 20 20 20
				210		
			2.00	0.00	00.0	
		n		2.08	2.19 <	
		Ba	8.44 <	1.74	4.00 <	< 0.0913
		Be <	< 0.120	12.9		< 0.00675
		Са	261	0.06	328	1.65
		<ul><li>Cd</li></ul>	< 2.66	19.5	13.0 <	< 0.150
		v C	< 3.88	197	119 <	< 0.219
		ບັ	2.66	6.67	16.0 <	< 0.141
		Cu	4.44	8.10	16.5	< 0.0578
		Fe	53.7	5.24	181	0.225
		×	33700	455	8850	1.60
			7.55	13.8	10.0	0.100
		Mg	232 <	14.6	21.5 <	< 0.767
		Mn	120	2.38	77.5	0.0250
		Mo	42.6 <	10.0	< 10.5 <	< 0.526
		Na	330000	121000	151000	1.58
		Ni	< 4.64 <	4.98	7.50 <	< 0.262
		Pb	43.1	74.8	< 35.7 <	< 1.79
		S	72800 <	238	24000 <	< 12.5
		Sb <	< 29.8	150	93.5 <	< 1.68
		Se	< 66.0 <	20.8	< 74.4 <	< 3.72
		Si	409	481	715	2.13
		Sn	43.1 <	27.4	< 28.7 <	< 1.44
		Sr	1.78	0.952	2.00 <	< 0.00825
		Ti	199	AN	NA	0.0500
		TI	< 6.96 <	7.17	< 75.3 <	< 3.77
		~	3.55	0.67	64.0	< 0.0585
		Zn	92.4 <	1.39	< 1.46 <	< 0.0730
Note:	1.Samples were	digested and	1.Samples were digested and reported on an as received basis.	eceived basis.		

Proiect:	T4594K
Receipt Date:	8/23/2005
Client:	IPST
IPST Contact:	Xiaoyan Zeng
Matrix:	Solids

Ti	(mg/kg)	455000	459000	201000
Client ID:		Zeng 1 08/22/05	Zeng 1 08/22/05	Zeng 2 08/22/05
Lab ID:		CAG-05-121-B	Duplicate	CAG-05-121-C

Note:

Samples were digested using H<sub>2</sub>SO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.
 Samples were reported on an as received basis.
 Samples were analyzed by Inductively Coupled Plasma Emission Spectroscopy.

Project:	1146A4416
Receipt Date:	11/30/2004
Client:	IPST
IPST Contact:	Xiaoyan Zeng
Matrix:	Solids

	liont ID.
CAG-04-152-11	P041202A
CAG-04-152-12	P041202B
CAG-04-152-13	P041202C
CAG-04-152-14	P041021A

(mg/kg) ï

338000 316000 304000 330000 279000

Note:

1. Samples were digested using  $H_2SO_4$  and  $(\text{NH}_4)_2SO_{4.}$ 

P041021B

CAG-04-152-15

Samples were reported on an as received basis.
 Samples were analyzed by Inductively Coupled Plasma Emission Spectroscopy.

LD 03/01/04 "1 <sup>st</sup> Grinded"		LD 07/19/04		
			LP 04224A	LP040924A
	"2 <sup>nd</sup> Grinded"			
	Reported	Reported	Reported	Reported
	Conc.	Conc.	Conc.	Conc.
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
	0.180		4.24	3.67 <
	0.277	0.566	< 0.291	0.598 <
	3.07	4.18	6.10	5.90
	0.0637	< 0.00887	< 0.00939	< 0.00733 <
	0.000506	< 0.000656	< 0.000694	< 0.000542 <
	0.446	3.13	6.97	1.69
	0.0112	< 0.0146	< 0.0154	< 0.0120 <
	0.0164	< 0.0212	< 0.0225	< 0.0175 <
	0.0105	0.0292	< 0.0145	< 0.0113 <
	0.0487		0.0103	0.0100
	0.0581	0.0632	0.0592	0.0261
	1.30		29.6	33.3
	0.00412	0.00972	0.00772	0.00803 <
	0.0575	< 0.0746	< 0.0789	< 0.0616
	0.00187	0.00243	0.00257	0.00201 <
	0.0394	< 0.0512	< 0.0541	< 0.0423 <
	53.0	362	617	568
	0.0196	< 0.0254	< 0.0269	< 0.0210
	0.937	139	136	115 <
	0.126	< 0.163	< 0.172	< 0.135 <
	15.4	49.1	112	81.7
	0.108	< 0.140	< 0.148	0.205
	0.00187	0.00243	0.00514	0.00201 <
	0.0450	0.0146	0.00772	0.0341
	0.00438	0.0923	0.0926	0.0823 <
	0.0206	0.00972	0.0566	0.0903

Samples were filtered through 0.45um filters, digested and reported on an as received t
 Samples were analyzed by Inductively Coupeld Plasma Emission Spectroscopy.

## APPENDIX A EXPERIMENTAL DATA

P.Blank			Reported	Conc.	(mg/kg)	0.597	2.83	0.325	0.0913	0.00675	2.58	0.150	0.219	0.141	0.200	0.625	2.75	0.0550	0.825	0.0145	0.526	3.23	0.425	12.5	1.68	1.58	6.10	0.00825	0.450	0.0585	0.200	
CAG-05-077-26	unlabeled	LP040924A	Reported	Conc.	(mg/kg)	3.67 <	0.598 <	5.90	0.00733 <	0.000542 <	1.69	0.0120 <	0.0175 <	0.0113 <	0.0100	0.0261	33.3	0.00803 <	0.0616	0.00201 <	0.0423 <	568	0.0210	115 <	0.135 <	81.7	0.205	0.00201 <	0.0341	0.0823 <	0.0903	sis.
CAG-05-077-25	LP 04224A		Reported	Conc.	(mg/kg)	4.24	0.291	6.10	0.00939 <	0.000694 <	6.97	0.0154 <	0.0225 <	0.0145 <	0.0103	0.0592	29.6	0.00772	0.0789 <	0.00257	0.0541 <	617	0.0269 <	136	0.172 <	112	0.148	0.00514	0.00772	0.0926	0.0566	<ol> <li>Samples were filtered through 0.45um filters, digested and reported on an as received basis.</li> <li>Samples were analyzed by Inductively Coupeld Plasma Emission Spectroscopy.</li> </ol>
CAG-05-077-24	LD 07/19/04		Reported	Conc.	(mg/kg)	1.37	0.566 <	4.18	0.00887 <	0.000656 <	3.13	0.0146 <	0.0212 <	0.0292 <	0.0122	0.0632	2.06	0.00972	0.0746 <	0.00243	0.0512 <	362	0.0254 <	139	0.163 <	49.1	0.140 <	0.00243	0.0146	0.0923	0.00972	sted and reported o asma Emission Spe
CAG-05-077-23	LD 03/01/04	"2 <sup>nd</sup> Grinded"	Reported	Conc.	(mg/kg)	0.180	0.277	3.07	0.0637 <	0.000506 <	0.446	0.0112 <	0.0164 <	0.0105	0.0487	0.0581	1.30	0.00412	0.0575 <	0.00187	0.0394 <	53.0	0.0196	0.937	0.126 <	15.4	0.108 <	0.00187	0.0450	0.00438	0.0206	<ol> <li>Samples were filtered through 0.45um filters, digested and reported on an as re- 2. Samples were analyzed by Inductively Coupeld Plasma Emission Spectroscopy.</li> </ol>
CAG-05-077-22	LD 03/01/04	"1 <sup>st</sup> Grinded"	Reported	Conc.	(mg/kg)	4.71	0.683	9.98	0.0182	0.000545 <	0.457	0.0303 <	0.0177 <	0.246 <	0.0182	0.0606	53.7	0.00808 <	0.0620 <	0.00202	0.0425 <	260	0.0211 <	92.7 <	0.135 <	91.5	0.206 <	0.00202	0.0141	0.125 <	0.129	vere filtered through vere analyzed by Inc
				icp	element	AI	As	В	Ba	Be <	Ca	Cd	Co <	c	Cu	Fe	×		Mg <	Mn	Mo <	Na	Ni <	S	Sb <	Si	Sn	Sr	Ti	~	Zn	<ol> <li>Samples v</li> <li>Samples v</li> </ol>
T4503K	5/5/2005	IPST	Xiaoyan Zeng	Aq.Liquid		_					-																_		-	-		Note:
Project:	Receipt Date:		IPST Contact:	Matrix:																												

Project:	T4503K		CAG-05-077-1	CAG-05-077-2	CAG-05-077-3	CAG-05-077-4	CAG-05-077-5	CAG-05-077-6
Receipt Date:	5/5/2005		D 03/01/04	D 07/19/04	D 03/28/05	D 03/30/05	D 04/02/05	P 040224A
Client:	IPST		Reported	Reported	Reported	Reported	Reported	Reported
IPST Contact:	Xiaoyan Zeng	icp	Conc.	Conc.	Conc.	Conc.	Conc.	Conc.
Matrix:	Solids	element	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
		AI	183	440	345	3300	620	297
		- As	< 53.0	< 54.8 <	< 51.8	125 <	53.5	< 52.3
		В	20.2	54.3	74.2	8320	10400	263
		Ba	230	< 1.77	12.4	12.5	12.3	9.26
		Be	0.469	0.484 <	0.124	< 0.125 <	0.128	19.0
		Са	1030	562	1090	939	1010	420
		- Cd	< 2.81	39.2 <	2.75	3.25	6.63	25.9
		ပိ	5.63	< 4.23 <	< 4.00	< 4.06 <	4.14	269
		ں ت	10.3	106	7.33	325	6.16	10.2
		CU	34.7	21.8	21.5	25.6	40.7	20.4
		Fe	924	127	291	1290	1970	354
		Y	3550	13900	29600	32900	32300	8190
		Li	16.4	< 1.07	2.29	2.79	2.84	12.0
		Mg	213	< 14.9	227	102	135 <	< 14.2
		Mn	227	523000	293	202	300	125
		Mo	< 9.87	34.9 <	< 9.64	31.6	43.1	10.2
		Na	92900	61500	368000	361000	365000	181000
		Ni	31.4	82.4	12.4	48.3	35.5 <	< 4.84
		s	< 235	751	24700	14400	8810	30600
		Sb .	< 31.5	< 32.5	40.3	104 <	31.8	240
		Si	372	853	618	3300	1070	4530
		Sn .	< 27.0	< 27.8	42.1	76.7 <	27.2	< 26.6
		Sr	8.44	3.39	5.49	4.65	5.21	2.31
		Ti	440000	53.3	52.2	35.8	62.5	277000
		^	4.69	< 1.13	40.3	37.2	28.9	118
		Zn	33.3	33.4	31.1	30.2	38.4 <	< 1.35
	Note:	1. Samples	<ol> <li>Samples were digested and reported on an as received basis.</li> <li>Samples(CAG-05-077-6 7 8 9 10) were dimested for Total Titanium using</li> </ol>	eported on an as rec	eived basis. or Total Titanium I	sing		

	using
1. Samples were digested and reported on an as received basis.	2. Samples(CAG-05-077-6,7,8,9,10) were digested for Total Titanium using

 $H_2SO_4$  and (NH\_4)\_2SO\_4 (per Xiaoyan's approval).

3. Samples were analyzed by Inductively Coupled Plasma Emission Spectroscopy.

	CAG-05-077-7	CAG-05-077-8	CAG-05-077-9	CAG-05-077-10	CAG-05-077-11	P.Blank
	P 040924A	CP 040224A	CP 040924A	CD 03/01/04	CD 07/19/04	
	Reported	Reported	Reported	Reported	Reported	Reported
icp	Conc.	Conc.	Conc.	Conc.	Conc.	Conc.
element	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
AI	95.6	223	232	397	268 <	< 0.597
As	97.0	< 54.7	< 55.4 <	39.4 <	51.5	4.78
В	58.9	130	71.6	47.8	58.7	1.23
Ba	16.4	8.70	9.31	10.1 <	1.66	< 0.0913
Be	9.17	19.8	19.1	33.1	0.455 <	< 0.00675
Са	565	378	373	530	447	3.95
Cd	18.8	24.2	35.8	63.5	36.9 <	< 0.150
Co	113	257	284	453 <	3.98	< 0.219
Cr	10.1	9.67	6.86	77.4	93.4 <	< 0.141
Cu	18.3	22.2	21.1	30.3	11.4	0.0750
Fe	516	368	391	572	53.7	1.08
X	3890	9140	10200	15500	10600	2.43
Li	13.0	12.1	10.8	13.2	2.28 <	< 0.0550
Mg	71.9	< 14.8	< 15.0 <	10.7 <	14.0	< 0.767
Mn	213	215	144	131	429000 <	< 0.0145
Mo	< 10.2 <	< 10.2	12.7 <	7.34 <	9.59	< 0.526
Na	96000	203000	193000	266000	131000 <	< 0.657
Ni	15.4	19.3	26.0	17.8	70.6	1.18
S	< 241	32300	27100	23200	30200 <	< 12.5
Sb	91.2	211	< 32.9	213 <		1.98
Si	1640	982	985	1210	537	2.78
Sn	173 <	< 27.8	< 28.2 <	20.0	26.2	1.55
Sr	3.86	2.42	2.45	3.14	2.28 <	< 0.00825
Ti	454000	313000	347000	282000	23.7	0.0250
<	47.3	124	121	203 <	1.07	< 0.0585
Zn	15.9	< 1.41	< 1.43 <	1.02	16.8	0.375

Project:	T4503K		CAG-05-077-1	CAG-05-077-2	CAG-05-077-3	CAG-05-077-4	CAG-05-077-5	CAG-05-077-6
Receipt Date:	5/5/2005		D 03/01/04	P 0/61/20 D	D 03/28/05	D 03/30/05	D 04/02/05	P 040224A
Client:	IPST		Reported	Reported	Reported	Reported	Reported	Reported
IPST Contact:	Xiaoyan Zeng	icp	Conc.	Conc.	Conc.	Conc.	Conc.	Conc.
Matrix:	Solids	element	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
		AI	183	440	345	3300	620	297
		As	< 53.0	< 54.8	< 51.8	125 <	< 53.5 <	< 52.3
		В	20.2	24.3	74.2	8320	10400	263
		Ba	530	< 1.77	12.4	12.5	12.3	9.26
		Be	0.469	0.484	< 0.124 <	< 0.125 <	< 0.128	19.0
		Са	1030		1090	939	1010	420
		Cd	< 2.81	> 2.9.2	< 2.75	3.25	6.63	25.9
		Co	5.63	< 4.23	< 4.00 <	< 4.06 <	< 4.14	269
		Cr	10.3	106	7.33	325	6.16	10.2
		Cu	34.7	21.8	21.5	25.6	40.7	20.4
		Fe	924	127	291	1290	1970	354
		¥	3550	13900	29600	32900	32300	8190
		Li	16.4	< 1.07	2.29	2.79	2.84	12.0
		Mg	213	< 14.9	227	102	135 <	< 14.2
		Mn	227	523000	293	202	300	125
		Mo	< 9.87	34.9	< 9.64	31.6	43.1	10.2
		Na	92900	61500	368000	361000	365000	181000
		Ni	31.4	82.4	12.4	48.3	35.5 <	< 4.84
		S	< 235	751	24700	14400	8810	30600
		Sb •	< 31.5	< 32.5	40.3	104 <	< 31.8	240
		Si	372	853	618	3300	1070	4530
		Sn	< 27.0	< 27.8	42.1	76.7 <	< 27.2 <	< 26.6
		Sr	8.44	3.39	5.49	4.65	5.21	2.31
		Ti	440000	53.3	52.2	35.8	62.5	277000
		>	4.69	< 1.13	40.3	37.2	28.9	118
		Zn	33.3	33.4	31.1	30.2	38.4 <	< 1.35
	Note:	1. Samples	were digested and r	. Samples were digested and reported on an as received basis	ceived basis.			
		2. Samples	(CAG-05-077-6,7,8,	<ol><li>Samples(CAG-05-077-6,7,8,9,10) were digested for I otal 1 itanium using</li></ol>	tor lotal litanium (	nsing		

	2. Samples(CAG-05-077-6,7,8,9,10) were digested for Total Titanium	H <sub>2</sub> SO <sub>4</sub> and (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (per Xiaoyan's approval).
	samples(C	SO4 and (
:	di N	Ť

3. Samples were analyzed by Inductively Coupled Plasma Emission Spectroscopy.

#### APPENDIX A EXPERIMENTAL DATA

	CAG-05-077-7	CAG-05-077-8	CAG-05-077-9	CAG-05-077-10	CAG-05-077-11	P.Blank
	P 040924A	CP 040224A	CP 040924A	CD 03/01/04	CD 07/19/04	
	Reported	Reported	Reported	Reported	Reported	Reported
icp	Conc.	Conc.	Conc.	Conc.	Conc.	Conc.
element	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
AI	95.6	223	232	397	268 <	< 0.597
As	97.0 <	54.7	< 55.4 <	39.4	< 51.5	4.78
В	58.9	130	71.6	47.8	58.7	1.23
Ba	16.4	8.70	9.31	10.1	< 1.66 <	< 0.0913
Be	9.17	19.8	19.1	33.1	0.455 <	< 0.00675
Са	565	378	373	530	447	3.95
Cd	18.8	24.2	35.8	63.5	36.9 <	< 0.150
Co	113	257	284	453 -	< 3.98 <	< 0.219
Cr	10.1	9.67	6.86	77.4	93.4 <	< 0.141
Cu	18.3	22.2	21.1	30.3	11.4	0.0750
Fe	516	368	391	572	53.7	1.08
X	3890	9140	10200	15500	10600	2.43
Li	13.0	12.1	10.8	13.2	2.28 <	< 0.0550
Mg	71.9 <	14.8	< 15.0 <	10.7		< 0.767
Mn	213	215	144	131	429000 <	< 0.0145
Mo	< 10.2 <	10.2	12.7 <	7.34	< 9.59 <	< 0.526
Na	96000	203000	193000	266000	131000 <	< 0.657
Ni	15.4	19.3	26.0	17.8	70.6	1.18
S	< 241	32300	27100	23200	30200 <	< 12.5
Sb	91.2	211	< 32.9	213	< 30.5	1.98
Si	1640	982	985	1210	537	2.78
Sn	173 <	27.8	< 28.2 <	20.0	< 26.2	1.55
Sr	3.86	2.42	2.45	3.14	8	< 0.00825
Ti	454000	313000	347000	282000	23.7	0.0250
٧	47.3	124	121	203 -	< 1.07 <	< 0.0585
Zn	15.9 <	1.41	< 1.43 <	1.02	16.8	0.375

Project:			CAG-04-152-1	CAG-04-152-2	CAG-04-152-3	CAG-04-152-4	CAG-04-152-5
Receipt Date:	11/30/2004		P041025A	P041026A	P041103A	P041104A	P041122A
Client:	IPST		Reported	Reported	Reported	Reported	Reported
IPST Contact:	Xiaoyan Zeng	icp	Conc.	Conc.	Conc.	Conc.	Conc.
Matrix:	Solids	element	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
		AI IA	< 55.1	< 57.2 <	57.2 <	: 57.7 <	57.0
		В	0866	10400	10300	11700	10300
		Ba	16.5	13.8	10.3	11.3 <	8.71
		Be	1.25	1.20	0.759	1.03	1.14
		Ca	673	986	286	2010	1200
		Cd	< 13.8	< 14.4 <	14.4	14.5 <	14.3
		Co	< 20.2	< 20.9	31.5 <	21.1 <	20.8
		ں ت	< 13.0	< 13.5 <	13.5 <	13.6 <	13.4
		Cu	23.8	28.7	28.0	28.9	32.4
		Fe	1340	1400	1380	1560	1440
		Ч	29600	30100	22600	28200	34600
		Mg	120	117	100	197	149
		Mn	234	250	251	272	245
		Na	347000	362000	299000	339000	346000
		Ni	32.5	< 25.0	28.2	25.3 <	25.0
		- PD	< 165	< 171 <	171	198 <	171
		S	80900	84900	77600	88600	65800
		Si	953	1050	066	1130	1020
		Sn	150	< 138 <	138 <	139 <	137
		Ti	1880	1100	220	108	109
		۲ ا	59.7	61.8	55.5	70.5	57.5
		Zn	43.5	82.8	23.4	43.0	38.9
	Note:	<ol> <li>Samples w</li> <li>Samples w</li> </ol>	ere digested and rep ere analvzed bv Indi	<ol> <li>Samples were digested and reported on an as received basis.</li> <li>Samples were analyzed by Inductively Council Plasma Emission Spectroscopy.</li> </ol>	ed basis. na Emission Spectro	SCODV	
						coopj.	

	⊢	CAG-04-152-6	CAG-04-152-7	CAG-04-152-8	CAG-04-152-9	CAG-04-152-10	CAG-04-152-11
		P041025B	P041026B	P041103B	P041104B	P041122B	P041202A
		Reported	Reported	Reported	Reported	Reported	Reported
icp		Conc.	Conc.	Conc.	Conc.	Conc.	Conc.
element		(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
AI	V	56.6	< 49.8	< 56.1 <	< 58.2 <	57.4	137
В	-	10100	10200	9360	11400	8600	67.0
Ba	V	< 8.66	18.8	15.0 <	< 8.89 <	8.77	6.81
Be	-	6.08	1.76	0.789	1.02	0.725	23.3
Са	-	1070	1090	934	1080	861	502
Cd	V	14.2	< 12.5	< 14.1 <	< 14.6 <	14.4 <	10.8
Co	-		< 18.2	< 20.5 <	< 21.3 <	21.0	186
Cr	V	13.3	< 11.7	< 13.2 <	< 13.7 <	13.5	10.7
Cu	-	27.9	26.6	33.1	29.7	23.6	13.2
Fe	-	1320	1360	1270	1470	1150	422
X		30000	29800	27900	32900	29000	10300
Mg		113	139	146	139	166 <	55.3
Mn	-	240	240	234	259	203	6.66
Na		358000	344000	321000	372000	300000	211000
Ni	V	24.8	< 21.8	42.7 <	< 25.5	53.8 <	18.8
Pb	V	170	< 149	< 168 <	< 174 <	172 <	129
S		64500	66600	51200	84100	48100	26900
Si		1030	1040	843	1090	753	563
Sn		197	< 120	< 135 <	< 140 <	138 <	104
Ti		22000	2740	193	115	89.3	91100
V		74.5	57.5	54.7	68.8	53.2	88.1
Zn		32.9	33.8	25.1	42.3	40.8 <	5.26

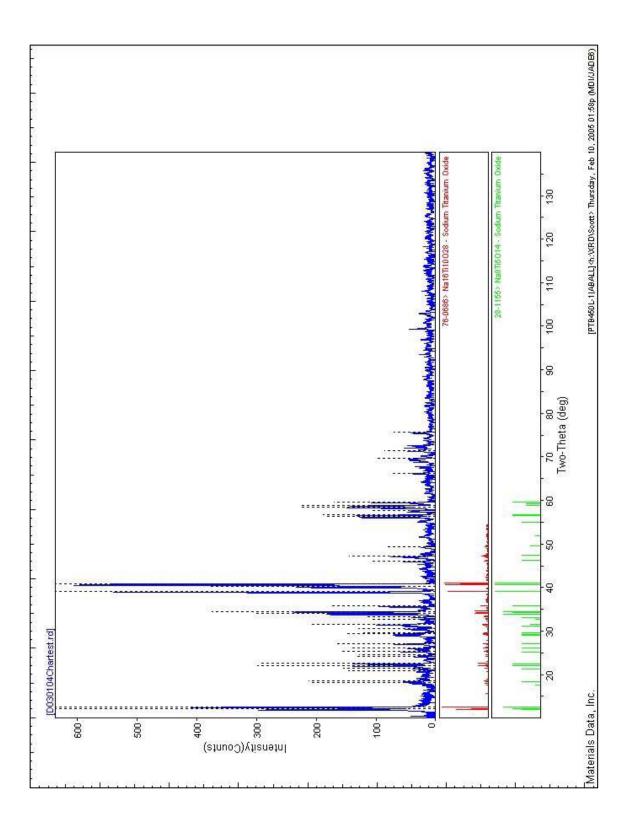
	CAG-04-152-12	CAC	CAG-04-152-13		CAG-04-152-14	S C	CAG-04-152-15	_	P.Blank
	P041202B	₽.	P041202C		P041021A		P041021B		
R	Reported	Rep	Reported	—	Reported	Rep	Reported	Ŗ	Reported
0	Conc.	Conc.	J.	-	Conc.	Conc.	nc.	Ŭ	Conc.
	(mg/kg)		(mg/kg)		(mg/kg)		(mg/kg)		(mg/kg)
	57.7		67.5		296		197	v	0.597
_	30.9		94.0	v	10.2	v	10.7	v	0.109
_	8.82 <	v	8.88	v	8.54 <	v	8.95	v	0.0913
	35.9		36.8		19.5		19.4	v	0.00675
	588		564		631		618		2.02
	14.5	v	14.6	v	14.0	v	14.7	v	0.150
	245		276		160		139	v	0.219
	18.3		24.2		20.3		19.6	v	0.141
_	13.7		15.6		17.3		19.2	v	0.0578
_	392		458		250		262		0.509
_	10400		10700		11500		11500		3.71
_	74.2 <	v	74.6	v	71.8 <	v	75.2	v	0.767
_	95.5		111		169		122	v	0.0145
_	201000		215000		216000		203000		0.712
	25.3 <	v	25.4	v	24.5	v	25.6	v	0.262
_	173 <	v	174	v	167 <	v	175	v	1.79
_	25700		38400		21000		22500	v	12.5
_	718		1010	_	500		946		2.22
_	236		190	v	135 <	v	141		1.86
	136000		145000		73300		73600	v	0.0218
	137		145		62.9		87.7	v	0.0585
	> 90'.2	v	7.10	v	6.84	v	7.16		0.126

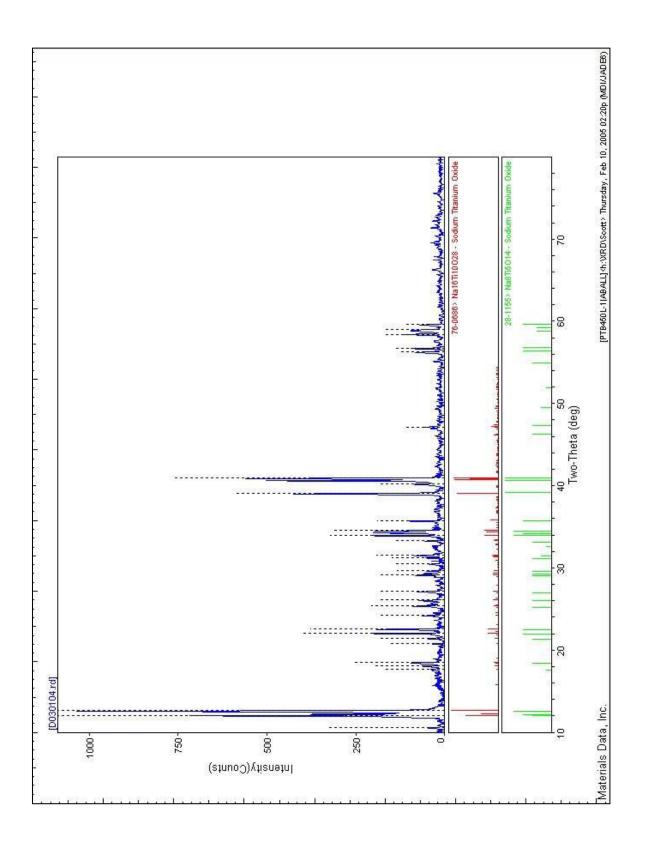
Project:		_	CAG-04-152-1	2-1	CAG-04-152-2	CAG-04-152-3	CAG-04-152-4	CAG-04-152-5
Receipt Date:	11/30/2004		P041025A	4	P041026A	P041103A	P041104A	P041122A
Client:	ISG		Reported		Reported	Reported	Reported	Reported
IPST Contact:	Xiaoyan Zeng	icp	Conc.		Conc.	Conc.	Conc.	Conc.
Matrix:	Solids	element	(mg/kg)		(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
		AI	v	55.1 <	57.2	< 57.2	< 27.7	< 27.0
		В	5	9980	10400	10300	11700	10300
		Ba		16.5	13.8	10.3	11.3	< 8.71
		Be		1.25	1.20	0.759	1.03	1.14
		Са		973	986	987	2010	1200
		Cd	v	13.8 <	14.4	< 14.4	< 14.5	< 14.3
		Co	V	20.2 <	20.9	31.5	< 21.1	< 20.8
		Cr	v	13.0 <	13.5	< 13.5	< 13.6	< 13.4
		Cu		23.8	28.7	28.0	28.9	32.4
		Fe		1340	1400	1380	1560	1440
		Y	26	29600	30100	22600	28200	34600
		Mg		120	117	100	197	149
		Mn		234	250	251	272	245
		Na	347	347000	362000	299000	339000	346000
		Ni		32.5 <	25.0	28.2	< 25.3	< 25.0
		Pb	v	165 <	171	< 171	198	< 171
		S	8(	80900	84900	77600	88600	65800
		Si		953	1050	066	1130	1020
		Sn		150 <	138	< 138	< 139	< 137
		Ti		1880	1100	220	108	109
		N		59.7	61.8	55.5	70.5	57.5
		Zn		43.5	82.8	23.4	43.0	38.9
	Note:	1. Samples w 2. Samples w	ere digested al ere analyzed b	y Indu	<ul> <li>Samples were digested and reported on an as received basis</li> <li>Samples were analyzed by Inductively Coupled Plasma Emiss</li> </ul>	<ol> <li>Samples were digested and reported on an as received basis.</li> <li>Samples were analyzed by Inductively Coupled Plasma Emission Spectroscopy.</li> </ol>	scopy.	

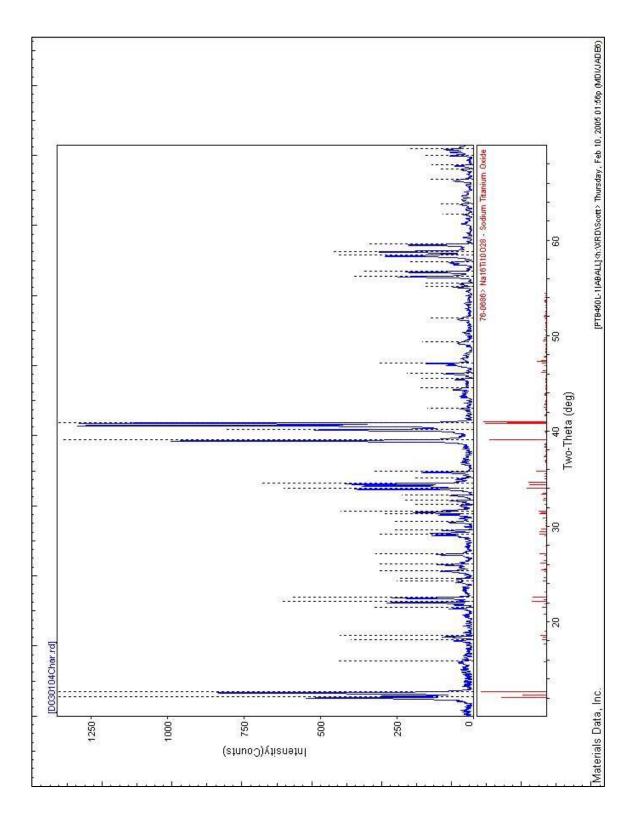
DE-FC26-02NT41492

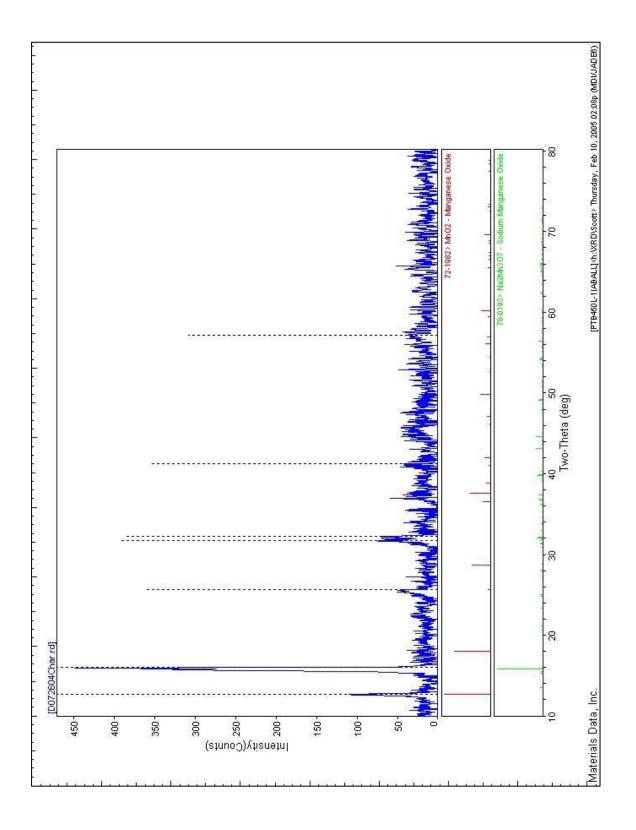
		CAG-04-152-6	CAG-04-152-7	:2-7	CAG-04-152-8	CAG-04-152-9	CAG-04-152-10	CAG-04-152-11
		P041025B	P041026B	В	P041103B	P041104B	P041122B	P041202A
		Reported	Reported		Reported	Reported	Reported	Reported
icp		Conc.	Conc.		Conc.	Conc.	Conc.	Conc.
element		(mg/kg)	(mg/kg)	_	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
AI	۷	56.6 <	v	49.8 <	< 56.1	< 58.2	< 57.4	137
В		10100	-	10200	9360	11400	8600	67.0
Ba	۷	8.66		18.8	15.0 <	< 8.89	< 8.77	6.81
Be		6.08		1.76	0.789	1.02	0.725	23.3
Са		1070		1090	934	1080	861	502
Cd	۷	14.2 <	v	12.5 <	< 14.1	< 14.6	< 14.4 <	10.8
Co		> 1.74	v	18.2 <	20.5	< 21.3	< 21.0	186
Cr	۷	13.3 <	v	11.7 <	13.2	< 13.7	< 13.5	10.7
Cu		27.9		26.6	33.1	29.7	23.6	13.2
Fe		1320		1360	1270	1470	1150	422
X		30000	S	29800	27900	32900	29000	10300
Mg		113		139	146	139	166 <	55.3
Mn		240		240	234	259	203	6.66
Na		358000	34	344000	321000	372000	300000	211000
Ni	۷	24.8 <	v	21.8	42.7	< 25.5	53.8 <	18.8
Pb	۷	170 <	v	149 <	168	< 174	< 172 <	129
S		64500	9	66600	51200	84100	48100	26900
Si		1030		1040	843	1090	753	563
Sn		> 161	v	120 <	< 135	< 140	< 138 <	104
Ti		22000		2740	193	115	89.3	91100
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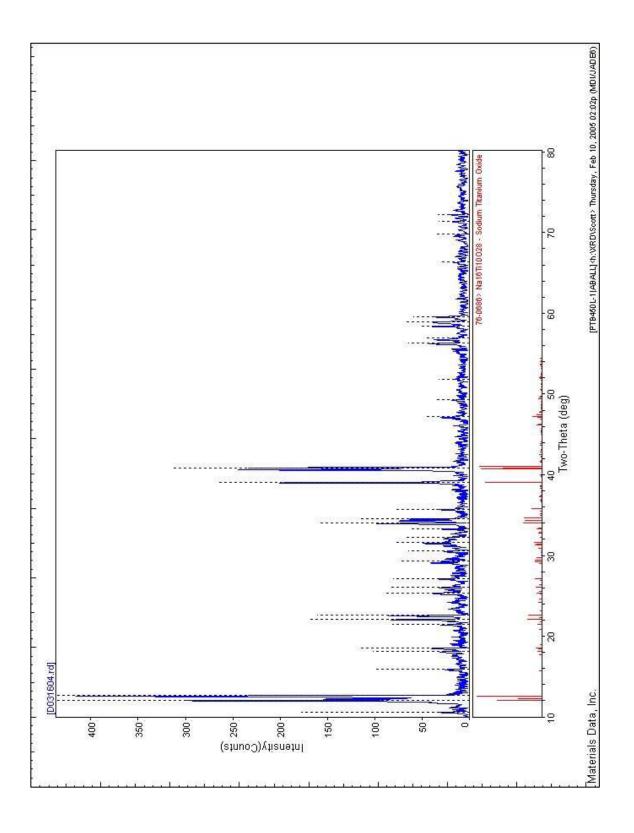
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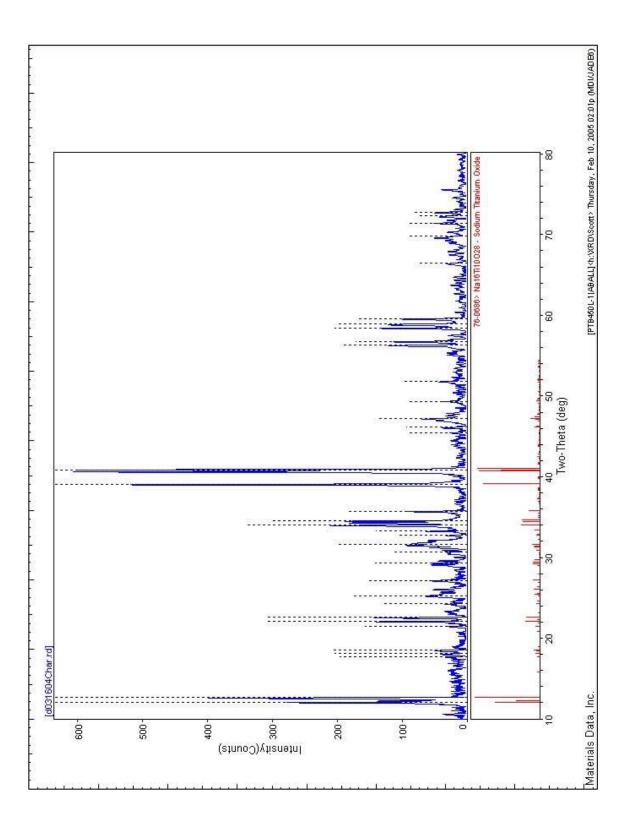


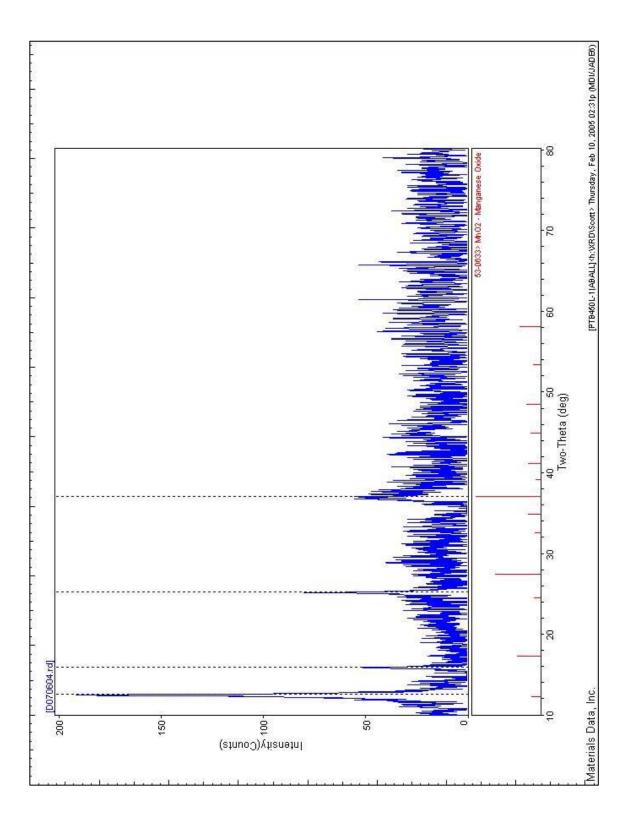


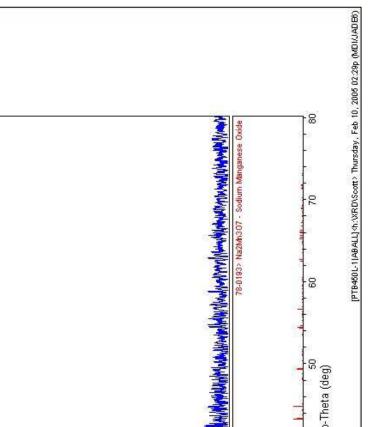


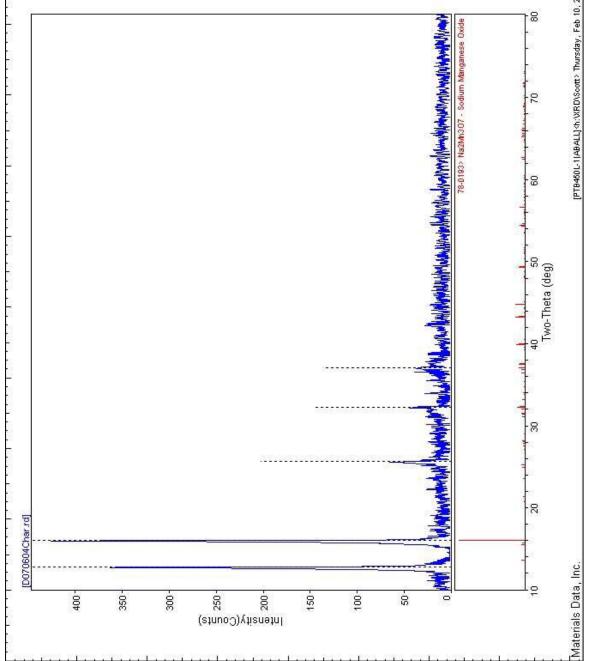


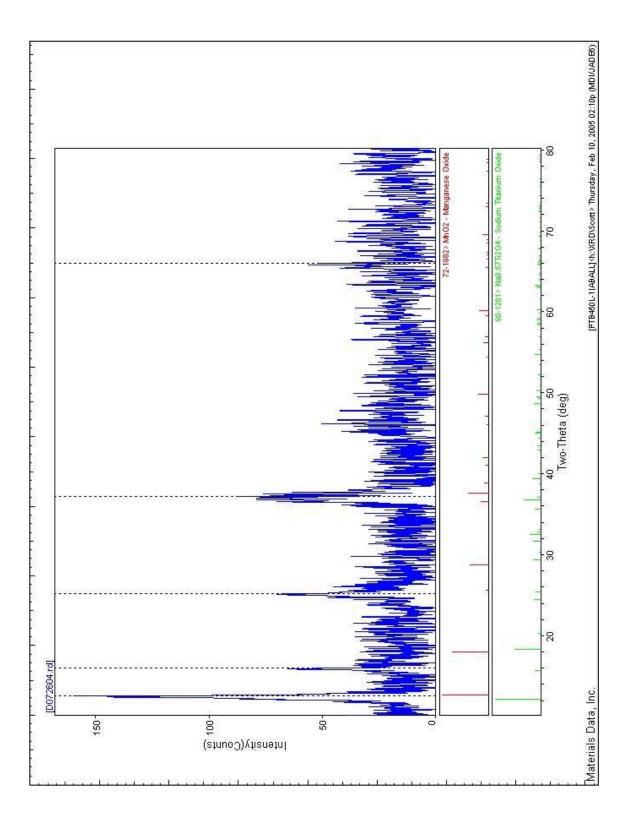


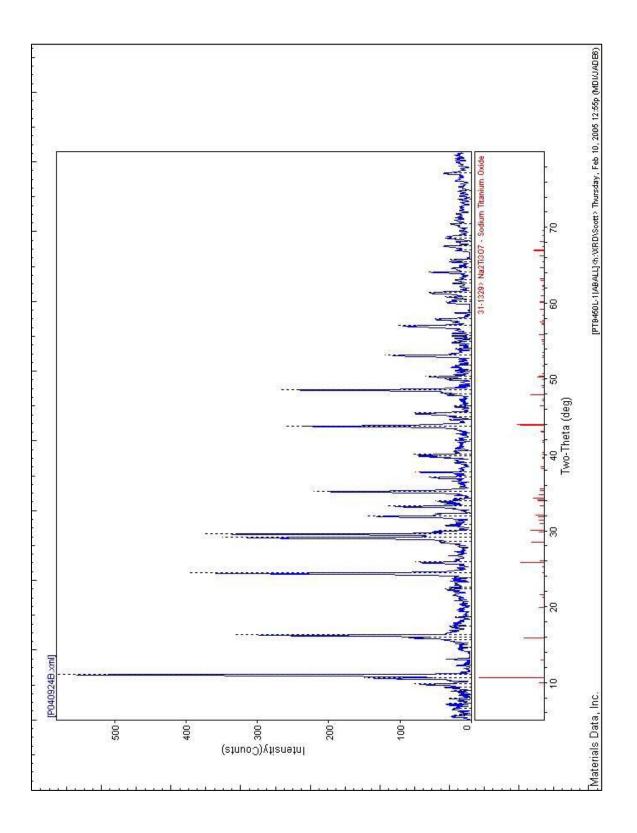


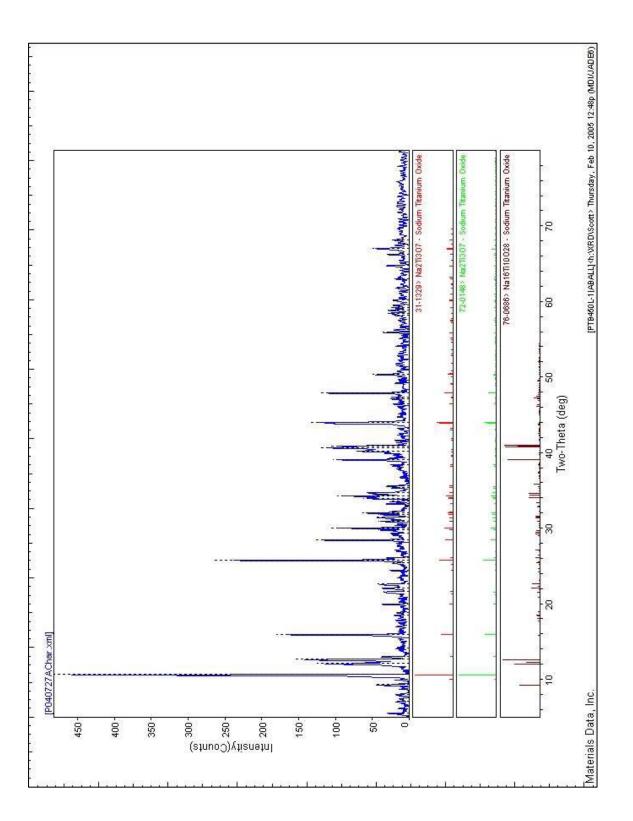


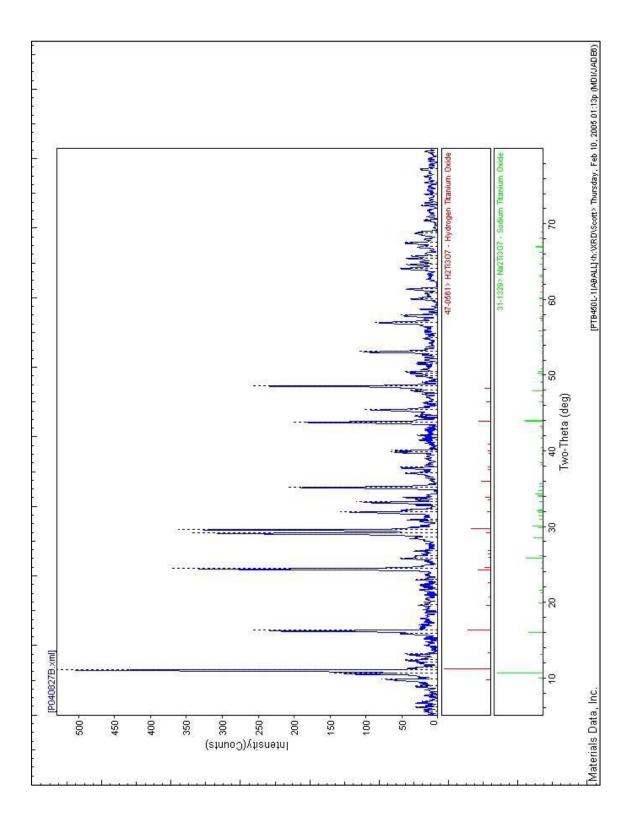


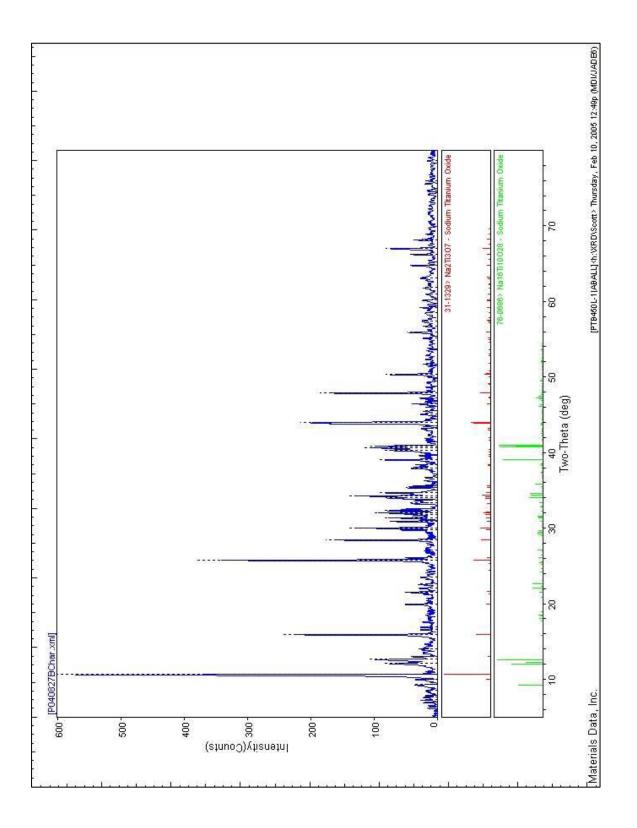


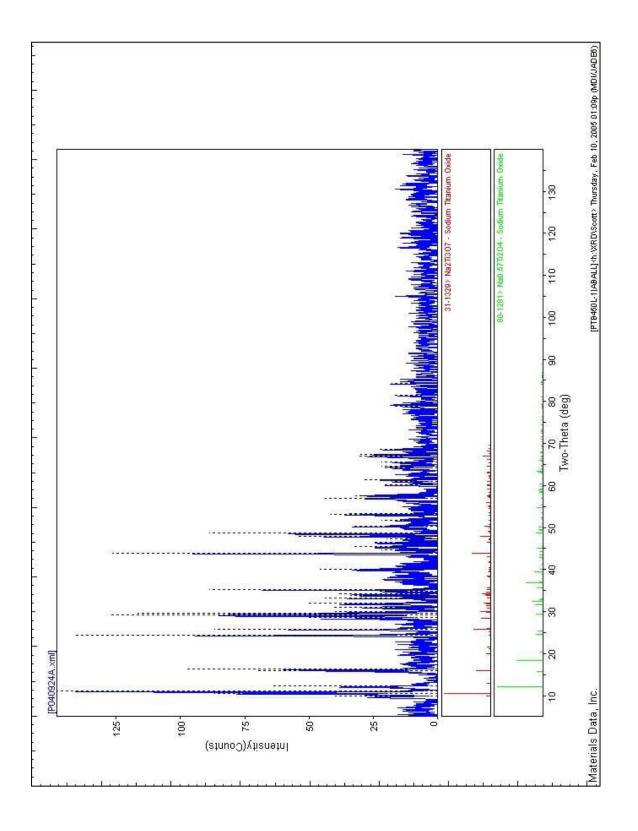




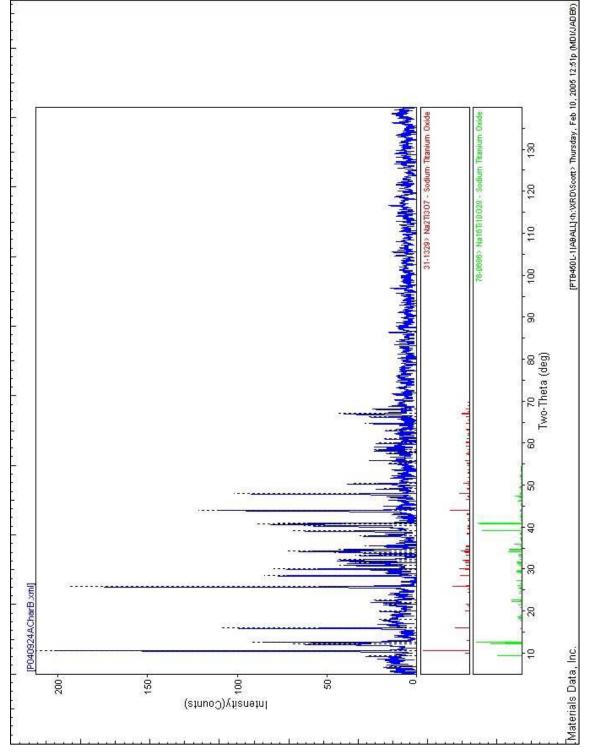


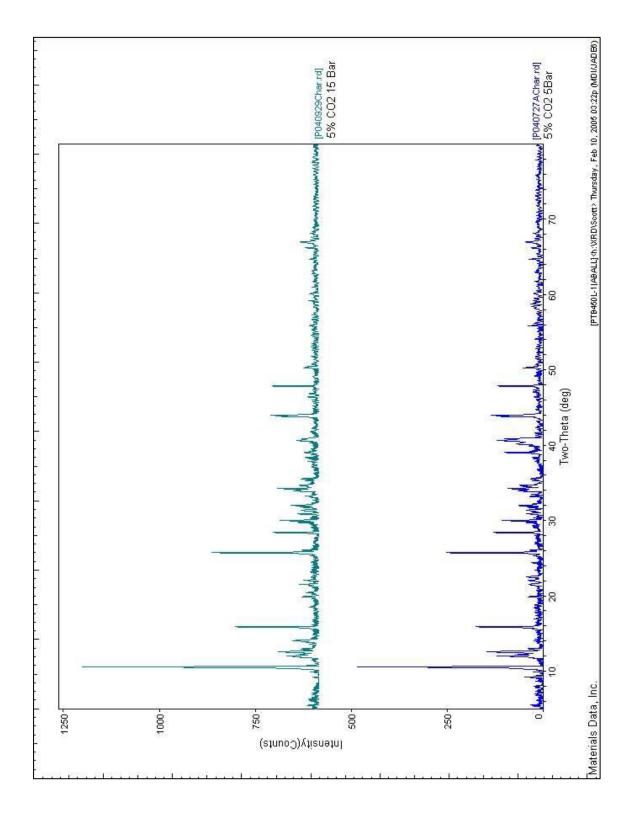


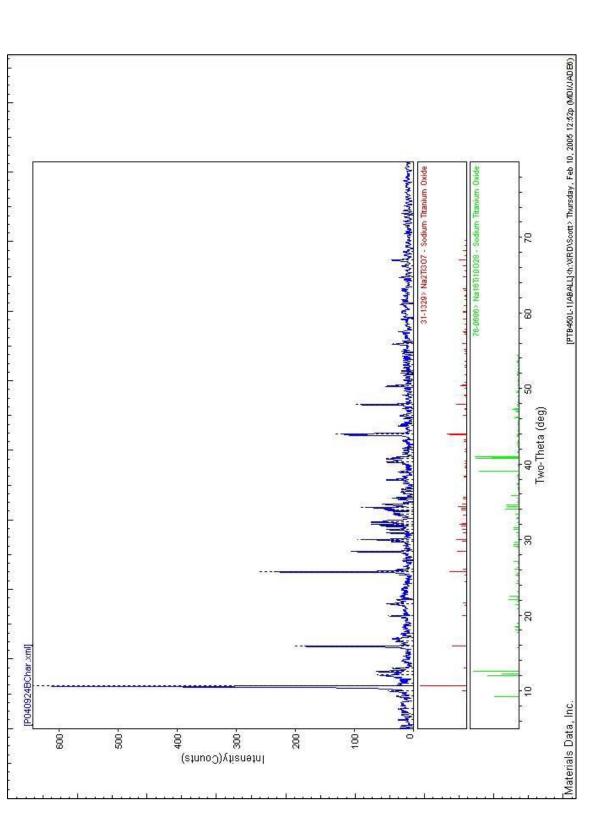


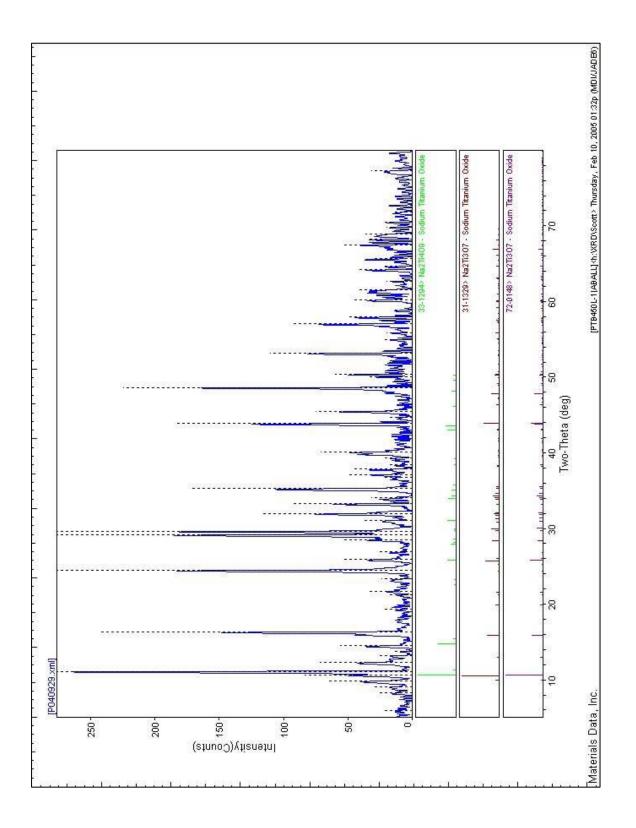


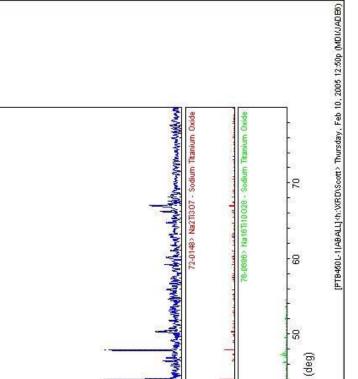


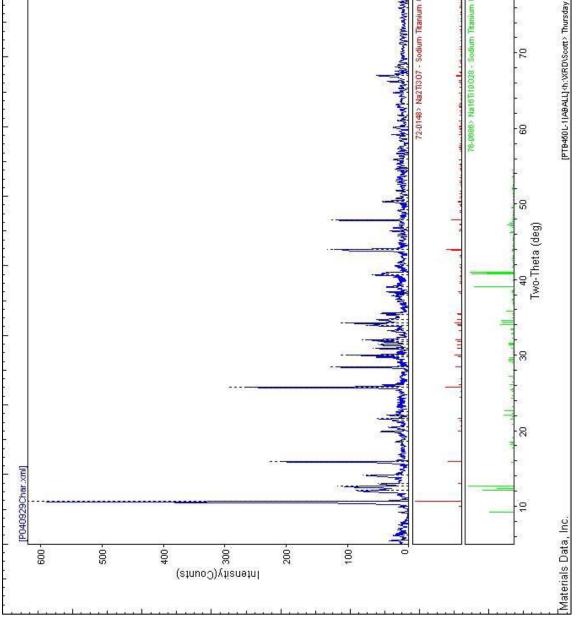




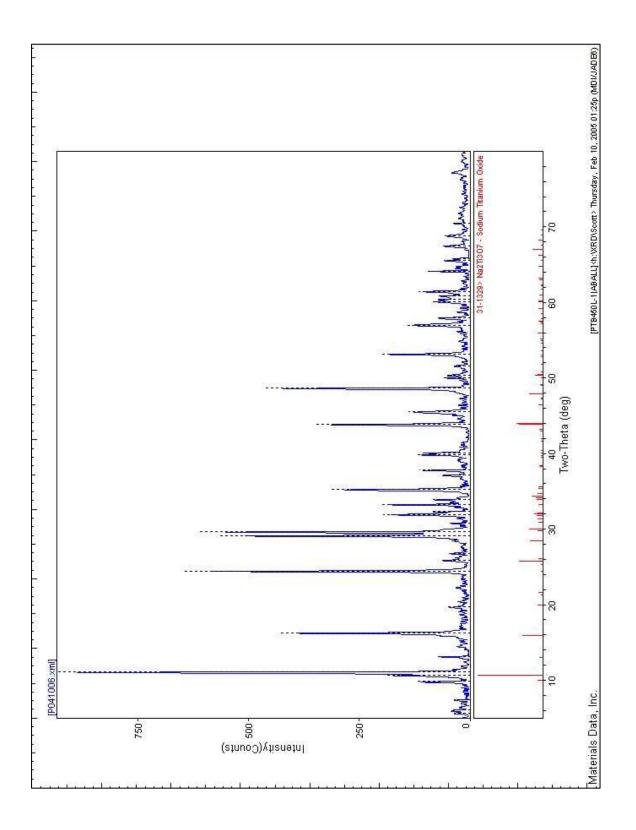




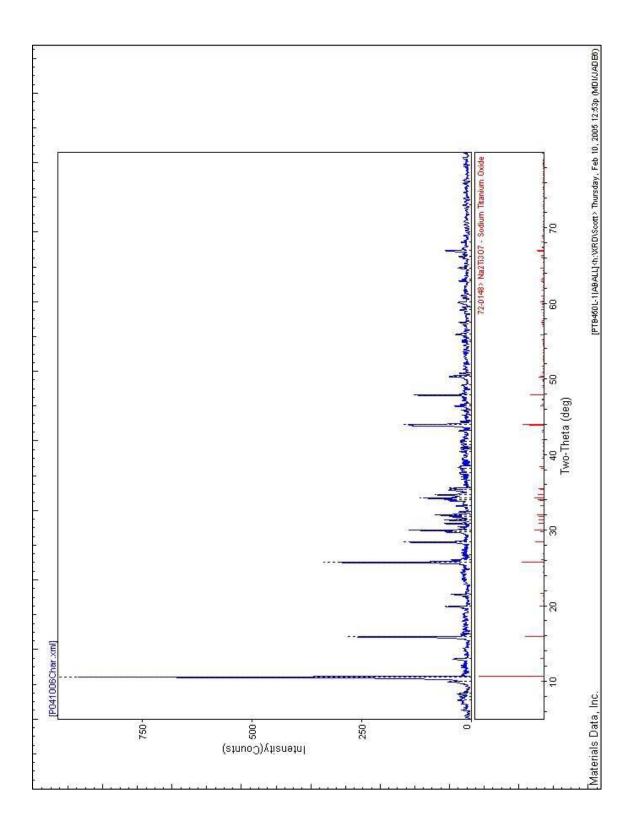




#### APPENDIX A EXPERIMENTAL DATA



#### APPENDIX A EXPERIMENTAL DATA



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## Project DE-FC26-02NT41492

## **APPENDIX B**

## **Jacobs Engineering Report**



# Institute of Paper Science & Technology at the Georgia Institute of Technology

# Atlanta, Georgia

# Causticizing for Black Liquor Gasification – Mill Integration Study

# **Final Report**

# Jacobs Job No. 16BD7500

# February 26, 2007

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#### 1.0 EXECUTIVE SUMMARY

Jacobs has prepared a mill integration study for the Institute of Paper Science & Technology (IPST) at Georgia Tech for in situ causticizing during black liquor gasification. Two in situ causticizing options are compared to the base case of high temperature black liquor gasification (HTBLG) with conventional causticizing. Borate is an auto-causticizing agent that can replace up to 20% of the conventional lime cycle. Titanate remains as a suspended solid throughout the process and can replace 100% of the conventional lime cycle.

The reference mill basis is identical to that used in the Larson Study from October, 2003 entitled "A Cost-Benefit Assessment of Biomass Gasification Power Generation in the Pulp and Paper Industry"<sup>1</sup>. The base case for this mill integration study is HTBLG with conventional causticizing since the borate and titanate only perform successfully under the high temperature gasification conditions.

The base case +/- 30% total installed cost estimate is \$1.2MM and includes oxygen enrichment, a new kiln burner system, and new refractory brick to increase the kiln capacity.

The borate option +/- 30% total installed cost estimate is \$170,000 and includes a borate mix down system for adding borate to the green liquor prior to slaking.

The titanate option +/-30% total installed cost estimate is \$31.6MM and includes a full 3-stage leaching system and non-process elements (NPE) acid leaching purge system to replace the conventional lime cycle process. Concentrator upgrades are also required to handle the additional liquor throughput brought on from titanate recycle to the heavy black liquor.

Titanate bears no advantage to the mill water balance except when compared to a conventional lime kiln wet scrubber system. In this case there is a 40 to 50% reduction in water lost to the sewer or atmosphere with the titanate option.

The primary drivers for the economic analyses are the avoided kiln fuel oil cost and the chemical costs for the borate and titanate options. Both the internal rate of return (IRR) and net present value (NPV) analyses were performed on each case and also performed relative to the HTBLG base case. Considering the stand-alone NPVs over the total project life of 25 years, the titanate option clearly has the best NPV of \$10.6MM primarily from the substantial fuel savings over the base case. The borate option has a high stand-alone IRR of 135% due to the minimal capital investment required. The borate option still achieves 20% of the fuel savings of the titanate option. Relative to the base case the titanate option is more economically attractive with an NPV of \$25.2MM and an IRR of 23.9%.



<sup>&</sup>lt;sup>1</sup> Larson, Eric D.; Consonni, Stefano; and Katofsky, Ryan E.; *A Cost-Benefit Assessment of Biomass Gasification Power Generation in the Pulp and Paper Industry – Final Report*, Princeton University, Princeton, New Jersey, 8 October 2004.

#### Economic Analysis Results Summary

#### TOTAL NET CASH FLOW

	Stand-Alone		Relativ	e to Base	
	IRR (%)	NPV (\$ million)	IRR (%)	NPV (\$ million)	
Base - HTBLG	N/A	-14.6	N/A	0	
Borate	135%	1.4	N/A	16.1	
Titanate	15.9%	10.6	23.9%	25.2	

Borate is a proven partial auto-causticizing agent through various trials around the world. Titanate has been proven successful in the lab. Pilot plant trials are needed to refine the process scope of titanate recovery and confirm overall performance of the proposed system.

#### 2.0 INTRODUCTION

The Institute of Paper Science and Technology (IPST) at Georgia Tech has investigated the performance of several compounds that causticize sodium carbonate in situ during the gasification of black liquor. Two of these compounds have proven successful for high temperature black liquor gasification (HTBLG). These include sodium titanate and sodium borate.

Titanate is insoluble and remains in suspension when mixed into the black liquor. By adding sufficient amounts, titanate directly causticizes sodium carbonate during gasification at levels equal to conventional causticizing. The smelt must then be dissolved and the titanate suspended solids are separated and leached to produce white liquor and to recover titanate for recycle. Non-process elements (NPEs) must be acid leached and purged to prevent build-up in the system. The solids loading for titanate direct causticizing is significant being on the order of three times that of calcium oxide causticizing.

Borate has only been tested at the 20% causticizing level; hence, it is causticizing booster rather than a full replacement of the lime causticizing system. Borate remains soluble throughout the liquor system reacting with carbonate during gasification and then forming sodium hydroxide and converting back to its original form during smelt dissolving. Therefore it is considered an autocausticizing agent. Also, because borate is soluble and remains in the liquor cycle, only small amounts



of makeup are required to maintain adequate liquor concentration. The makeup system is a minor capital expense.

The purpose of this mill integration study is to develop the most likely process configuration for the borate and titanate options based on the reference mill design basis, perform capital cost estimates for the options, and then to perform economic evaluations for the options as compared to the base case. The base case is HTBLG with a conventional causticizing operation that has been upgraded with oxygen enriched fuel oil firing in the lime kiln.

The reference mill basis used for this study is the same as that used in the study entitled "A Cost-Benefit Assessment of Biomass Gasification Power Generation in the Pulp and Paper Industry – Final Report" by E. Larson, S. Consumi, and R. Katofsky, October 8, 2003 (from this point forward referred to as the Larson Study). This was done so that the economics of this study could be used to compare to the results of the Larson Study.

#### 3.0 DESIGN BASIS AND MILL CHARACTERIZATION

The reference mill used for this study is an integrated pulp and paper mill producing uncoated freesheet paper from a 65/35 mix of hardwood and softwood. The mill produces about 5.4 MM lbs/day of black liquor solids (BLS). The HTBLG case data from the Larson Study is used for the base case in this study. Table 1 shows the basic data used for the study.

#### Table 1

#### Reference Mill Basis Data (Larson Study)

Product Flow	md mtpd	1725
Unbleached Pulp Rate	bd stpd	1580
Mill Hardwood/Softwood Mix	% HW, % SW	65% HW, 35% SW
Digester Yield	% for softwood	48.75
	% for hardwood	49.75
Wood To Process (91% of total)	bd stpd	3,208
Hog Fuel (9% of total)	bd stpd	317
Total Wood Used	bd stpd	3,525
Black Liquor Solids Concentration	% solids	80
BL Solids Flow Rate	lb BLS per day	5,419,646
	kg BLS per day	2,458,311
	BLS mtpd	2,458
BL Specific Gravity		1.428
BL Flow	lpm	1,495
BL Energy Content	kJ per kg of BLS (HHV)	13,874
	Btu per lb of BLS (HHV)	5,966
	MW, HHV	394.7
BL Solids Composition, mass%	С	32.97
	н	3.70
	0	36.88
	S	4.27
	Na	20.03
	К	1.93
	Ash/Cl	0.22

Table 2 shows the reference mill HTBLG chemical recovery data.

#### Table 2

#### HTBLG Chemical Recovery Data (Larson Study)

Wood charge, mt/d	3,198
Causticization efficiency, %	81%
Active Alkali (as Na <sub>2</sub> O), mtpd	584
Active Alkali (as Na <sub>2</sub> O)/Wood	0.183
Lime availability, %	90%
White Liquor in lime mud, mtpd	749
Water for slaking, mtpd	137.5
Green Liquor TTA, g/l as Na <sub>2</sub> O	130
Water in White Liquor, mtpd	5,240
White Liquor TTA, g/l as $Na_2O$	133
TTA in Weak Wash, mtpd	87.9

Black Liquor	mtpd	mtph
BLS	2,458	102
S	105	4.38
Na	492.4	20.52
К	47.5	1.98
CI	2.7	0.11
Ash	2.7	0.11
*Smelt	mtpd	mtph
Na <sub>2</sub> S	120.0	5.0
NaOH	20.0	0.8
Na <sub>2</sub> CO <sub>3</sub>	1005.6	41.9
NaCl	4.5	0.2
Ash	2.7	0.1
TTA	1152.8	48.0

\* Note - the Larson Study assumes that potassium and sodium are equivalent and both elements are included in the smelt sodium compounds.

#### 4.0 PROCESS DESCRIPTION

#### 4.1 Base Case

The base case process is based on HTBLG followed by conventional calcium oxide causticizing. See Figure 2. Since HTBLG will increase smelt sodium carbonate by about 16%, the lime requirement for slaking increases by a like amount. This puts an increase load on the lime kiln. Considering that many mills are kiln limited and the hypothetical mill is at its kiln design limit, the Larson Study includes oxygen enrichment, a new kiln burner system, and new refractory brick to increase the kiln capacity.

The flow rates for smelt, green liquor, white liquor, and lime are taken directly from the Larson Study for the base case. Dregs flow rate is assumed to be 0.2 mtph based on literature factors and the pulp production.

#### 4.2 Borate Case (Auto Causticizing)

Borate autocausticizing is a partial causticization process (20% of lime is replaced with borate). This means that the conventional lime caustic plant continues to run but at a reduced rate. Borate in the form of sodium tetraborate pentahydrate (Na<sub>2</sub>B4O<sub>7</sub>-5H<sub>2</sub>O) is added to the liquor system to achieve the desired level of lime substitution. Once this level is achieved, borate can be made up to the liquor system in small amounts to account for natural system losses.

For the borate case, borate is fed to a small mix tank from a supersack/screw feeder. A side stream of clarified green liquor is sent to the mix tank to dissolve and absorb the borate. This green liquor/borate stream then flows to the slaker by gravity. See Figure 3.

A spreadsheet balance was used to develop the chemical flows and borate makeup. See Appendix C for details on borate chemistry. Borate makeup is based on lime substitution, lime availability, white liquor causticity, borate loss rate, and borate reaction efficiency.

#### 4.3 Titanate Case (Direct Causticizing)

Titanate direct causticizing is for full 100% substitution of lime, hence, the conventional caustic plant is shut down. For the economical use of titanate, it must be recovered and recycled back to the black liquor prior to gasification. Following smelt dissolving, titanate remains in the green liquor as a suspended solid. By assuming physical properties of the titanate being similar to lime mud, we can extrapolate to a mill-scale process utilizing three staged leaching tanks for reaction residence time with each stage followed by disc filtration.

The green liquor/titanate slurry goes to a first stage leaching tank. See Figure 4. The leaching tank is agitated to keep the solids in suspension. Each tank is sized for

60 minutes of residence time to allow adequate mass transfer and leaching of the sodium hydroxide. From the first stage leaching tank, the slurry is pumped to a disc filter. Solids discharge from the filter at 85% solids. The filtrate from the first stage filtrate tank is essentially white liquor that is transferred to the digester area. The first stage filter discharge solids are diluted and gravity fed to the second stage leaching tank. The second and third leaching stages are configured the same as the first stage. Filtrate moves countercurrent to the solids flow through the system. Hot water or evaporator condensate is added to the third stage filter showers. Titanate solids off the third stage filter are conveyed to a black liquor mix tank prior to the gasifier. A portion of the titanate solids stream (10%) is transferred to an acid slurry mix tank.

The purpose of the acid slurry tank is to mix hydrochloric acid with the titanate solids. The acid leaches out the NPEs from the titanate. The acid slurry is transferred to a disc filter. Filtrate from the NPE purge filter flows by gravity to the NPE purge filtrate tank. Caustic is added to neutralize the acid. The neutralized filtrate then flows to the sewer. Solids from the NPE purge filter are conveyed to a new black liquor mix tank. Titanium dioxide makeup is added to the black liquor mix tank as well via the screw conveyor. It is assumed that the mill already has available hydrochloric acid and caustic make-down and delivery systems.

Potassium remains in the system either as potassium titanate or potassium hydroxide and carbonate. Potassium lowers the melting point of recovery boiler ash and is a primary cause of boiler tube pluggage in Tomlison recovery boilers. In a HTBLG system, the potassium poses no problem.

A new agitated heavy (50%) black liquor mix tank is required to recycle the titanate prior to the black liquor concentrator. This allows the 85% solids titanate recycle stream to be uniformly mixed prior to concentrating the black liquor to 80% solids for gasification. The titanate suspended solids flow is substantial, adding about 40% to the overall mass flow of the black liquor. The black liquor volume flow increases about 20%. Although no increase to the evaporation capacity of the black liquor concentrator is required, modifications are required to increase the hydraulic capacity. Primarily pump and motor upgrades are required. An allowance is included in the capital estimate to cover concentrator upgrades for the increased liquor flow. The additional suspended solids should enhance the crystallization process and reduce fouling for 80% solids liquor production by providing sites for crystallization to take place rather than on heat transfer surface areas.

A WinGEMS<sup>®2</sup> balance was used to calculate material flows and temperatures for the titanate recovery and NPE purge process. See Appendix D for titanate chemistry details and Appendix E for the WinGEMS flowsheet. Detailed chemical flows are shown in Figure 4 below. The WinGEMS balance is based on HTBLG smelt chemical flow data from the Larson Study and stoichiometric titanate requirements for causticization. In addition, results from IPST experimental data were also used

<sup>&</sup>lt;sup>2</sup> WinGEMS<sup>®</sup> is a heat and material balance simulation product from Pacific Simulation, 121 W Sweet Ave, Moscow, ID 83843, www.pacsim.com

for the balance around the caustic leaching stages and the NPE acid leaching stage. Table 3 shows the basis and assumptions for executing the WinGEMS material balance.

#### Table 3

#### Titanate WinGEMS Balance Basis and Assumptions

Smelt	(w/o potassium)
Na <sub>2</sub> CO <sub>3</sub> , mt/hr	4.76
NaOH, mt/hr	0.79
Na <sub>2</sub> S, mt/hr	4.73
HCl, mt/hr	0
NPEs (Dissolved), mt/hr	3.15
Inerts (Suspended), mt/hr	1.46
Black Liquor Sodium Carbonate Converted, %	88.0
1st Leaching Stage Caustic Recovery, %	86.1
2nd Leaching Stage Caustic Recovery, %	8.9

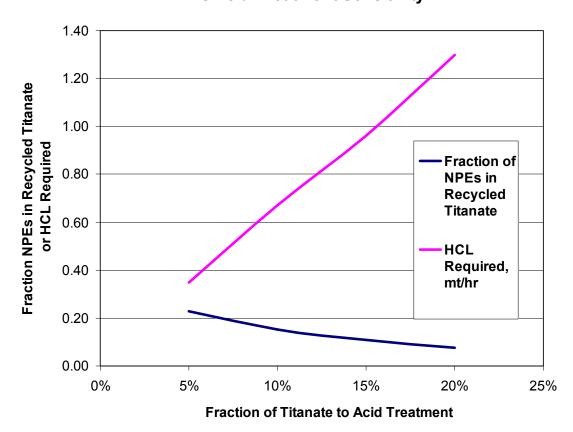
3rd Leaching Stage Caustic Recovery, %	3.6
Titanate Split to NPE Purge, %	10
HCI ratio to Treated Solids, kg/kg	0.1

The Titanate split to acid treatment for NPE purge was varied to observe the effect on the steady-state level of NPEs in the recycled titanate. Table 4 and Figure 1 below show the effect on NPE levels at different purge fractions.

#### Table 4

Fraction to Acid Treatment	Fraction of NPEs in Recycled Titanate	HCL Required, mt/hr	NaOH Required, mt/hr
5%	0.23	0.35	0.25
10%	0.15	0.67	0.47
15%	0.11	0.96	0.67
20%	0.08	1.30	0.91

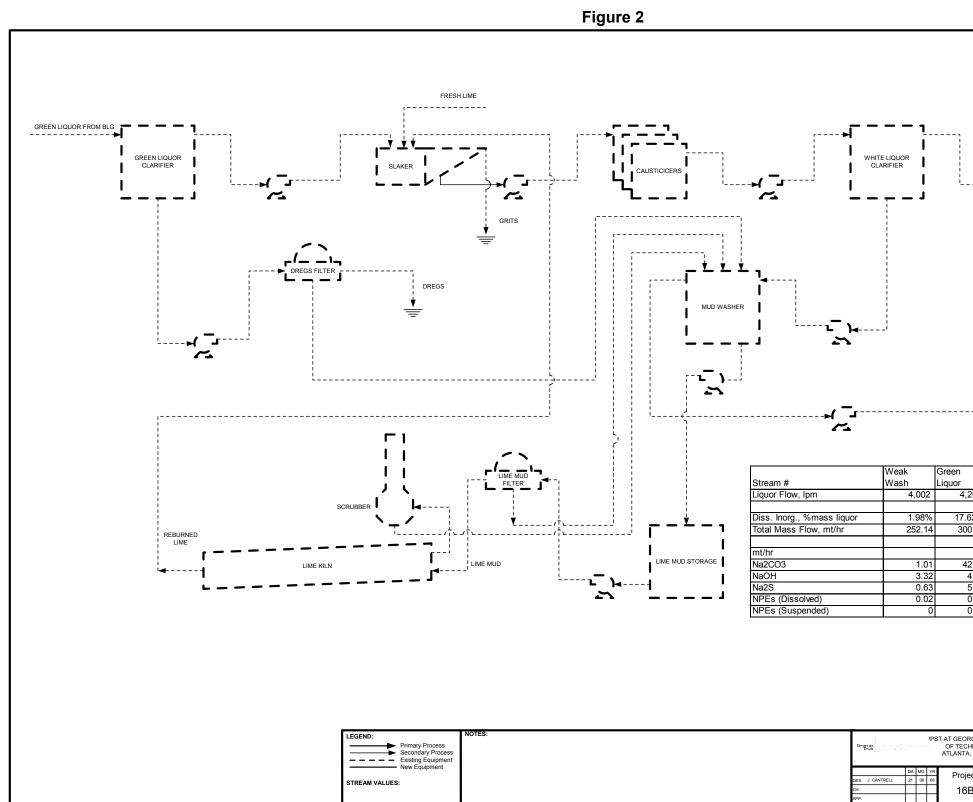
#### Figure 1





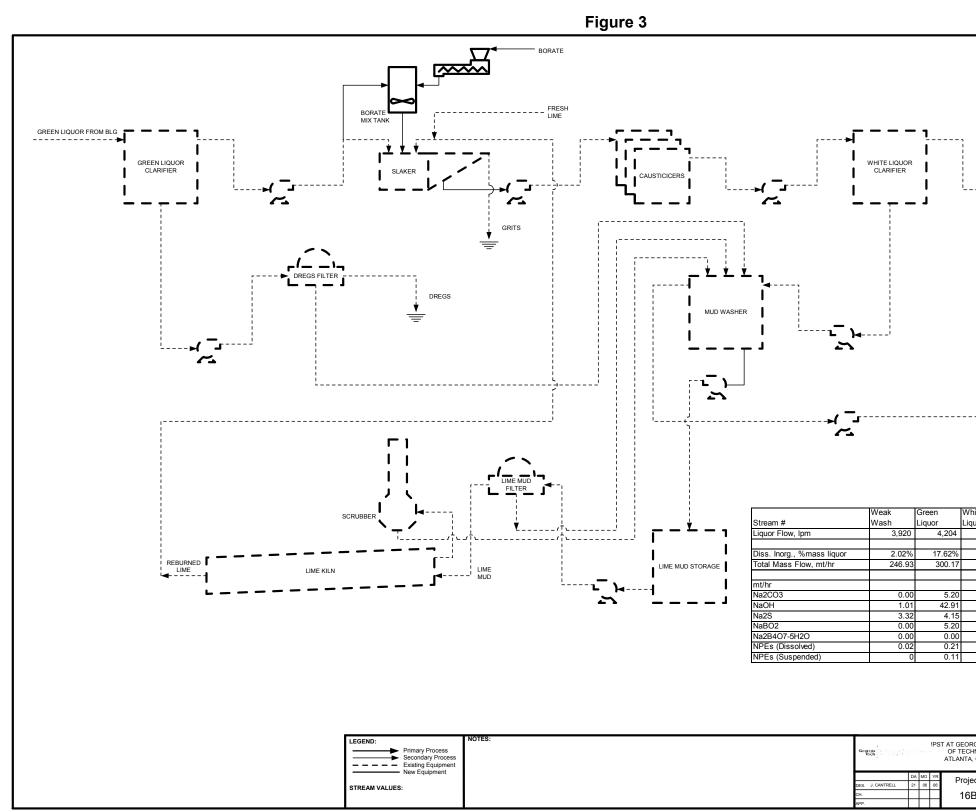
At 5% fraction to acid treatment, the NPEs level in the recycled titanate is 23%. A higher level of NPEs in the system means a higher dead-load through the process. This causes higher loads on the causticizing equipment and higher hydraulic/pumping loads on the black liquor concentrator system. Of course the acid and caustic costs decrease, but there is still more operational risk with the higher dead-load through the process.

At 10% fraction to acid treatment, the NPEs level decreases to 15%. Further increases in acid treatment fractions yield lower decreases in the NPEs level. It appears that 10% fraction to acid treatment is good conservative minimum for the purpose of this mill integration study. In a traditional lime based causticizing system, the amount of NPEs or inerts carried in the reburned lime is typically 10 to 15% as well.



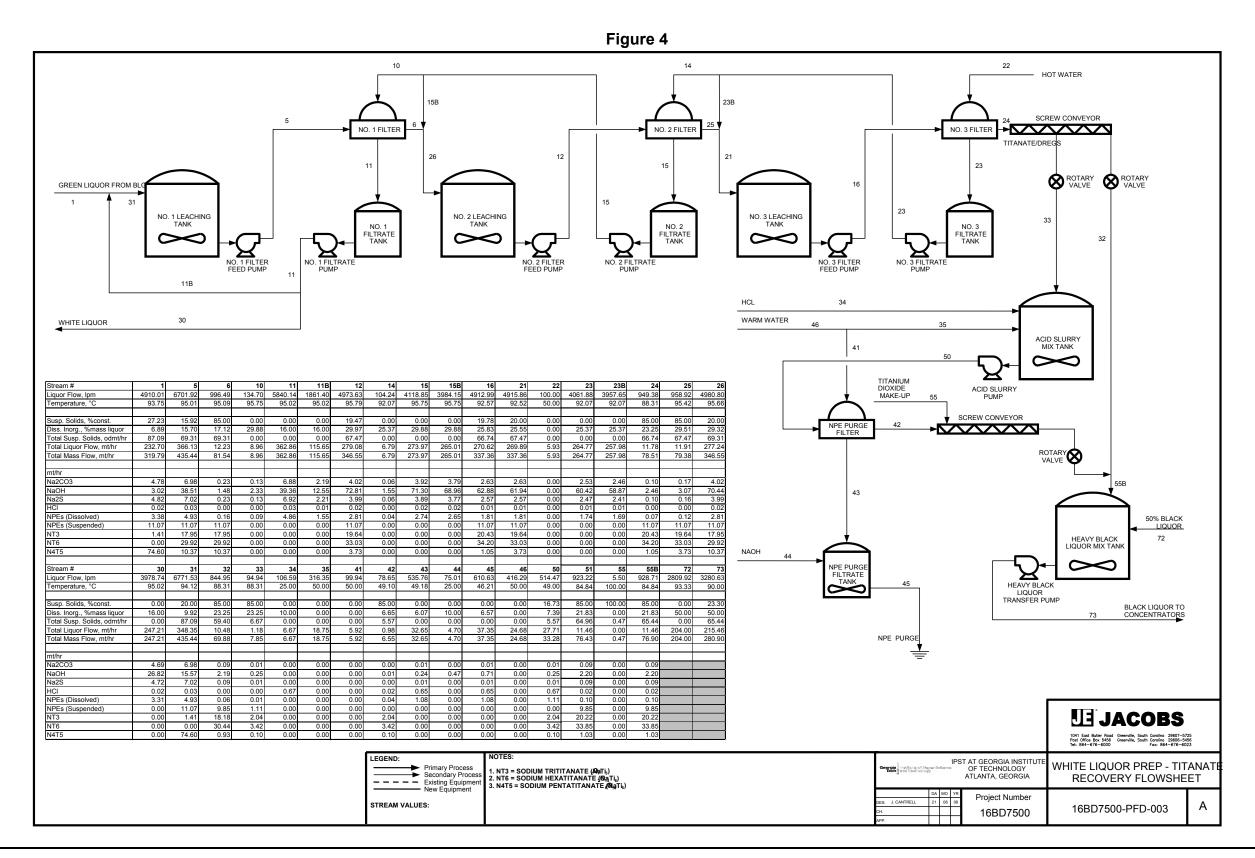
#### Jacobs Job No. 16BD7500 February 26, 2007 Rev. 1

	یک ۲۰		WHITE LIQUO	R TO DIGESTER	
	WEA	K W4	ASH TO SMELT DI	Reburned	
	White Liquor			►	Lime Mud
204	White			Reburned	Lime Mud
204	White Liquor	37		Reburned	Lime Mud
204 62%	White Liquor 3,6	37		Reburned	Lime Mud
204 62%	White Liquor 3,6	37	Dregs	Reburned Lime	
204 62% 0.17	White Liquor 3,6 15.59 253	37 9% .15	Dregs	Reburned Lime	
204 62% 0.17 2.91	White Liquor 3,6 15.5 253 8	37	Dregs	Reburned Lime	
204 62% 0.17 2.91 4.15	White Liquor 3,6 15.5 253 8 26	37 9% .15 .00	Dregs	Reburned Lime	
204 62% 0.17 2.91 4.15 5.63 0.21	White Liquor 3,6 253 8 265 5 0	37 9% .15 .00 .28	Dregs	Reburned Lime	
204 <u>62%</u> 0.17 <u>2.91</u> 4.15 5.63 0.21 0.11	White Liquor 3,6 253 253 8 26 5 0 0 0 0	37 9% .15 .00 .28 .00	Dregs 0.20 0.20	Reburned Lime	33.8 33.8 



#### Jacobs Job No. 16BD7500 February 26, 2007 Rev. 1

<b></b>		TO SMELT DIS	₽		
hite		Reburned		Borate	2
quor Dregs 3,637	5	Lime	Lime Mud	Makeu	qu
15.59%					
253.15	0.20	15.84	27.04		
5.20					
8.00 26.28		ļ			
5.20					0.14
0.00 0.19				<u> </u>	0.14
0.11					
RGIA INSTITUTE HNOLOGY		041 East Butler Road ast Office Box 5456 el: 864-676-6000	Greenville, South Carolin Greenville, South Carolin Fax: 8	- BOF	
A, GEORGIA		FLC	DWSHEET		
ect Number					^
BD7500		16BD7500	)-PFD-002		A



#### 4.4 Water Balance

Water usages for the three options are compared in Table 5 along with a base case that uses a scrubber on the kiln flue gas instead of an electrostatic precipitator (ESP).

	Table 5			
	Base w/ Kiln Scrubber Ipm	<b>Base</b> Ipm	<b>Borate</b> Ipm	<b>Titanate</b> Ipm
Water In Dregs PreCoat Filter Mud Washer Mud Filter Kiln Scrubber	85 2,781 1,502 709	85 2,781 1,502	85 3,027 1,201	
BLG Smelt Dissolving No. 3 Leach Filter Dilute Acid Water to NPE Purge Dilute Caustic	105			4,088 99 100 411 71
Total	5,077	4,368	4,314	4,769
Water Out White Liquor Smelt Dissolving Tank Stack Kiln Stack Slaker Stack Titanate to Black Liquor NPE Purge to Sewer	4,018 60 975 24	4,018 60 266 24	4,018 60 212 24	4,018 169 582
Total	5,077	4,368	4,314	4,769
Total Water Lost to Sewer or Atmosphere	1,059	350	296	582

The state of the art mill with an ESP on the lime kiln flue gas uses minimal water because the recycle lime dust is returned dry. The base case assumes a state of the art mill with a lime kiln ESP. The borate case water usage is even less due to a lower lime requirement. The base case with a conventional kiln scrubber has the highest water usage due to evaporative losses. The titanate case water usage is an improvement upon a kiln scrubber but it does require more water than the base case with a kiln ESP. See Figure 5 below.

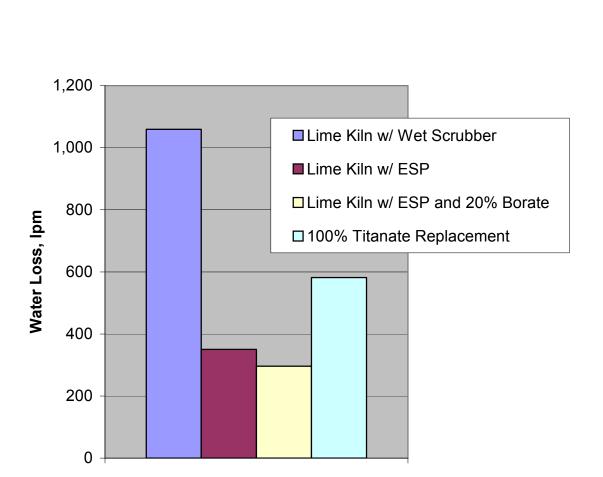


Figure 5



#### 5.0 BASIS OF ESTIMATED COST

The estimates are +/- 30% accuracy factored total installed cost (TIC). The estimates are based on preliminary process flow diagrams, priced equipment lists, and project scope descriptions. Equipment pricing was obtained from Andritz for disc filters and leaching tank agitators. Pump pricing was obtained from ITT Goulds. All other equipment pricing was obtained from Jacobs' historical database. Piping, structural, electrical, and controls material and equipment were factored based on the process equipment direct cost. The estimates assume an engineering, procurement, and construction management (EPC) type contract to execute the project. The estimates assume a site in the southeastern United States, non-union, and no escalation is included. Other estimating assumptions are listed in Table 6 below.

#### Table 6

#### **Capital Estimates Assumptions**

General Information Basis of Productivity Basis of Premium Time Per Diem Requirements Constructability	Jacobs Standards and Historical Data 100% of the hours worked on 50-hour weeks Per Diem at \$5.00 per hour on 100% of hours Unknown – depending on site
Construction Support Labor	20% of direct labor
Non Payroll Insurance, Taxes, Permit Sales Tax Building Permits Environmental Permits	s 5% of TIC Allowance provided for building permits Unknown – depending on site
Construction Management	4% of TIC
Engineering	15% of TIC for borate, 10% of TIC for titanate
Outside Consultants	DCS configuration, soils testing, and outside survey
Owner's Cost	4% of TIC
Spare Parts	5% of equipment cost
Check-Out & Commissioning	5% of engineering and allowances for vendors
Allowance for Unforeseen	10% on all costs which equates to 8.33% of TIC
Escalation	0%, Estimated in today's costs (October, 2006)

#### 6.0 CAPITAL COST ESTIMATES

The capital cost estimates are summarized in Table 7. The base case capital cost is taken from the Larson Study and factored up to account for inflation from 2002 to 2006.

Table 7

Capital Cost Summary	

Case	MM\$
Base	1.20
Borate	0.17
Titanate	31.55

The following sections show the detailed capital cost estimates for borate and titanate cases.



#### 6.1 Borate Auto Causticizing

JOB: BORATE SYSTEM - (HYPOTHETICAL MILL ) CLIENT: GEORGIA TECH LOCATION: ATLANTA, GEORGIA JOB NUMBER: 16BD7500 CONSTRUCTION DURATION: N/A ESTIMATE TYPE: CLASS 5 G:\ESTIMATI\GEORGIA TECH\16BD7500\[EMAIL\_BORATE SYSTEM\_R0.xis]PRIME CODE TCS

ESTIMATE DATE: 10/01/06 REVISION NO.: 0 ESTIMATOR: WAYNE FAILS PROJECT MANAGER: JAMES CANTRELL EST. FILE #: 06188

PRIME CODE	DESCRIPTION	W-H	QTY	UNIT	LABOR	EQUIPMENT	MATERIAL	SUBCONTRACT	TOTAL COST
	DIRECT COSTS								
50	MAJOR EQUIPMENT	217	0	0	\$10,505	\$49,820	\$747	\$0	\$61,07
51	DEMOLITION	0	0	0	\$0	\$0	\$0	\$0	\$
52	SITE EARTHMOVING	0	0	0	\$0	\$0	\$0	\$0	\$
53 54	SITE IMPROVEMENTS PILING, CAISSONS	0	0	0 0	\$0 \$0	\$0 \$0	\$0 \$0	\$0 \$0	9
55	BUILDINGS	0	1	LOT	\$0 \$0	\$0 \$0	\$0 \$0	\$0 \$0	4
56	CONCRETE	29	2	CY	\$1,221	\$0	\$611	\$0	\$1,83
57	MASONRY, REFRACTORY	0	0	0	\$0	\$0	\$0	\$0	
58	STRUCTURAL STEEL	11	0	TN	\$458	\$0	\$749	\$0	\$1,20
59	ROOFING AND SIDING	0	0	0	\$0	\$0	\$0	\$0	
60		0	0	0	\$0 \$0	\$0	\$0	\$0	
61 62	PROCESS DUCTWORK (NON-BUILDING) PIPING	126	0	0 LF	\$0 \$6,107	\$0 \$0	\$0 \$5,973	\$0 \$0	\$12,08
63	INSULATION - PIPE, EQUIPMENT & DUCTWORK	0	0	0	\$0,107	\$0 \$0	\$0,973 \$0	\$0 \$0	\$12,00
64	INSTRUMENTATION	41	ő	ŏ	\$1,832	\$6,107	\$1,832	\$0 \$0	\$9,77
65	ELECTRICAL	118	520	LF	\$5,219	\$1,272	\$3,069	\$0	\$9,56
66	PAINTING, PROTECTIVE COATINGS	0	0	0	\$0	\$0	\$0	\$0	
67	FURNITURE, LAB & SHOP EQUIPMENT	0	0	0	\$0	\$0	\$0	\$0	:
	TOTAL DIRECT COSTS	542			\$25,343	\$57,199	\$12,981	\$0	\$95,5
	\$ / WH CONSTRUCTION INDIRECT COSTS	\$46.75							
75	CONSTRUCTION SUPPORT LABOR	108			\$2,488	\$0	\$0	\$0	\$2,4
76	TEMPORARY CONSTRUCTION FACILITIES (IN WAGE RATES)				\$0	\$0	\$0	\$0	:
78	PREMIUM TIME				\$1,663	\$0	\$0	\$0	\$1,66
79	CRAFT FRINGE BENEFITS (IN WAGE RATES)				\$0	\$0	\$0	\$0	5
	CRAFT PER DIEM (\$5 PER HOUR ON 100 % OF THE HOURS)				\$0	\$0	\$0	\$3,253	\$3,25
80	PAYROLL TAXES & INSURANCE (IN WAGE RATES)				\$0	\$0	\$0	\$0	
83 84	SMALL TOOLS (IN WAGE RATES) CONSUMABLE SUPPLIES (IN WAGE RATES)				\$0 \$0	\$0 \$0	\$0 \$0	\$0 \$0	
85	CONSTRUCTION EQUIPMENT (IN WAGE RATES)				\$0 \$0	\$0 \$0	\$0 \$0	\$0 \$0	
87	FIELD STAFF (IN WAGE RATES)				\$0 \$0	<u>\$0</u> \$0	<u>\$0</u> \$0	<u>\$0</u> \$0	
81	NON-PAYROLL TAX, INSURANCE & PERMITS				\$0 \$0	\$0	\$649	\$2,000	\$2,64
93	CONSTRUCTION HOME OFFICE COST (IN WAGE RATES)				\$0 \$0	\$0	\$0	\$0	¢_,0
71	CRAFT START-UP ASSISTANCE				\$773	\$0	\$0	\$0	\$7
99	CONTRACTOR'S CONSTRUCTION OVERHEAD & FEE		10.00%	TCC	\$2,891	\$0	\$2,045	\$525	\$5,40
	TOTAL CONSTRUCTION INDIRECT COSTS	108			\$7,815	\$0	\$2,694	\$5,778	\$16,28
	TOTAL CONSTRUCTION COSTS (TCC)	651			\$33,158	\$57,199	\$15,675	\$5,778	\$111,8
	\$ / WH	\$58.73							
	PROJECT INDIRECT COSTS								
88	CONSTRUCTION MANAGEMENT		4.00%	TIC	\$0	\$0	\$0	\$6,966	\$6,9
90	ENGINEERING PROFESSIONAL SERVICES		15.00%	TIC	\$0	\$0	\$0	\$26,096	\$26,0
90	STUDY COST		0.00%	TIC	\$0	\$0	\$0	\$0	
96 91	OUTSIDE CONSULTANT SERVICES OWNER'S COST		4.00%	TIC	\$0 \$0	\$0 \$0	\$0 \$0	\$2,000 \$6,966	\$2,00
91 70	SPARE PARTS		4.00%	TIC	\$0 \$0	\$0 \$2.860	\$0 \$0	\$6,966 \$0	\$6,90 \$2.80
70	NON-CRAFT START-UP ASSISTANCE				\$0 \$0	<u>\$2,000</u> \$0	\$0 \$0	\$0 \$1,305	\$2,0
98	ALLOWANCE FOR UNFORESEEN		9.08%	TIC	\$3,316	\$6,006	\$1,567	\$4,911	\$15,80
98	ESCALATION (EXCLUDED - DATES UNKNOWN)		0.00%	TIC	\$0	\$0	\$0	\$0	
	ROUND OFF				\$526	(\$65)	(\$242)	(\$21)	\$19
	TOTAL PROJECT COSTS	651			\$37,000	\$66,000	\$17,000	\$54,000	\$174,00

\$ / WH

\$58.73

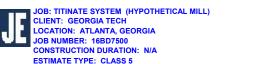
JE PRIME CODE	SUB CODE	AREA 001 BORATE SYSTEM DESCRIPTION	QTY.	UNIT	TOTAL W.H.'s	TOTAL DIRECT LABOR	TOTAL PROCESS EQUIPMENT	TOTAL MATERIAL	TOTAL SUB CONTRACTS	TOTAL ALL COSTS
		DIRECT COST SUMMARY								
50 56 58 62 64 65	01100 03000 05000 15100 17000 16000	MAJOR EQUIPMENT CONCRETE STRUCTURAL STEEL PIPING INSTRUMENTATION ELECTRICAL	0 1.936785 0.263033 0 0 520		217 29 11 126 41 118	\$10,505 \$1,221 \$458 \$6,107 \$1,832 \$5,219	\$49,820 \$0 \$0 \$6,107 \$1,272	\$747 \$611 \$749 \$5,973 \$1,832 \$3,069	\$0 \$0 \$0 \$0 \$0 \$0	\$61,072 \$1,832 \$1,207 \$12,080 \$9,772 \$9,560

	TOTAL - DIRECT COST SUMMARY	<b>542</b>	\$25,343	\$57,199	<b>\$12,981</b>	\$0	\$95,523
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#### G:\ESTIMATI\GEORGIA TECH\16BD7500\[EMAIL\_BORATE SYSTEM\_R0.xls]PRIME CODE TCS

	JE PRIME CODE	AREA 001 BORATE SYSTEM DESCRIPTION	QTY. UNIT	W.H./ UNIT	TOTAL W.H.'s	COST/ W.H.	TOTAL DIRECT LABOR	PROCESS EQUIPMENT UNIT COST	TOTAL PROCESS EQUIPMENT	MATERIAL UNIT COST	TOTAL MATERIAL	SUB CONTRACT UNIT COST	TOTAL SUB CONTRACTS	UNIT COST	TOTAL ALL COSTS
		DIRECT COST- DETAILS													
1		MAJOR EQUIPMENT													
2 3 4	50 50	BORATE FEEDER MOTOR - 1/2 HP @ 1800 RPM	1 EA 1 EA	160 INCL	160 0	\$48.34 \$48.34	\$7,735 \$0	\$35,000 INCL	\$35,000 \$0	\$0.00 \$0.00	\$0 \$0	\$0.00 \$0.00	\$0 \$0	\$42,735 \$0	\$42,735 \$0
5 6 7	50 50 50	BORATE MIX TANK - (70 GALS, 2' DIA. X 3' HT, 316L S.S.)	1 EA	24	24	\$48.34	\$1,160	\$2,000	\$2,000	\$0.00	\$0	\$0.00	\$0	\$3,160	\$3,160
8 9	50 50 50	BORATE MIX TANK AGITATOR MOTOR - 1/2 HP @ 1800 RPM	1 EA 1 EA	24 4	24 4	\$48.34 \$48.34	\$1,160 \$193	\$10,000 INCL	\$10,000 \$0	\$0.00 \$0.00	\$0 \$0	\$0.00 \$0.00	\$0 \$0	\$11,160 \$193	\$11,160 \$193
10 11 12	50	FREIGHT	1 LOT	N/A	0	\$48.34	\$0	\$2,820	\$2,820	\$0.00	\$0	\$0.00	\$0	\$2,820	\$2,820
13 18	50	SHIMS AND GROUT	1 LOT	5	5	\$48.34	\$256	\$0	\$0	\$747	\$747	\$0.00	\$0	\$1,004	\$1,004
19 20	50	TOTAL - MAJOR EQUIPMENT			217	\$48.34	\$10,505		\$49,820		\$747		\$0		\$61,072
21 170		CONCRETE													
71 76	56	FACTORED FROM INSTALLED PROCESS EQUIPMENT COST	1 LOT	29.05	29	\$42.04	\$1,221	\$0	\$0	\$611	\$611	\$0	\$0	\$1,832	\$1,832
177 178 170	56	TOTAL - CONCRETE	2 CY	15.00	29	\$42.04	\$1,221		\$0		\$611		\$0		\$1,832
179 180 192		STRUCTURAL STEEL													
193 215	58	FACTORED FROM INSTALLED PROCESS EQUIPMENT COST	1 LOT	10.52	11	\$43.53	\$458	\$0	\$0	\$749	\$749	\$0	\$0	\$1,207	\$1,207
216 217 218	58	TOTAL - STRUCTURAL STEEL	0.26 TN	40.00	11	\$43.53	\$458		\$0		\$749		\$0		\$1,207
219 253		PIPING													
254 288	62	FACTORED FROM INSTALLED PROCESS EQUIPMENT COST	1 LOT	126.33	126	\$48.34	\$6,107	\$0	\$0	\$5,973	\$5,973	\$0	\$0	\$12,080	\$12,080
289 290	62	TOTAL - PIPING, AVG. Ø"	LF		126	\$48.34	\$6,107		\$0		\$5,973		\$0		\$12,080
291 292 304 305		INSTRUMENTATION													
817 818	64	FACTORED FROM INSTALLED PROCESS EQUIPMENT COST	1 LOT	41.28	41	\$44.38	\$1,832	\$6,107	\$6,107	\$1,832	\$1,832	\$0	\$0	\$9,772	\$9,772
19	64	TOTAL - INSTRUMENTATION			41	\$44.38	\$1,832		\$6,107		\$1,832		\$0		\$9,772
321 322		ELECTRICAL													
323 325	65	MOTOR CONTROL CENTERS	2 EA	4.00	8	\$44.38	\$355	\$600.00	\$1,200	\$0.00	\$0	\$0.00	\$0	\$777.53	\$1,555
28 29	65	MINOR ELECTRICAL - WIRING DEVICES	4 EA	0.50	2	\$44.38	\$89	\$0.00	\$0	\$50.00	\$200	\$0.00	\$0	\$72.19	\$289
31 32	65	GROUND RODS / WIRE	20 LF	0.10	2	\$44.38	\$89	\$0.00	\$0	\$3.50	\$70	\$0.00	\$0	\$7.94	\$159
35 36	65	WIRE AND CABLE	500 LF	0.05	25	\$44.38	\$1,110	\$0.00	\$0	\$1.50	\$750	\$0.00	\$0	\$3.72	\$1,860
337 338 341	65	CONDUIT	500 LF	0.15	75	\$44.38	\$3,329	\$0.00	\$0	\$3.75	\$1,875	\$0.00	\$0	\$10.41	\$5,204
342 343	65	TESTING AND STARTUP	1 LOT	5.60	6	\$44.38	\$249	\$0.00	\$0	\$0.00	\$0	\$0.00	\$0	\$248.54	\$249
344 349	65	FREIGHT	1 LOT	N/A	0	\$44.38	\$0	\$72.00	\$72	\$173.70	\$174	\$0.00	\$0	\$245.70	\$246
350 351 352	65	TOTAL - ELECTRICAL	520 LF	0.23	118	\$44.38	\$5,219		\$1,272		\$3,069		\$0		\$9,560
377 378 379		TOTAL - DIRECT COST			542	\$46.75	\$25,343		\$57,199		\$12,981		\$0		\$95,523
513					542	φ <b>40.</b> / J	<b>⊅</b> ∠0,343		\$07,199		\$12, <del>3</del> 81		φU		\$90,0 <u>2</u> 3

#### 6.2 Titanate Direct Causticizing



ESTIMATE TYPE: CLASS 5 G:\ESTIMATI\GEORGIA TECH\16BD7500\[EMAIL\_TITANATE SYSTEM\_R0.xis]PRIME CODE TCS ESTIMATE DATE: 10/01/06 REVISION NO.: 0 ESTIMATOR: WAYNE FAILS PROJECT MANAGER: JAMES CANTRELL EST. FILE #: 06188

PRIME CODE	DESCRIPTION	W-H	QTY	UNIT	LABOR	EQUIPMENT	MATERIAL	SUBCONTRACT	TOTAL COST
	DIRECT COSTS								
50	MAJOR EQUIPMENT	5,540	0	0	\$267,824	\$11,840,337	\$177,605	\$1,000,000	\$13,285,76
51	DEMOLITION	0	0	0	\$0	\$0	\$0	\$0	
<u>52</u> 53	SITE EARTHMOVING SITE IMPROVEMENTS	0	0	0	\$0 \$0	\$0 \$0	\$0 \$0	\$0 \$0	
54	PILING, CAISSONS	0	0	0	\$0	\$0	\$0	\$0	
<u>55</u> 56	BUILDINGS CONCRETE	8,241 6,320	<u>1</u> 421	LOT CY	\$346,500 \$265,715	\$0 \$0	\$283,500 \$132.858	\$0 \$0	\$630,0 \$398.5
50 57	MASONRY, REFRACTORY	6,320 0	421	0	\$205,715 \$0	\$0 \$0	\$132,858 \$0	\$0 \$0	\$398,0
58	STRUCTURAL STEEL	2,289	57	TON	\$99,643	\$0	\$163,016	\$0	\$262,6
59	ROOFING AND SIDING	0	0	0	\$0	\$0 ©0	\$0 \$0	\$0 ©0	
60 61	FIRE PROOFING PROCESS DUCTWORK (NON-BUILDING)	0	0	0 0	\$0 \$0	\$0 \$0	\$0 \$0	\$0 \$0	
62	PIPING	29,642	7,852	LF	\$1,432,965	\$0	\$1,326,399	\$0	\$2,759,3
63	INSULATION - PIPE, EQUIPMENT & DUCTWORK	0	0	0	\$0	\$0	\$0	\$0	
64 65	INSTRUMENTATION ELECTRICAL	8,980 2,715	0 12,940	0 LF	\$398,573 \$120,513	\$1,328,577 \$434,860	\$398,573 \$55,984	\$0 \$0	\$2,125,7 \$611,3
66	PAINTING, PROTECTIVE COATINGS	2,715	12,340	0	\$0	\$0 \$0	\$0 \$0	\$0 \$0	φ011,0
67	FURNITURE, LAB & SHOP EQUIPMENT	0	0	0	\$0	\$0	\$0	\$0	
	TOTAL DIRECT COSTS	63,728			\$2,931,733	\$13,603,774	\$2,537,935	\$1,000,000	\$20,073,4
	\$ / WH CONSTRUCTION INDIRECT COSTS	\$46.00							
75	CONSTRUCTION SUPPORT LABOR	12,746			\$292,456	\$0	\$0	\$0	\$292,4
76	TEMPORARY CONSTRUCTION FACILITIES (IN WAGE RATES)				\$0	\$0	\$0	\$0	
78	PREMIUM TIME				\$192,365	\$0	\$0	\$0	\$192,3
79	CRAFT FRINGE BENEFITS (IN WAGE RATES) CRAFT PER DIEM (\$5 PER HOUR ON 100 % OF THE HOURS)				\$0 \$0	\$0 \$0	\$0 \$0	\$0 \$382,367	\$382,3
80	PAYROLL TAXES & INSURANCE (IN WAGE RATES)				\$0 \$0	\$0 \$0	\$0 \$0	\$0	ψ002,
83	SMALL TOOLS (IN WAGE RATES)				\$0	\$0	\$0	\$0	
84	CONSUMABLE SUPPLIES (IN WAGE RATES)				\$0	\$0	\$0	\$0	
<u>85</u> 87	CONSTRUCTION EQUIPMENT (IN WAGE RATES) FIELD STAFF (IN WAGE RATES)				\$0 \$0	\$0 \$0	\$0 \$0	\$0 \$0	
81	NON-PAYROLL TAX, INSURANCE & PERMITS				\$0 \$0	\$0	\$126,897	\$30,000	\$156,8
93	CONSTRUCTION HOME OFFICE COST (IN WAGE RATES)				\$0	\$0	\$0	\$0	
71 99	CRAFT START-UP ASSISTANCE CONTRACTOR'S CONSTRUCTION OVERHEAD & FEE		10.00%	тсс	\$20,304 \$294,195	\$0 \$0	\$0 \$399,725	\$0 \$141,237	\$20, \$835,
	TOTAL CONSTRUCTION INDIRECT COSTS	12,746			\$799,321	\$0	\$526,621	\$553,604	\$1,879,
	TOTAL CONSTRUCTION COSTS (TCC) \$ / WH	76,473 \$60.60			\$3,731,054	\$13,603,774	\$3,064,556	\$1,553,604	\$21,952,
	PROJECT INDIRECT COSTS								
			4.000/	TIO			•••	A4 000 007	<b>*</b> 4 000
88 90	CONSTRUCTION MANAGEMENT ENGINEERING PROFESSIONAL SERVICES		4.00% 10.00%	TIC TIC	\$0 \$0	\$0 \$0	\$0 \$0	\$1,262,297 \$3,156,840	\$1,262, \$3,156,
90	STUDY COST		0.00%	TIC	\$0 \$0	\$0	\$0 \$0	\$0	φ0,100,
96	OUTSIDE CONSULTANT SERVICES		0.22%	TIC	\$0	\$0	\$0	\$70,000	\$70,0
91 70	OWNER'S COST SPARE PARTS		4.00% 2.16%	TIC TIC	\$0 \$0	\$0 \$680,189	\$0 \$0	\$1,262,297 \$0	\$1,262, \$680,
70	NON-CRAFT START-UP ASSISTANCE		0.98%	TIC	\$0 \$0	\$000,109	\$0 \$0	\$307,842	\$000, \$307,
98	ALLOWANCE FOR UNFORESEEN		9.09%	TIC	\$373,105	\$1,428,396	\$306,456	\$761,288	\$2,869,2
98	ESCALATION (EXCLUDED - DATES UNKNOWN)		0.00%	TIC	\$0 (\$160)	\$0 (\$250)	\$0	\$0 (\$167)	
	ROUND OFF				(\$160)	(\$359)	(\$12)	(\$167)	(\$6

TOTAL PROJECT COSTS	76,473	\$4,104,000	\$15,712,000	\$3,371,000	\$8,374,000	\$31,561,000

JE PRIME CODE	AREA 001 TITANATE SYSTEM DESCRIPTION	QTY.	UNIT	TOTAL W.H.'s	TOTAL DIRECT LABOR	TOTAL PROCESS EQUIPMENT	TOTAL MATERIAL	TOTAL SUB CONTRACTS	TOTAL ALL COSTS
	DIRECT COST SUMMARY								
50	MAJOR EQUIPMENT	0	0	5,540	\$267,824	\$11,840,337	\$177,605	\$1,000,000	\$13,285,767
55.380	BUILDINGS	1,800	SF	8,241	\$346,500	\$0	\$283,500	\$0	\$630,000
56	CONCRETE	421	CY	6,320	\$265,715	\$0	\$132,858	\$0	\$398,573
58	STRUCTURAL STEEL	57	TON	2,289	\$99,643	\$0	\$163,016	\$0	\$262,660
62	PIPING	7,852	LF	29,642	\$1,432,965	\$0	\$1,326,399	\$0	\$2,759,363
64	INSTRUMENTATION	0	0	8,980	\$398,573	\$1,328,577	\$398,573	\$0	\$2,125,723
65	ELECTRICAL	12,940	LF	2,715	\$120,513	\$434,860	\$55,984	\$0	\$611,357

TOTAL - DIRECT COST SUMMARY	63,728	\$2,931,733	\$13,603,774	\$2,537,935	\$1,000,000	\$20,073,442

## G:\ESTIMATI\GEORGIA TECH\16BD7500\[EMAIL\_TITANATE SYSTEM\_R0.xis]PRIME CODE TCS

YSTEM	_R0.xls	<b>PRIME</b>	CODE	TCS
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LINE NO.	JE PRIME CODE	AREA 001 TITANATE SYSTEM DESCRIPTION	QTY. UNIT	W.H./ UNIT	TOTAL W.H.'s	COST/ W.H.	TOTAL DIRECT LABOR	PROCESS EQUIPMENT UNIT COST	TOTAL PROCESS EQUIPMENT	MATERIAL UNIT COST	TOTAL MATERIAL	SUB CONTRACT UNIT COST	TOTAL SUB CONTRACTS	UNIT COST	TOTAL ALL COSTS
		DIRECT COST- DETAILS													
1		MAJOR EQUIPMENT													
2 3 4	50 50	NO. 1 LEACHING TANK (26' $\Phi$ X $$ 26' L, 100,000 GALS, 316L S.S.)	1 EA	360	360	\$48.34	\$17,403	\$260,000	\$260,000	\$0.00	\$0	\$0.00	\$0	\$277,403	\$277,403
5	50	NO. 1 LEACHING TANK AGITATOR8' TURBINE 4-BLADE IMPELLER, 316L S.S.	1 EA	120	120	\$48.34	\$5.801	\$9,500,000	\$9.500.000	\$0.00	\$0	\$0.00	\$0	\$9.505.801	\$9.505.801
6 7	50 50	MOTOR - 150 HP @ 1200 RPM	1 EA	40	40	\$48.34	\$1,934	\$4,400	\$4,400	\$0.00	\$0	\$0.00	\$0	\$6,334	\$6,334
8	50	NO. 1 FILTER FEED PUMP 1900 GPM, 98' TDH GOULDS JC 8X10-18-4J, 316L S.S.													
9	50	15.375" IMPELLER MOTOR - 100 HP @ 1200 RPM	1 EA 1 EA	60 30	60 30	\$48.34 \$48.34	\$2,901 \$1,450	\$28,086 \$4,518	\$28,086 \$4,518	\$0.00 \$0.00	\$0 \$0	\$0.00 \$0.00	\$0 \$0	\$30,987 \$5,968	\$30,987 \$5,968
10 11	50 50	NO. 1 FILTER						+ .,							
12	50	ADRITZ SIZE CD3712, 10,200 M3/D MOTOR - 60 HP @ 1200 RPM	1 EA 1 EA	48 24	48 24	\$48.34 \$48.34	\$2,320 \$1,160	INCL. INCL.	\$0 \$0	\$0.00 \$0.00	\$0 \$0	\$0.00 \$0.00	\$0 \$0	\$2,320 \$1,160	\$2,320 \$1,160
13 14	50 50	NO. 1 FILTER FILTRATE TANK	1 EA	42	42	\$48.34	\$2,030	INCL.	\$0	\$0.00	\$0	\$0.00	\$0	\$2,030	\$2,030
15 16	50 50	NO. 1 FILTRATE PUMP 1600 GPM, 98' TDH GOULDS 3175 6X8-14, 316L S.S.													
17	50	11.75" IMPELLER MOTOR - 60 HP @ 1200 RPM	1 EA 1 EA	48 24	48 24	\$48.34 \$48.34	\$2,320 \$1,160	\$28,638 \$2,399	\$28,638 \$2,399	\$0.00 \$0.00	\$0 \$0	\$0.00 \$0.00	\$0 \$0	\$30,958 \$3,559	\$30,958 \$3,559
18 19	50 50	NO. 1 VACUUM PUMP	1 EA	360	360	\$48.34	\$17,403	INCL.	¢2,000 \$0	\$0.00	\$0 \$0	\$0.00	\$0 \$0	\$17,403	\$17,403
20 21	50 50 50	MOTOR - 500 HP @ 1800 RPM	1 EA	120	120	\$48.34	\$5,801	\$28,200	\$28,200	\$0.00	\$0 \$0	\$0.00	\$0 \$0	\$34,001	\$34,001
22	50	NO. 2 LEACHING TANK 26' Φ X 26' L, 100,000 GALS, 316L S.S.	1 EA	360	360	\$48.34	\$17,403	\$260,000	\$260,000	\$0.00	\$0	\$0.00	\$0	\$277,403	\$277,403
23 24	50 50	NO. 2 LEACHING TANK AGITATOR	1 27	000	000	φ+0.0+	¢17,400	φ200,000	¢200,000	φ0.00	ψŪ	φ0.00	ţ,	φ211,400	φ211,400
		8' TURBINE 4-BLADE IMPELLER, 316L S.S. MOTOR - 150 HP @ 1800 RPM	1 EA	120	120 40	\$48.34	\$5,801	INCL.	\$0	\$0.00	\$0 \$0	\$0.00	\$0 ©0	\$5,801	\$5,801
25 26	50 50	0	1 EA	40	40	\$48.34	\$1,934	\$4,400	\$4,400	\$0.00	\$0	\$0.00	\$0	\$6,334	\$6,334
27	50	NO. 2 FILTER FEED PUMP 1400 GPM, 98' TDH													
		GOULDS JC 6X6-14HS-4J, 316L S.S. 10.875" IMPELLER	1 EA	60	60	\$48.34	\$2,901	\$25,278	\$25,278	\$0.00	\$0	\$0.00	\$0	\$28,179	\$28,179
28 29	50 50	MOTOR - 75 HP @ 1800 RPM	1 EA	30	30	\$48.34	\$1,450	\$2,803	\$2,803	\$0.00	\$0	\$0.00	\$0	\$4,253	\$4,253
30	50	NO. 2 FILTER ADRITZ SIZE CD3712, 10,200 M3/D	1 EA	48	48	\$48.34	\$2,320	INCL.	\$0	\$0.00	\$0	\$0.00	\$0	\$2,320	\$2,320
31 32	50 50	MOTOR - 60 HP @ 1800 RPM	1 EA	24	24	\$48.34	\$1,160	INCL.	\$0	\$0.00	\$0	\$0.00	\$0	\$1,160	\$1,160
33 34	50 50	NO. 2 FILTER FILTRATE TANK	1 EA	42	42	\$48.34	\$2,030	INCL.	\$0	\$0.00	\$0	\$0.00	\$0	\$2,030	\$2,030
35	50	NO. 2 FILTRATE PUMP 1200 GPM, 98' TDH GOULDS 3175 6X8-12, 316L S.S.													
	50	10.9375" IMPELLER	1 EA	48	48	\$48.34	\$2,320	\$24,884	\$24,884	\$0.00	\$0	\$0.00	\$0	\$27,204	\$27,204
36 37	50 50	MOTOR - 60 HP @ 1800 RPM	1 EA	24	24	\$48.34	\$1,160	\$1,790	\$1,790	\$0.00	\$0		\$0	\$2,950	\$2,950
38 39 40	50 50 50	NO. 2 VACUUM PUMP MOTOR - 500 HP @ 1800 RPM	1 EA 1 EA	360 120	360 120	\$48.34 \$48.34	\$17,403 \$5,801	INCL. \$28,200	\$0 \$28,200	\$0.00 \$0.00	\$0 \$0	\$0.00 \$0.00	\$0 \$0	\$17,403 \$34,001	\$17,403 \$34,001
40	50	NO. 3 LEACHING TANK 26' Φ X 26' L, 100,000 GALS, 316L S.S.	1 EA	360	360	\$48.34	\$17,403	\$260,000	\$260,000	\$0.00	\$0	\$0.00	\$0	\$277,403	\$277,403
42	50							,	,,	+0	ţŭ		÷	,	,

LINE NO.	JE PRIME CODE	AREA 001 TITANATE SYSTEM DESCRIPTION	QTY. UNIT	W.H./ UNIT	TOTAL W.H.'s	COST/ W.H.	TOTAL DIRECT LABOR	PROCESS EQUIPMENT UNIT COST	TOTAL PROCESS EQUIPMENT	MATERIAL UNIT COST	TOTAL MATERIAL	SUB CONTRACT UNIT COST	TOTAL SUB CONTRACTS	UNIT COST	TOTAL ALL COSTS
43	50	NO. 3 LEACHING TANK AGITATOR													
44	50	8' TURBINE 4-BLADE IMPELLER, 316L S.S. MOTOR - 150 HP @ 1800 RPM	1 EA 1 EA	120 40	120 40	\$48.34 \$48.34	\$5,801 \$1,934	INCL. \$4,400	\$0 \$4,400	\$0.00 \$0.00	\$0 \$0	\$0.00 \$0.00	\$0 \$0	\$5,801 \$6,334	\$5,801 \$6,334
45 46	50 50	NO. 3 FILTER FEED PUMP 1400 GPM, 98' TDH GOULDS JC 6X6-14HS-4J, 316L S.S.													
47 48	50 50	10.875" IMPELLER MOTOR - 75 HP @ 1800 RPM	1 EA 1 EA	60 30	60 30	\$48.34 \$48.34	\$2,901 \$1,450	\$25,279 \$2,803	\$25,279 \$2,803	\$0.00 \$0.00	\$0 \$0	\$0.00 \$0.00	\$0 \$0	\$28,180 \$4,253	\$28,180 \$4,253
49 50	50 50	NO. 3 FILTER ADRITZ SIZE CD3712, 10,200 M3/D MOTOR - 60 HP @ 1800 RPM	1 EA 1 EA	48 24	48 24	\$48.34 \$48.34	\$2,320 \$1,160	INCL. INCL.	\$0 \$0	\$0.00 \$0.00	\$0 \$0	\$0.00 \$0.00	\$0 \$0	\$2,320 \$1,160	\$2,320 \$1,160
51 52	50 50	NO. 3 FILTER FILTRATE TANK	1 EA	42	42	\$48.34	\$2,030	INCL.	\$0 \$0	\$0.00	\$0	\$0.00	\$0	\$2,030	\$2,030
53 54	50 50	NO. 3 FILTRATE PUMP 1100 GPM, 98' TDH													
		GOULDS 3175 6X8-12, 316L S.S. 10.875" IMPELLER	1 EA	48	48	\$48.34	\$2,320	\$24,884	\$24,884	\$0.00	\$0	\$0.00	\$0	\$27,204	\$27,204
55 56	50 50	MOTOR - 50HP @ 1800 RPM	1 EA	24	24	\$48.34	\$1,160	INCL.	\$0	\$0.00	\$0	\$0.00	\$0	\$1,160	\$1,160
57 58 59	50 50 50	NO. 3 VACUUM PUMP MOTOR - 500 HP @ 1800 RPM	1 EA 1 EA	360 120	360 120	\$48.34 \$48.34	\$17,403 \$5,801	INCL. \$28,200	\$0 \$28,200	\$0.00 \$0.00	\$0 \$0	\$0.00 \$0.00	\$0 \$0	\$17,403 \$34,001	\$17,403 \$34,001
60	50	NO. 3 FILTER SCREW CONVEYOR 20"Ф X 30' L, 316L S.S.	1 EA	240	240	\$48.34	\$11,602	\$787,637	\$787,637	\$0.00	\$0	\$0.00	\$0	\$799,240	\$799,240
61 62	50 50	MOTOR - 150 HP @ 1800 RPM	1 EA	40	40	\$48.34	\$1,934	\$4,400	\$4,400	\$0.00	\$0	\$0.00	\$0	\$6,334	\$6,334
63	50	ROTARY VALVE, ACID MIX TANK FEED (150 CUFT/HR, 10", 316L S.S.)	1 EA	64	64	\$48.34	\$3,094	\$17,250	\$17,250	\$0.00	\$0	\$0.00	\$0	\$20,344	\$20,344
64 65	50 50		1 EA	6	6	\$48.34	\$290	INCL.	\$0	\$0.00	\$0	\$0.00	\$0	\$290.06	\$290
66 67	50 50	ACID SLURRY MIX TANK ) 6' Φ X 9' L, 1,900 GALS, HASTELLOY C)	1 EA	64	64	\$48.34	\$3,094	INCL.	\$0	\$0.00	\$0	\$0.00	\$0	\$3,094	\$3,094
68 69	50 50	ACID SLURRY MIX TANK AGITATOR - 72" TURBINE 4-BLADE IMPELLER, HASTELLOY C MOTOR - 20 HP @ 1800 RPM	1 EA 1 EA	40 15	40 15	\$48.34 \$48.34	\$1,934 \$725	\$30,000 INCL.	\$30,000 \$0	\$0.00 \$0.00	\$0 \$0	\$0.00 \$0.00	\$0 \$0	\$31,934 \$725.14	\$31,934 \$725
70 71	50 50 50	ACID SLURRY PUMP	T EX	15	15	φτ0.0τ	φ123	INGE.	φU	ψ0.00	ψŪ	ψ0.00	ψŬ	ψ720.1 <del>4</del>	ψ123
		160 GPM, 98' TDH GOULDS 3175 3X6-12, CD4MCuN 9.8125" IMPELLER	1 EA	40	40	\$48.34	\$1,934	\$20,603	\$20,603	\$0.00	\$0	\$0.00	\$0	\$22,537	\$22,537
72 73	50 50	MOTOR -20 HP @ 1800 RPM	1 EA	15	15	\$48.34	\$725	\$803	\$803	\$0.00	\$0	\$0.00	\$0	\$1,528	\$1,528
74 75 76	50 50 50	NPE PURGE FILTER (ANDRITZ SIZE EIRS 3030) MOTOR - 1/2 HP @ 1800 RPM	1 EA 1 EA	24 6	24 6	\$48.34 \$48.34	\$1,160 \$290	INCL. INCL.	\$0 \$0	\$0.00 \$0.00	\$0 \$0	\$0.00 \$0.00	\$0 \$0	\$1,160 \$290.06	\$1,160 \$290
70 77 78	50 50 50	NPE PURGE FILTRATE TANK (6' $\Phi$ X $$ 9' L, HASTELLOY	1 EA	64	64	\$48.34	\$3,094	INCL.	\$0	\$0.00	\$0	\$0.00	\$0	\$3,094	\$3,094
79	50	NPE PURGE FILTRATE TANK AGITATOR48" TURBINE 4-BLADE IMPELLER, HASTELLOY C	1 EA	20	20	\$48.34	\$967	\$20,000	\$20,000	\$0.00	\$0	\$0.00	\$0	\$20,967	\$20,967
80 81	50 50	MOTOR - 2 HP @ 1800 RPM	1 EA	6	6	\$48.34	\$290	INCL.	\$0	\$0.00	\$0	\$0.00	\$0	\$290.06	\$290
82 83	50 50 50	TITANATE SCREW CONVEYOR (9"Φ X 30' L, HASTELLOY C) MOTOR - 5 HP @ 1800 RPM	1 EA 1 EA	240 5	240 5	\$48.34 \$48.34	\$11,602 \$242	\$160,000 INCL.	\$160,000 \$0	\$0.00 \$0.00	\$0 \$0	\$0.00 \$0.00	\$0 \$0	\$171,602 \$241.71	\$171,602 \$242
84 85 86 87	50 50 50 50	TITANATE ROTARY VALVE (150 CUFT/HR, 10", HASTELLOY C) MOTOR - 1.5 HP @ 1800 RPM	1 EA 1 EA	72 4	72 4	\$48.34 \$48.34	\$3,481 \$193	\$60,000 INCL.	\$60,000 \$0	\$0.00 \$0.00	\$0 \$0	\$0.00 \$0.00	\$0 \$0	\$63,481 \$193.37	\$63,481 \$193
87 88	50 50	HEAVY BLACK LIQUOR MIX TANK (12 $\Phi$ X 30' L, 55,000 GAL 316L SS)	1 EA	360	360	\$48.34	\$17,403	\$143,000	\$143,000	\$0.00	\$0	\$0.00	\$0	\$160,403	\$160,403

LINE NO.	JE PRIME CODE	AREA 001 TITANATE SYSTEM DESCRIPTION	QTY. UNIT	W.H./ UNIT	TOTAL W.H.'s	COST/ W.H.	TOTAL DIRECT LABOR	PROCESS EQUIPMENT UNIT COST	TOTAL PROCESS EQUIPMENT	MATERIAL UNIT COST	TOTAL MATERIAL	SUB CONTRACT UNIT COST	TOTAL SUB CONTRACTS	UNIT COST	TOTAL ALL COSTS
89 90 91 92	50 50 50 50	HEAVY BLACK LIQUOR TANK AGITATOR ( 6' Ø, 316L SS ) MOTOR - 150 HP @ 1800 RPM	1 EA 1 EA	120 64	120 64	\$48.34 \$48.34	\$5,801 \$3,094	\$15,000 \$4,400	\$15,000 \$4,400	\$0.00 \$0.00	\$0 \$0	\$0.00 \$0.00	\$0 \$0	\$20,801 \$7,494	\$20,801 \$7,494
93 94	50 50	HEAVY BLACK LIQUOR TANK TRANSFER PUMP ( GOULD 3175 6X8-12, 316L SS ) MOTOR - 50 HP @ 1800 RPM	1 EA 1 EA	48 20	48 20	\$48.34 \$48.34	\$2,320 \$967	\$25,279 \$2,803	\$25,279 \$2,803	\$0.00 \$0.00	\$0 \$0	\$0.00 \$0.00	\$0 \$0	\$27,599 \$3,770	\$27,599 \$3,770
95 96	50 50	ALLOWANCE FOR CONCENTRATOR UPGRADE	1 LOT	S/C	0	\$48.34	\$0	\$0	\$0	\$0.00	\$0	\$1,000,000	\$1,000,000	\$1,000,000	\$1,000,000
97 98 99	50	FREIGHT	1 LOT	N/A	0	\$48.34	\$0	W/EQUIP	\$0	\$0.00	\$0	\$0.00	\$0	\$0.00	\$0
99 100 105	50	SHIMS AND GROUT	1 LOT	135	135	\$48.34	\$6,532	\$0	\$0	\$177,605	\$177,605	\$0.00	\$0	\$184,137	\$184,137
105 106 107	50	TOTAL - MAJOR EQUIPMENT			5,540	\$48.34	\$267,824		\$11,840,337		\$177,605		\$1,000,000		\$13,285,767
108 209 210		BUILDINGS													
210 211 216	55.380	MOTOR CONTROL CENTER (30' X 60')	1,800 SF	4.58	8,241	\$42.04	\$346,500	\$0.00	\$0	\$157.50	\$283,500	\$0.00	\$0	\$350.00	\$630,000
210 217 218	55.380	TOTAL - BUILDINGS	1,800 SF	4.58	8,241	\$42.04	\$346,500		\$0		\$283,500		\$0		\$630,000
218 219 257 258		CONCRETE													
263 264	56	FACTORED FROM INSTALLED PROCESS EQUIPMENT COST	1 LOT	6,320	6,320	\$42.04	\$265,715	\$0	\$0	\$132,858	\$132,858	\$0	\$0	\$398,573	\$398,573
265 266	56	TOTAL - CONCRETE	421 CY	15.00	6,320	\$42.04	\$265,715		\$0		\$132,858		\$0		\$398,573
260 267 279 280		STRUCTURAL STEEL													
302 303	58	FACTORED FROM INSTALLED PROCESS EQUIPMENT COST	1 LOT	2,289	2,289	\$43.53	\$99,643	\$0	\$0	\$163,016	\$163,016	\$0	\$0	\$262,660	\$262,660
303 304 305	58	TOTAL - STRUCTURAL STEEL	57 TON	40	2,289	\$43.53	\$99,643		\$0		\$163,016		\$0		\$262,660
306 340 341		PIPING													
375 376	62	FACTORED FROM INSTALLED PROCESS EQUIPMENT COST	1 LOT	27,482	27,482	\$48.34	\$1,328,577	\$0	\$0	\$1,299,348	\$1,299,348	\$0	\$0	\$2,627,925	\$2,627,925
377 378	62	TOTAL - PIPING, AVG. Ø 12"	7,852 LF	3.78	29,642	\$48.34	\$1,432,965		\$0		\$1,326,399		\$0		\$2,759,363
379 391 392		INSTRUMENTATION													
404 405	64	FACTORED FROM INSTALLED PROCESS EQUIPMENT COST	1 LOT	8,980	8,980	\$44.38	\$398,573	\$1,328,577	\$1,328,577	\$398,573	\$398,573	\$0	\$0	\$2,125,723	\$2,125,723
406 407	64	TOTAL - INSTRUMENTATION			8,980	\$44.38	\$398,573		\$1,328,577		\$398,573		\$0		\$2,125,723
408 409		ELECTRICAL													
410 411	65	3450KVA SUBSTATION	1 EA	170	170	\$44.38	\$7,545	\$140,000	\$140,000	\$0.00	\$0	\$0.00	\$0	\$147,545	\$147,545
412 413	65	2400V SWITCHGEAR	1 LOT	40	40	\$44.38	\$1,775	\$65,000	\$65,000	\$0.00	\$0	\$0.00	\$0	\$66,775	\$66,775
414 415	65	1500KVA SUBSTATION	1 EA	120	120	\$44.38	\$5,326	\$67,000	\$67,000	\$0.00	\$0	\$0.00	\$0	\$72,326	\$72,326
416 417 418	65	15KV SWITCH	1 EA	40	40	\$44.38	\$1,775	\$28,000	\$28,000	\$0.00	\$0	\$0.00	\$0	\$29,775	\$29,775

LINE NO.	JE PRIME CODE	AREA 001 TITANATE SYSTEM DESCRIPTION	QTY. UNIT	W.H./ UNIT	TOTAL W.H.'s	COST/ W.H.	TOTAL DIRECT LABOR	PROCESS EQUIPMENT UNIT COST	TOTAL PROCESS EQUIPMENT	MATERIAL UNIT COST	TOTAL MATERIAL	SUB CONTRACT UNIT COST	TOTAL SUB CONTRACTS	UNIT COST	TOTAL ALL COSTS
419	65	480V SWITCHGEAR	1 EA	90	90	\$44.38	\$3,994	\$49,000	\$49,000	\$0.00	\$0	\$0.00	\$0	\$52,994	\$52,994
420 421 422	65	LOW VOLTAGE MOTOR CONTROL CENTERS	20 EA	12.00	240	\$44.38	\$10,652	\$1,500	\$30,000	\$0.00	\$0	\$0.00	\$0	\$2,033	\$40,652
423 424	65	MEDIUM VOLTAGE MOTOR CONTROL CENTERS	3 EA	16.00	48	\$44.38	\$2,130	\$17,000	\$51,000	\$0.00	\$0	\$0.00	\$0	\$17,710	\$53,130
425 427	65	MINOR ELECTRICAL - WIRING DEVICES	88 EA	0.50	44	\$44.38	\$1,953	\$0.00	\$0	\$50.00	\$4,400	\$0.00	\$0	\$72.19	\$6,353
428 431	65	GROUND RODS / WIRE	440 LF	0.10	44	\$44.38	\$1,953	\$0.00	\$0	\$3.50	\$1,540	\$0.00	\$0	\$7.94	\$3,493
432 433	65	WIRE AND CABLE	12,500 LF	0.05	625	\$44.38	\$27,739	\$0.00	\$0	\$1.50	\$18,750	\$0.00	\$0	\$3.72	\$46,489
434 437	65	CONDUIT	7,500 LF	0.15	1,125	\$44.38	\$49,931	\$0.00	\$0	\$3.75	\$28,125	\$0.00	\$0	\$10.41	\$78,056
438 439	65	TESTING AND STARTUP	1 LOT	129	129	\$44.38	\$5,739	\$0.00	\$0	\$0.00	\$0	\$0.00	\$0	\$5,739	\$5,739
440 445	65	FREIGHT	1 LOT	N/A	0	\$44.38	\$0	\$4,860	\$4,860	\$3,169	\$3,169	\$0.00	\$0	\$8,029	\$8,029
446 472 473	65	TOTAL - ELECTRICAL	12,940 LF	0.21	2,715	\$44.38	\$120,513		\$434,860		\$55,984		\$0		\$611,357
474 475		TOTAL - DIRECT COST			63,728	\$46.00	\$2,931,733		\$13,603,774		\$2,537,935		\$1,000,000		\$20,073,442

#### 7.0 OPERATING AND MAINTENANCE COSTS

The operating and maintenance costs for each option are estimated from the following sources of information:

- Chemicals usages from WinGEMS or spreadsheet mass balances
- Lime kiln fuel oil usage for HTBLG (Larson Study)
- Electricity usage based on total connected equipment horsepower times 80% for each case
- Chemicals, fuel oil, and electricity costs from current market pricing (August, 2006)
- Annual maintenance cost equal to 5% of capital cost

Table 8 shows the chemicals, fuel oil, and electricity costs used for the economics analysis based on 2006 prices.

#### Table 8

Chemicals, Fuel Oil, and Electricity Costs (2006)

#6 Fuel Oil , \$/MMBtu	\$8.51
Electricity , \$/MWh	\$58.60
Borate, \$/mt	\$425.00
Titanium Dioxide, \$/mt	\$480.00
Hydrochloric Acid, \$/mt	\$135.00
Sodium Hydroxide, \$/mt	\$370.00

Table 9 shows chemicals, fuel oil, and electricity usage or savings as compared to the base case.

Table 9

Annual Chemicals, Fuel Oil, and Electricity Usages

	Borate	Titanate	
Fuel Oil Savings	217,386	1,086,928	MMBtu/yr
Electricity Savings	4,310	7,038	MWh/yr
Borate Usage	1,177		mt/yr
Titanium Dioxide Usage		3,951	mt/yr
Hydrochloric Acid Usage		5,559	mt/yr
Sodium Hydroxide Usage		3,912	mt/yr

Table 10 shows the costs or savings items for each option. Avoided cost savings are treated as positive cash flow. The annual maintenance cost for the base case is based on 5% of the capital cost of a new lime kiln and caustic plant of similar capacity. This capital cost is approximately \$35,000,000.

#### Table 10

#### Annualized O&M Costs

		Annual \$	
	Base	Borate	Titanate
Avoided Cost Savings			
Avoided Lime Kiln Fuel Oil		1,849,503	9,247,514
Avoided Electricity Purchases		252,567	412,428
Total		2,102,070	9,659,943
Direct Operating Costs			
Borate		500,288	
Titanate			1,896,391
Hydrochloric Acid			750,454
Sodium Hydroxide			1,447,375
Incremental Waste Treatment Costs (.10 KW/lpm)	)		29,809
Operations & Maintenance	1,750,000	1,408,700	1,577,250
Total	1,750,000	1,908,988	5,701,279

#### 8.0 ECONOMIC ANALYSIS

#### 8.1 Approach and Assumptions

Both the internal rate of return (IRR) and net present value (NPV) analyses were performed on each case and also performed relative to the base case. The key inputs to the analyses are the capital costs from Section 5 and the annualized operating and maintenance costs from Section 6. Table 11 shows the economic assumptions used for the analyses.



#### Table 11

#### **Economic Assumptions**

#### **Financial Parameters**

Annual Inflation Rate	4.0%						
Debt Fraction of Capital	50%						
Equity Fraction of Capital	50%						
Interest Rate on Debt	8.0%						
Return on Equity	15%						
Resulting Discount Rate used for NPV calculations	9.9% (after tax)						
Income Tax Rate (combined Federal & State)	40%						
Economic Life (years)	25 20 year MACRS rate						
Depreciation Method	20-year MACRS rate schedule <sup>1</sup>						
Construction Time	1 yr						
Mill Assumptions							
Annual Operating Hours	8,330						
Annual O&M Costs, % of Capital Cost	5%						
Start-up Assumptions							
Year 1 of Operation	100%						

(1 - Modified Accelerated Cost Recovery System (MACRS) per IRS Tax Code)

#### 8.2 Economic Analysis Results

The IRR and NPV cash flow analyses were performed for each case and for relative comparison to the HTBLG base case. The annualized materials and energy flows used in the analyses are shown above in Table 9. The detailed cash flow calculations are shown in Appendix F.

As shown in Table 12, sensitivity analyses were performed for capital cost, fuel and electricity costs since these variables are subject to some volatility in the current and future economic environment.

#### Table 12

Economic Analysis Results Summary

#### TOTAL NET CASH FLOW

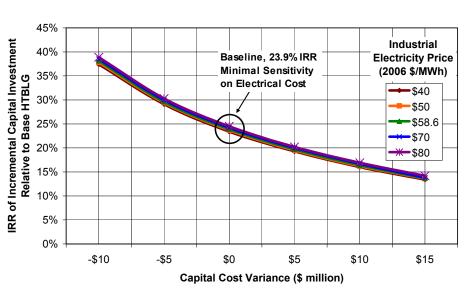
	Stand	d-Alone	Relative to Base			
	IRR (%)	NPV (\$ million)	IRR (%)	NPV (\$ million)		
Base - HTBLG	N/A	-14.6	N/A	0		
Borate	135%	1.4	N/A	16.1		
Titanate	15.9%	10.6	23.9%	25.2		

Considering the stand-alone NPVs over the total project life of 25 years, the titanate option clearly has the best NPV of \$10.6MM primarily from the substantial fuel savings over the base case. The borate option has a high stand-alone IRR of 135% due to the minimal capital investment required. The borate option still achieves 20% of the fuel savings of the titanate option. Relative to the base case the titanate option is more economically attractive with an NPV of \$25.2MM and an IRR of 23.9%.

The titanate carries some technical risks though because it is a new technology. The performance of titanate as a direct causticizing agent and the subsequent acid purging of NPEs was proven successful on the lab scale. Some basic assumptions are made about the titanate char physical properties in order to configure the process presented in this report. The actual performance of the process must be determined through pilot plant trials to refine the process configuration and minimize risk. Hence, the capital cost could vary depending on the final process scope from pilot plant work. Borate, on the other hand, has been proven effective in conventional Tomlison based recovery cycles but only for partial auto-causticization.



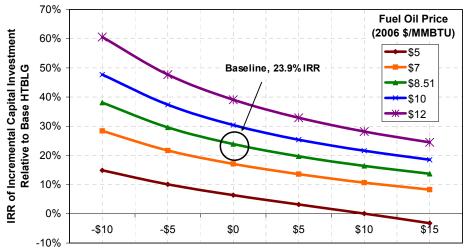
Below are sensitivity charts that show how the capital cost variance affects the economics.



## Figure 6

### **Electrical & Capital Cost Sensitivity**

Figure 7



Capital Cost Variance (\$ million)

Figure 6 shows IRR sensitivity to titanate capital cost variance. Also, the industrial electricity price was varied only around the baseline \$0 cost variance to check the sensitivity spread. Industrial electricity price variance has minimal effect on the IRR because it is simply not a large portion of the incremental operating cost. The fuel oil cost by far outweighs the effect of electricity cost. The IRR decreases from about 24% to 14% as the capital cost increases by \$15MM.

Figure 7 shows IRR sensitivity to titanate capital cost variance at varying fuel oil prices. Fuel oil price variance has a significant effect on the IRR. If fuel oil price rises to \$10 per MMBTU, then the IRR will increase from 23.9% to 31%. On the other hand a significant drop in fuel oil price will severely negate the economics of titanate as well. Therefore, fuel price trends must be carefully analyzed to predict economic performance for future projects.

### 9.0 Summary and Conclusions

The borate and titanate options are both effective auto and direct causticizing agents, respectively. Borate carries minimal capital investment and provides attractive payback and economics by alleviating the additional burden on the lime cycle that HTBLG causes and by saving some kiln fuel oil cost.

Titanate can replace up to 100% of the lime cycle and provide equal white liquor quality. This has been demonstrated on the lab scale. By assuming physical properties of the titanate being similar to lime mud we can extrapolate to a mill-scale process utilizing three staged agitated leaching tanks for reaction residence time followed by disc filtration. Acid leaching of a final titanate side stream achieves the required NPE purge of metals. Potassium remains in the system either as potassium titanate or potassium hydroxide and carbonate. This poses no problem without a Tomlison recovery boiler in the system. An additional hydraulic burden is put on the black liquor concentrator system due to the high flow rate of suspended titanate solids to 50% black liquor. It is not known exactly what the performance and maintenance impact will be with this additional 40% mass flow load increase. The additional suspended solids could enhance the crystallization process and reduce fouling for 80% solids liquor production by providing sites for crystallization to take place rather than on heat transfer surface areas. On the other hand, the added abrasive ness of the concentrated black liquor may pose a maintenance risk to the process equipment.

Titanate bears no advantage to the mill water balance except when compared to a conventional lime kiln wet scrubber system. In this case there is a 40 to 50% reduction in water lost to the sewer or atmosphere with the titanate option.

The titanate option economics are very favorable. The titanate recovery system is estimated at about \$32MM with an NPV and IRR, relative to the base case, of \$25.2MM and 23.9%. The main issue is scale-up from lab results. Pilot plant testing is required to firm up the process scope and capital cost estimate.

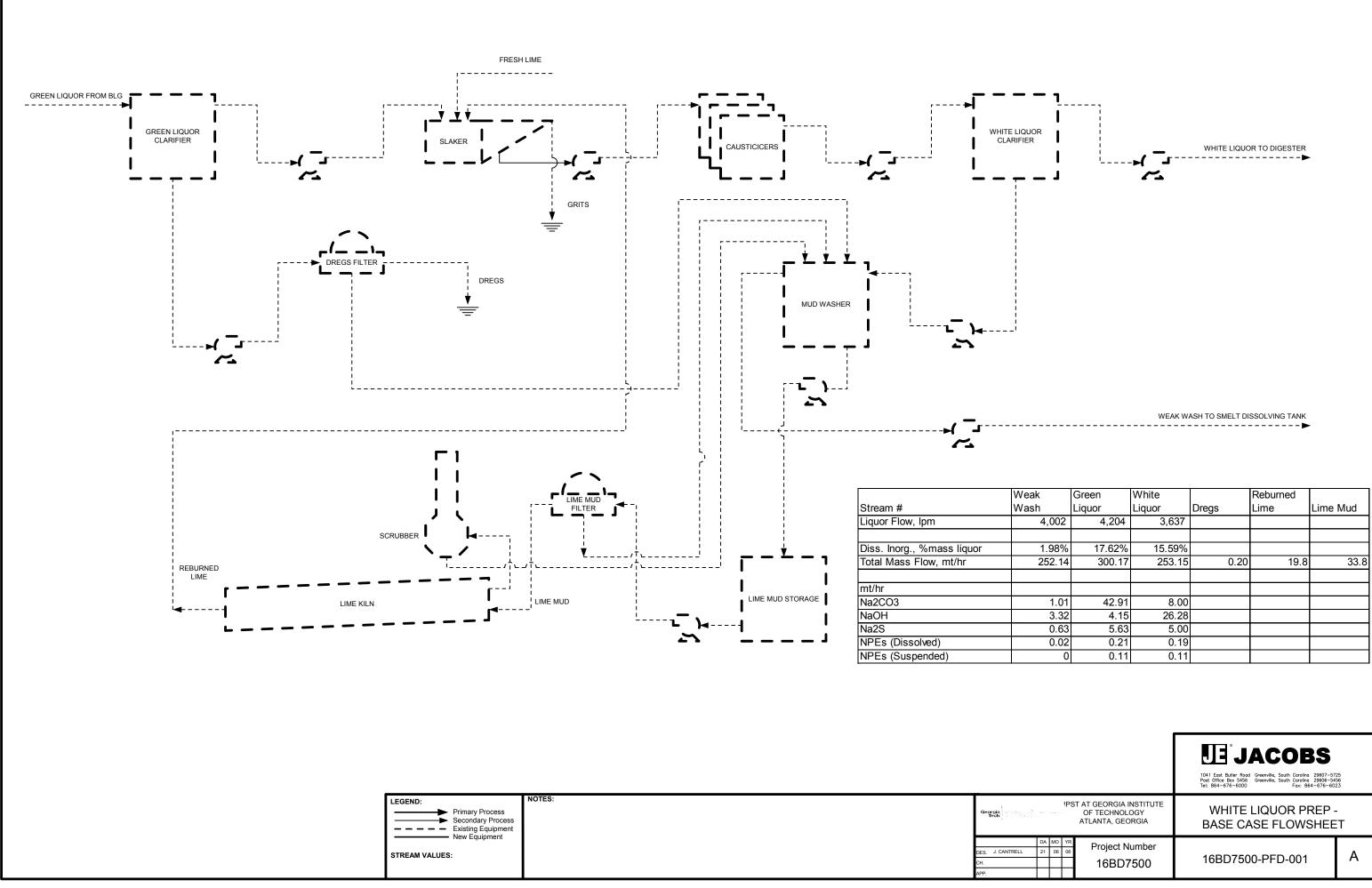


### 10.0 Abbreviations

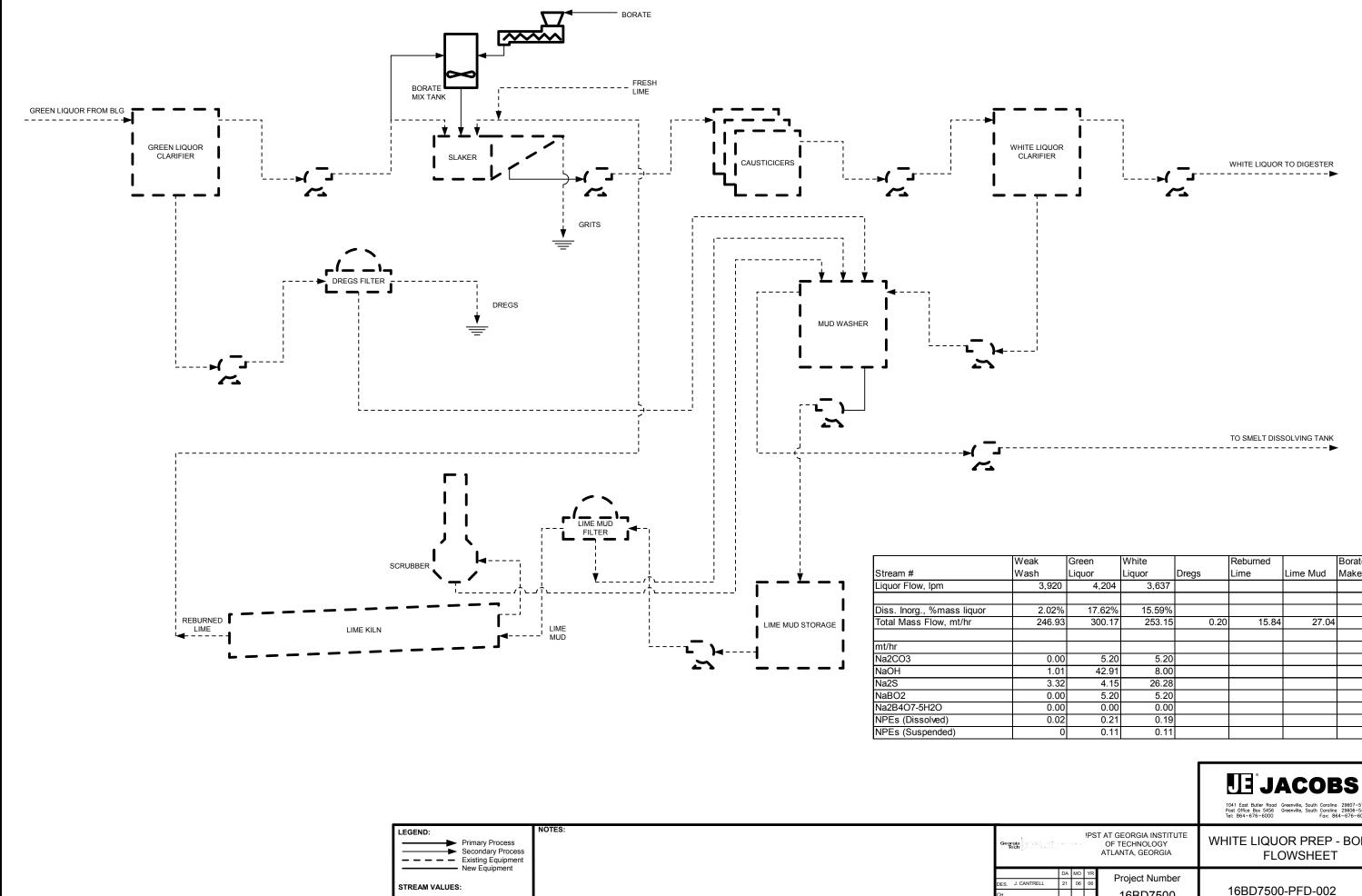
Black Liquor Solids Bone Dry	BLS bd
Electrostatic Precipitator Engineer, Procure, Construct	ESP EPC
Hardwood	HW
High Temperature Black Liquor Gasification	HTBLG
Higher Heating Value	HHV
Internal Rate of Return	IRR
Liters Per Minute	lpm
Machine Dry	md
Metric Ton	mt
Metric Tons Per Day	mtpd
Net Present Value	NPV
Non-Process Elements	NPEs
Short Tons Per Day	stpd
Softwood	SŴ
Total Installed Cost	TIC
Total Titratable Alkali	TTA

#### 11.0 APPENDICES

APPENDIX A – PROCESS FLOW DIAGRAMS

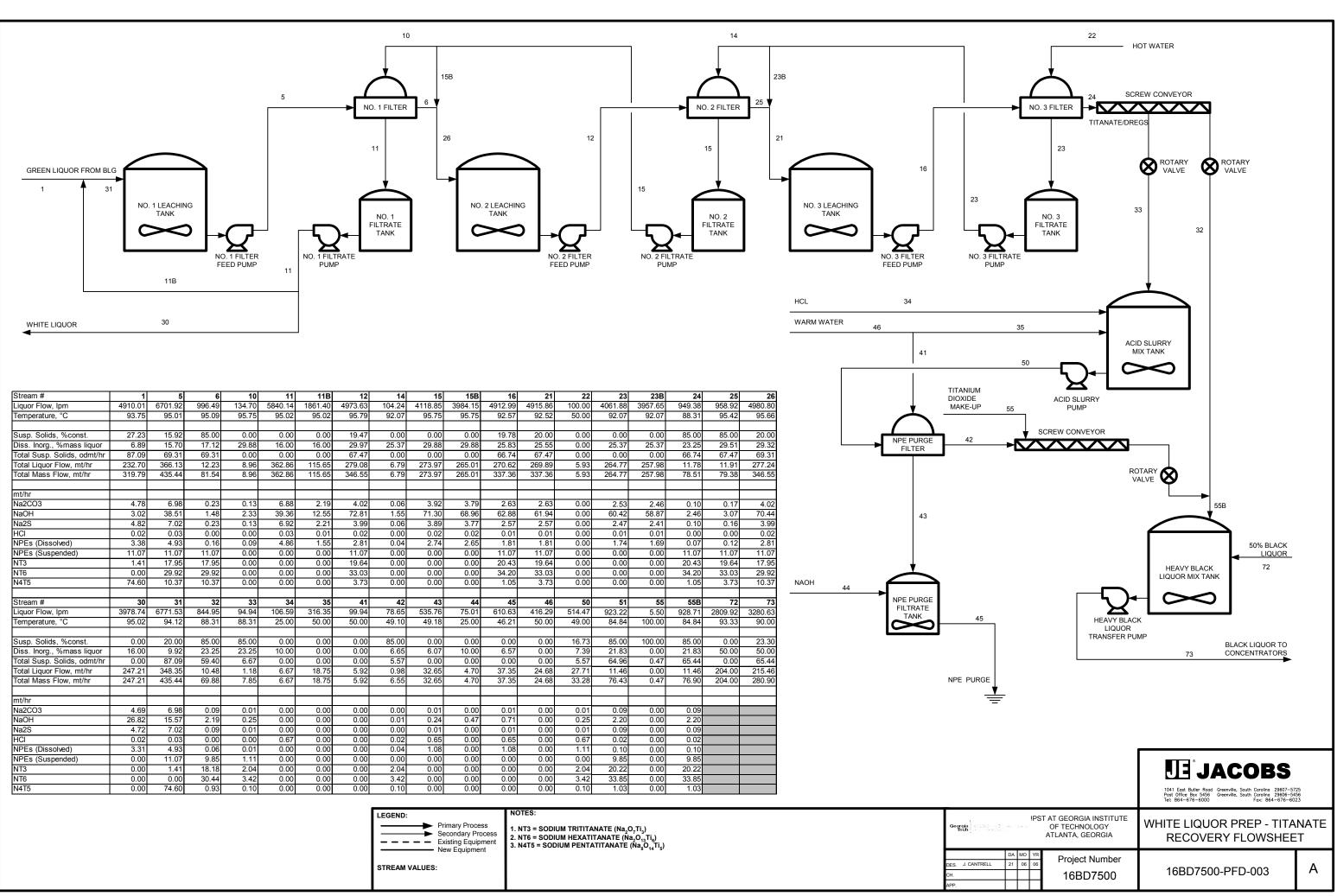


(	Green	White		Reburned	
า	Liquor	Liquor	Dregs	Lime	Lime Mud
4,002	4,204	3,637			
1.98%	17.62%	15.59%			
252.14	300.17	253.15	0.20	19.8	33.8
1.01	42.91	8.00			
3.32	4.15	26.28			
0.63	5.63	5.00			
0.02	0.21	0.19			
0	0.11	0.11			



	Green	White		Reburned		Borate
	Liquor	Liquor	Dregs	Lime	Lime Mud	Makeup
)	4,204	3,637				
6	17.62%	15.59%				
3	300.17	253.15	0.20	15.84	27.04	
0	5.20	5.20				
1	42.91	8.00				
2	4.15	26.28				
0	5.20	5.20				
0	0.00	0.00				0.14
2	0.21	0.19				
0	0.11	0.11				

				DE JACOBS 1041 East Butler Road Tel: 864-676-6000 Greenvile, South Carolina 29607-57 Greenvile, South Carolina 29607-57 Greenvile, South Carolina 29607-57 Fax: 864-676-600	56
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DA	MO	YR	Project Number		
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			16BD7500	16BD7500-PFD-002	



LEGEND:	NOTES:	
Primary Process     Secondary Process     Existing Equipment     New Equipment	1. NT3 = SODIUM TRITITANATE (Na <sub>2</sub> O <sub>7</sub> Ti <sub>3</sub> ) 2. NT6 = SODIUM HEXATITANATE (Na <sub>2</sub> O <sub>13</sub> Ti <sub>6</sub> ) 3. N4T5 = SODIUM PENTATITANATE (Na <sub>8</sub> O <sub>14</sub> Ti <sub>5</sub> )	Georgia de activitation de la constantia
STREAM VALUES:		DES. J. CANTRELL
		CH.
		APP.

### APPENDIX B – TYPICAL BASE MILL CAUSTIC ROOM POWER

Equipment	Connected HP (450 tpd RBL)
Green Liquor Clarifiers	7.5
GLC Overflow Pumps	80
GLC Underflow Pump	60
Green Liquor Storage Tank Pump	25
Slaker Scrubber Pump	15
Slaker Scrubber Recirc. Pump	60
Slaker Agitator	40
Slaker Grits Screw	3
Nos. 1 - 4 Causticizers Agitators	120
Causticized Liquor Pump	75
Dregs Precoat Filter	5
Dregs Filter Discharge Screw	25
Dregs Filtrate Pump	7.5
Dregs Filter Dump Tank Pump	2
Dregs Filter Purge Pump	125
Dregs Filter Vacuum Pump	75 50
Weak Wash Pump Weak Wash Agitator	50 4
White Liquor Clarifier	4
WLC Overflow Pump	50
WLC Underflow Pump	60
Mud Washer	4
Weak Wash Pump	25
Washed Mud Pump	40
Mud Storage Agitators	35
Lime Mud Recirc. Pump	25
LM to Dregs Filter Precoat Pump	20
LM to Mud Filter Precoat Pump	20
Mud Filter Feed Pumps	60
LM Filter	60
LM Filter Vacuum Pumps	800
LM Filter Filtrate Pumps	40
LM Filter Belt Conveyors	15
LM Filter Screw Conveyors	40
Mill Water Pump	75 125
Kiln Feed Conveyor Kiln ID Fan	900
Kiln Scrubber Recirc. Pump	80
Kiln Sump Pump	30
Kiln Drive	200
Kiln Trunion Cooling Water Pump	15
Kiln Primary Air Fan	55
Kiln Secondary Air Fan	55
Atomizing Air Blower	40
Purchase Lime Conveyor	10
Hot Lime Drag Conveyor	20
Lime Crusher	5
Lime Bucket Elevator	10
Total Connected Power	3700
Total Connected Power @ 525 tpd RBL Total Operating Power (80% of connected)	4320 3460
Titanate System Connected Power	2910
Total Operating Power (80% of connected)	2330
Difference	1130

APPENDIX C – BORATE STOICHIOMETRY

Sodium tetraborate (makeup) reacts with sodium carbonate in the gasifier:

 $Na_2B_4O_7 + 5 Na_2CO_3 \rightarrow 4 Na_3BO_3 + 5 CO_2$ 

> Sodium is bound up by sodium metaborate within the gasifier:

 $2 \text{ NaBO}_2 + \text{Na}_2\text{CO}_3 \leftrightarrow \text{Na}_4\text{B}_2\text{O}_7 + \text{CO}_2$ 

 $NaBO_2 + Na_2CO_3 \leftrightarrow Na_3BO_3 + CO_2$ 

> The caustic is later recovered by hydrolysis:

 $Na_3BO_3 + H_2O \leftrightarrow 2 NaOH(aq) + NaBO_2 (aq)$ 

> Borate is soluble and circulates with the pulping liquor

The amount of sodium tetraborate pentahydrate makeup required is as follows per U.S. Borax:

# Ton Neobor Makeup Ton of Lime Replaced = 1.3 x A x B x C / D

where: A = Lime Availability, wt% of CaO in lime	= 90%
B = White Liquor Causticity , mole%	= 81%
C = Borate Loss Rate, % of Borate Used	= 3%

Borate loss rate can be assumed equal to Na loss rate from the liquor cycle. However, the Na loss rate has to be expressed as a percentage of the total amount of Na passed through digester (or in circulation).

D = Borate AC Reaction Efficiency, % = 80%

APPENDIX D – TITANATE STOICHIOMETRY

Sodium is bound up by titanates within the gasifier:

 $Na_2CO_3 + 3 TiO_2 (s) \leftrightarrow Na_2O.3TiO_2 (s) + CO_2 (g)$ 

7 Na<sub>2</sub>CO<sub>3</sub> + 5 (Na<sub>2</sub>O-3TiO<sub>2</sub>) (s)  $\leftrightarrow$  3 (4Na<sub>2</sub>O-5TiO<sub>2</sub>) (s) + 7 CO<sub>2</sub> (g)

 $Na_2O-6TiO_2(s) + Na_2CO_3(s) \leftrightarrow 2 (Na_2O-3TiO_2) (s) + CO_2 (g)$ 

[Abbreviated NT3, N4T5, NT6]

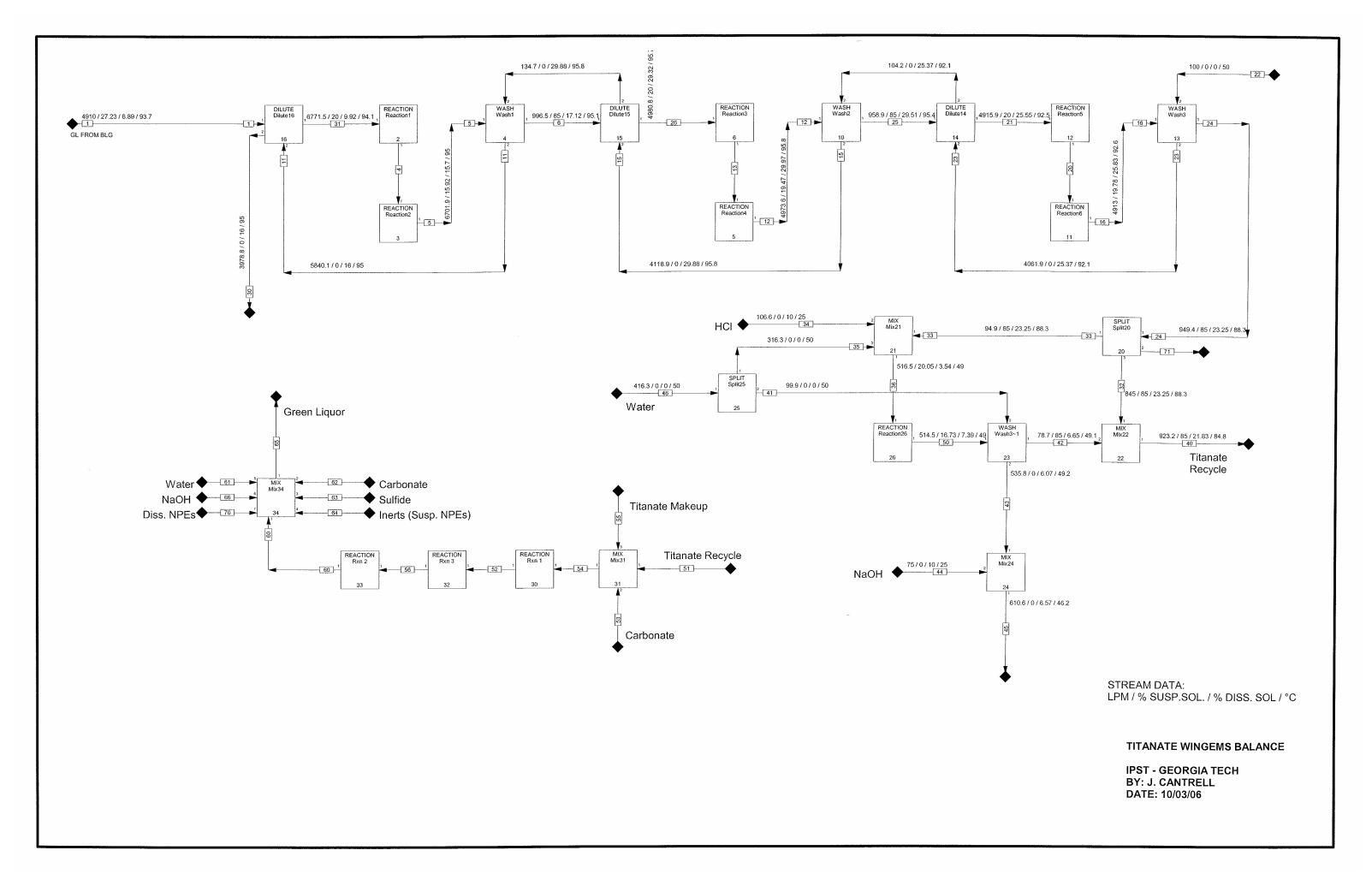
> The caustic is later recovered by hydrolysis:

3 (4Na<sub>2</sub>O-5TiO<sub>2</sub>)(s) + 7 H<sub>2</sub>O  $\leftrightarrow$  14 NaOH(aq) + 5 (Na<sub>2</sub>O-3TiO<sub>2</sub>)(s)

2 (Na<sub>2</sub>O-3TiO<sub>2</sub>) (s) + H<sub>2</sub>O  $\leftrightarrow$  2 NaOH (aq) + Na<sub>2</sub>O-6TiO<sub>2</sub> (s) (65%)



### APPENDIX E – WINGEMS TITANATE BALANCE FLOWSHEET



### APPENDIX F – DETAILED FINANCIAL ANALYSES

	Year	0	1	2	3	4	5	6	7	8	9	10	11	12
Total Net Cash Flow														
Base Case		(620,146)	(1,108,896)	(1,153,910)	(1,200,518)	(1,248,771)	(1,298,750)	(1,350,540)	(1,403,909)	(1,458,026)	(1,514,354)	(1,572,981)	(1,633,995)	(1,697,505)
NPV (\$ million)	(14.6	) (620,146)	(1,009,005)	(955,381)	(904,432)	(856,036)	(810,097)	(766,516)	(725,029)	(685,147)	(647,513)	(611,993)	(578,464)	(546,813)
IRR														
Borate		(89,921)	118,033	122,659	127,499	132,566	137,864	143,402	149,233	155,498	162,007	168,769	175,796	183,097
NPV (\$ million)	1.4	(89,921)	107,400	101,555	96,054	90,874	85,993	81,390	77,069	73,071	69,271	65,662	62,235	58,980
IRR	135%	5												
Titanate		(16,302,077)	2,026,089	2,089,821	2,161,543	2,241,917	2,330,857	2,428,281	2,542,567	2,697,876	2,858,186	3,023,697	3,194,744	3,371,163
NPV (\$ million)	10.6	(16,302,077)	1,843,575	1,730,269	1,628,436	1,536,841	1,453,875	1,378,202	1,313,072	1,267,770	1,222,113	1,176,417	1,130,997	1,085,944
IRR	15.9%	5												
Total Net Cash Flow Variance from Base														
Borate		530,224	1,226,929	1,276,569	1,328,018	1,381,337	1,436,614	1,493,942	1,553,142	1,613,524	1,676,361	1,741,751	1,809,791	1,880,601
NPV of Variance (\$ million)	16.1	530,224	1,116,405	1,056,937	1,000,486	946,910	896,090	847,906	802,098	758,218	716,784	677,656	640,699	605,793
IRR on Variance														
Titanate		(15,681,932)	3,134,985	3,243,731	3,362,061	3,490,688	3,629,607	3,778,821	3,946,476	4,155,903	4,372,541	4,596,679	4,828,739	5,068,668
NPV of Variance (\$ million)	25.2	(15,681,932)	2,852,580	2,685,650	2,532,868	2,392,876	2,263,972	2,144,718	2,038,101	1,952,917	1,869,625	1,788,411	1,709,461	1,632,757
IRR on Variance	23.9%	5												

	Year	13	14	15	16	17	18	19	20	21	22	23	24	25
Total Net Cash Flow														
Base Case		(1,763,591)	(1,832,377)	(1,903,951)	(1,978,443)	(2,055,952)	(2,136,616)	(2,220,544)	(2,326,614)	(2,420,162)	(2,514,719)	(2,613,103)	(2,715,469)	(2,799,128)
NPV (\$ million)		(516,925)	(488,705)	(462,051)	(436,878)	(413,097)	(390,632)	(369,405)	(352,185)	(333,344)	(315,167)	(297,995)	(281,774)	(264,290)
IRR														
Borate		190,683	198,566	206,758	215,270	224,117	233,309	242,865	250,078	260,011	270,738	281,887	293,476	308,834
NPV (\$ million)		55,891	52,959	50,176	47,536	45,031	42,655	40,403	37,855	35,813	33,931	32,146	30,453	29,160
IRR														
Titanate		3,553,686	3,742,040	3,936,975	4,138,239	4,346,599	4,561,824	4,784,705	4,522,678	4,690,856	4,937,644	5,193,091	5,457,546	6,331,983
NPV (\$ million)		1,041,619	998,023	955,426	913,803	873,351	834,027	795,974	684,608	646,101	618,829	592,215	566,308	597,857
IRR														
Total Net Cash Flow Variance from Base														
<b>-</b> /														
Borate		1,954,275	2,030,943	2,110,708	2,193,713	2,280,068	2,369,926	2,463,408	2,576,692	2,680,174	2,785,457	2,894,990	3,008,945	3,107,962
NPV of Variance (\$ million)		572,817	541,664	512,227	484,414	458,128	433,288	409,808	390,040	369,157	349,098	330,142	312,226	293,449
IRR on Variance														
Titanate		5,317,277	5,574,417	5,840,926	6,116,682	6,402,550	6,698,441	7,005,249	6,849,292	7,111,019	7,452,363	7,806,195	8,173,015	9,131,112
NPV of Variance (\$ million)		1,558,545	1,486,729	1,417,478	1,350,681	1,286,448	1,224,659	1,165,380	1,036,792	979,446	933,995	890,210	848,082	862,147
IRR on Variance														

#### Base Case

	Year	0	1	2	3	4	5	6	7	8	9	10	11	12
Avoided Cost Savings														
Subtotal - Avoided Cost Savings			0	0	0	0	0	0	0	0	0	0	0	0
Direct Operating Costs														
Operations & Maintenance			1,820,000	1,892,800	1,968,512	2,047,252	2,129,143	2,214,308	2,302,881	2,394,996	2,490,796	2,590,427	2,694,045	2,801,806
Subtotal - Operating Costs			1,820,000	1,892,800	1,968,512	2,047,252	2,129,143	2,214,308	2,302,881	2,394,996	2,490,796	2,590,427	2,694,045	2,801,806
Financing														
Interest		46,080	44,160	42,240	40,320	38,400	36,480	34,560	32,640	30,720	28,800	26,880	24,960	23,040
Principal		24,000	24,000	24,000	24,000	24,000	24,000	24,000	24,000	24,000	24,000	24,000	24,000	24,000
Cumulative Principal		24,000	48,000	72,000	96,000	120,000	144,000	168,000	192,000	216,000	240,000	264,000	288,000	312,000
Subtotal - Financing		70,080	68,160	66,240	64,320	62,400	60,480	58,560	56,640	54,720	52,800	50,880	48,960	47,040
Total Expenses Before Taxes		70,080	1,888,160	1,959,040	2,032,832	2,109,652	2,189,623	2,272,868	2,359,521	2,449,716	2,543,596	2,641,307	2,743,005	2,848,846
Income Taxes		(49,934)	(779,264)	(805,130)	(832,314)	(860,882)	(890,873)	(922,328)	(955,611)	(991,690)	(1,029,241)	(1,068,326)	(1,109,010)	(1,151,342)
Total Expenses After Taxes		20,146	1,108,896	1,153,910	1,200,518	1,248,771	1,298,750	1,350,540	1,403,909	1,458,026	1,514,354	1,572,981	1,633,995	1,697,505
Net Cash Flow from Operations		(20,146)	(1,108,896)	(1,153,910)	(1,200,518)	(1,248,771)	(1,298,750)	(1,350,540)	(1,403,909)	(1,458,026)	(1,514,354)	(1,572,981)	(1,633,995)	(1,697,505)
Equity Capital Invested		(600,000)												
Total Net Cash Flow		(620,146)	(1,108,896)	(1,153,910)	(1,200,518)	(1,248,771)	(1,298,750)	(1,350,540)	(1,403,909)	(1,458,026)	(1,514,354)	(1,572,981)	(1,633,995)	(1,697,505)
Discount Factor		1.0	1.1	1.2	1.3	1.5	1.6	1.8	1.9	2.1	2.3	2.6	2.8	3.1
NPV (\$ million)	(14.6)	(620,146)	(1,009,005)	(955,381)	(904,432)	(856,036)	(810,097)	(766,516)	(725,029)	(685,147)	(647,513)	(611,993)	(578,464)	(546,813)
IRR														
Total Capital Invested	1,200,000													
Discount Rate	1.099													

#### Base Case

	Year	15 16	17	18	19	20	21	22	23	24	25
Avoided Cost Savings											
Subtotal - Avoided Cost Savings		0 0	0	0	0	0	0	0	0	0	0
Direct Operating Costs											
Operations & Maintenance	3,151,65	3,277,717	3,408,826	3,545,179	3,686,986	3,834,466	3,987,844	4,147,358	4,313,252	4,485,782	4,665,214
Subtotal - Operating Costs	3,151,65	3,277,717	3,408,826	3,545,179	3,686,986	3,834,466	3,987,844	4,147,358	4,313,252	4,485,782	4,665,214
Financing											
Interest	17,28	15,360	13,440	11,520	9,600	7,680	5,760	3,840	1,920	0	
Principal	24,00	24,000	24,000	24,000	24,000	24,000	24,000	24,000	24,000	24,000	
Cumulative Principal	384,00	408,000	432,000	456,000	480,000	504,000	528,000	552,000	576,000	600,000	
Subtotal - Financing	41,28	39,360	37,440	35,520	33,600	31,680	29,760	27,840	25,920	24,000	
Total Expenses Before Taxes	3,192,93	31 3,317,077	3,446,266	3,580,699	3,720,586	3,866,146	4,017,604	4,175,198	4,339,172	4,509,782	4,665,214
Income Taxes	(1,288,98	30) (1,338,634)	(1,390,314)	(1,444,083)	(1,500,042)	(1,539,532)	(1,597,442)	(1,660,479)	(1,726,069)	(1,794,313)	(1,866,085)
Total Expenses After Taxes	1,903,95	51 1,978,443	2,055,952	2,136,616	2,220,544	2,326,614	2,420,162	2,514,719	2,613,103	2,715,469	2,799,128
Net Cash Flow from Operations	(1,903,95	51) (1,978,443)	(2,055,952)	(2,136,616)	(2,220,544)	(2,326,614)	(2,420,162)	(2,514,719)	(2,613,103)	(2,715,469)	(2,799,128)
Equity Capital Invested											
Total Net Cash Flow	(1,903,95	51) (1,978,443)	(2,055,952)	(2,136,616)	(2,220,544)	(2,326,614)	(2,420,162)	(2,514,719)	(2,613,103)	(2,715,469)	(2,799,128)
Discount Factor	4	.1 4.5	5.0	5.5	6.0	6.6	7.3	8.0	8.8	9.6	10.6
NPV (\$ million)	(462,05	(436,878)	(413,097)	(390,632)	(369,405)	(352,185)	(333,344)	(315,167)	(297,995)	(281,774)	(264,290)
IRR											

Total Capital Invested

Discount Rate

#### Borate Case

	Year	0	1	2	3	4	5	6	7	8	9	10	11	12
Avoided Cost Savings														
Avoided Lime Kiln Fuel Oil			1,923,483	2,000,422	2,080,439	2,163,657	2,250,203	2,340,211	2,433,820	2,531,172	2,632,419	2,737,716	2,847,225	2,961,114
Avoided Electricity Purchases			262,669	273,176	284,103	295,467	307,286	319,577	332,361	345,655	359,481	373,860	388,815	404,367
Subtotal - Avoided Cost Savings			2,186,152	2,273,598	2,364,542	2,459,124	2,557,489	2,659,789	2,766,180	2,876,827	2,991,900	3,111,576	3,236,040	3,365,481
Direct Operating Costs														
Borate			520,300	541,112	562,756	585,267	608,677	633,024	658,345	684,679	712,066	740,549	770,171	800,978
<b>Operations &amp; Maintenance</b>			1,465,048	1,523,650	1,584,596	1,647,980	1,713,899	1,782,455	1,853,753	1,927,903	2,005,019	2,085,220	2,168,629	2,255,374
Subtotal - Operating Costs			1,985,348	2,064,762	2,147,352	2,233,246	2,322,576	2,415,479	2,512,098	2,612,582	2,717,086	2,825,769	2,938,800	3,056,352
Financing														
Interest		6,682	6,403	6,125	5,846	5,568	5,290	5,011	4,733	4,454	4,176	3,898	3,619	3,341
Principal		3,480	3,480	3,480	3,480	3,480	3,480	3,480	3,480	3,480	3,480	3,480	3,480	3,480
Cumulative Principal		3,480	6,960	10,440	13,920	17,400	20,880	24,360	27,840	31,320	34,800	38,280	41,760	45,240
Subtotal - Financing		10,162	9,883	9,605	9,326	9,048	8,770	8,491	8,213	7,934	7,656	7,378	7,099	6,821
Total Expenses Before Taxes		10,162	1,995,231	2,074,367	2,156,679	2,242,294	2,331,346	2,423,971	2,520,311	2,620,517	2,724,742	2,833,147	2,945,899	3,063,173
Income Taxes		(7,240)	72,888	76,573	80,364	84,264	88,279	92,416	96,636	100,813	105,152	109,660	114,344	119,212
Total Expenses After Taxes		2,921	2,068,120	2,150,940	2,237,043	2,326,558	2,419,625	2,516,387	2,616,947	2,721,330	2,829,894	2,942,807	3,060,243	3,182,385
Net Cash Flow from Operations		(2,921)	118,033	122,659	127,499	132,566	137,864	143,402	149,233	155,498	162,007	168,769	175,796	183,097
Equity Capital Invested		(87,000)												
Total Net Cash Flow		(89,921)	118,033	122,659	127,499	132,566	137,864	143,402	149,233	155,498	162,007	168,769	175,796	183,097
Discount Factor		1.0	1.1	1.2	1.3	1.5	1.6	1.8	1.9	2.1	2.3	2.6	2.8	3.1
NPV (\$ million)	1.4	(89,921)	107,400	101,555	96,054	90,874	85,993	81,390	77,069	73,071	69,271	65,662	62,235	58,980
IRR	135%													
Total Capital Invested	174,000													
Discount Rate	1.099													

#### Borate Case

	Year	13	14	15	16	17	18	19	20	21	22	23	24	25
Avoided Cost Savings														
Avoided Lime Kiln Fuel Oil		3,079,558	3,202,741	3,330,850	3,464,084	3,602,648	3,746,753	3,896,624	4,052,489	4,214,588	4,383,172	4,558,499	4,740,838	4,930,472
Avoided Electricity Purchases		420,542	437,364	454,858	473,053	491,975	511,654	532,120	553,405	575,541	598,563	622,505	647,405	673,301
Subtotal - Avoided Cost Savings		3,500,100	3,640,104	3,785,709	3,937,137	4,094,622	4,258,407	4,428,744	4,605,893	4,790,129	4,981,734	5,181,004	5,388,244	5,603,773
Direct Operating Costs														
Borate		833,017	866,338	900,991	937,031	974,512	1,013,492	1,054,032	1,096,193	1,140,041	1,185,643	1,233,069	1,282,391	1,333,687
Operations & Maintenance		2,345,589	2,439,413	2,536,989	2,638,469	2,744,007	2,853,768	2,967,918	3,086,635	3,210,101	3,338,505	3,472,045	3,610,927	3,755,364
Subtotal - Operating Costs		3,178,606	3,305,750	3,437,980	3,575,499	3,718,519	3,867,260	4,021,951	4,182,829	4,350,142	4,524,147	4,705,113	4,893,318	5,089,051
Financing														
Interest		3,062	2,784	2,506	2,227	1,949	1,670	1,392	1,114	835	557	278	0	
Principal		3,480	3,480	3,480	3,480	3,480	3,480	3,480	3,480	3,480	3,480	3,480	3,480	
Cumulative Principal		48,720	52,200	55,680	59,160	62,640	66,120	69,600	73,080	76,560	80,040	83,520	87,000	
Subtotal - Financing		6,542	6,264	5,986	5,707	5,429	5,150	4,872	4,594	4,315	4,037	3,758	3,480	
Total Expenses Before Taxes		3,185,148	3,312,014	3,443,966	3,581,207	3,723,948	3,872,411	4,026,823	4,187,422	4,354,457	4,528,184	4,708,872	4,896,798	5,089,051
									100.000		100.010			
Income Taxes		124,269	129,525	134,985	140,661	146,558	152,687	159,056	168,393	175,661	182,812	190,245	197,970	205,889
Total Expanses After Taxes		0 000 447	2 444 520	0.570.054	0 704 007	0.070.500	4 005 000	4 405 070	4 955 945	4 500 440	4 740 000	4 000 440	E 004 700	5 004 040
Total Expenses After Taxes		3,309,417	3,441,539	3,578,951	3,721,867	3,870,506	4,025,098	4,185,879	4,355,815	4,530,118	4,710,996	4,899,116	5,094,768	5,294,940
Net Cash Flow from Operations		190.683	198,566	206,758	215,270	224,117	233,309	242,865	250,078	260,011	270,738	281,887	293.476	308,834
		100,000	130,300	200,700	210,270	224,117	200,000	242,000	200,070	200,011	210,100	201,007	200,470	000,004
Equity Capital Invested														
1.3.1.														
Total Net Cash Flow		190,683	198,566	206,758	215,270	224,117	233,309	242,865	250,078	260,011	270,738	281,887	293,476	308,834
Discount Factor		3.4	3.7	4.1	4.5	5.0	5.5	6.0	6.6	7.3	8.0	8.8	9.6	10.6
NPV (\$ million)		55,891	52,959	50,176	47,536	45,031	42,655	40,403	37,855	35,813	33,931	32,146	30,453	29,160
IRR														

Total Capital Invested

Discount Rate

#### Titanate Case

	Year	0	1	2	3	4	5	6	7	8	9	10	11	12
Avoided Cost Savings														
Avoided Lime Kiln Fuel Oil			9,617,415	10,002,112	10,402,196	10,818,284	11,251,015	11,701,056	12,169,098	12,655,862	13,162,096	13,688,580	14,236,124	14,805,569
Avoided Electricity Purchases			428,925	446,082	463,926	482,483	501,782	521,853	542,727	564,437	587,014	610,495	634,914	660,311
Subtotal - Avoided Cost Savings			10,046,340	10,448,194	10,866,122	11,300,767	11,752,797	12,222,909	12,711,826	13,220,299	13,749,111	14,299,075	14,871,038	15,465,879
Direct Operating Costs														
Titanium Dioxide			1,972,143	2,051,028	2,133,069	2,218,392	2,307,128	2,399,413	2,495,390	2,595,205	2,699,013	2,806,974	2,919,253	3,036,023
Hydrochloric Acid			780,481	811,700	844,168	877,935	913,053	2,399,413 949,575	987,558	1,027,060	1,068,142	1,110,868	1,155,303	1,201,515
Sodium Hydroxide			1,505,306	1,565,518	1,628,139	1,693,265	1,760,995	1,831,435	1,904,692	1,980,880	2,060,142	2,142,520	2,228,221	2,317,350
Incremental Waste Treatment Costs			30,999	32,239	33,529	34,870	36,265	37,716	39,224	40,793	42,425	44,122	45,887	47,722
Operations & Maintenance			1,640,340	1,705,954	1,774,192	1,845,159	1,918,966	1,995,724	2,075,553	2,158,576	2,244,919	2,334,715	2,428,104	2,525,228
Subtotal - Operating Costs			5,929,269	6,166,440	6,413,098	6,669,622	6,936,406	7,213,863	7,502,417	7,802,514	2,244,919 8,114,614	2,334,715 8,439,199	2,428,104 8,776,767	2,525,228 9,127,838
Subtotal - Operating Costs			5,525,205	0,100,440	0,413,030	0,009,022	0,930,400	7,215,005	7,502,417	7,002,014	0,114,014	0,433,133	0,770,707	9,127,000
Financing														
Interest		1,211,328	1,160,856	1,110,384	1,059,912	1,009,440	958,968	908,496	858,024	807,552	757,080	706,608	656,136	605,664
Principal		630,900	630,900	630,900	630,900	630,900	630,900	630,900	630,900	630,900	630,900	630,900	630,900	630,900
Cumulative Principal		630,900	1,261,800	1,892,700	2,523,600	3,154,500	3,785,400	4,416,300	5,047,200	5,678,100	6,309,000	6,939,900	7,570,800	8,201,700
Subtotal - Financing		1,842,228	1,791,756	1,741,284	1,690,812	1,640,340	1,589,868	1,539,396	1,488,924	1,438,452	1,387,980	1,337,508	1,287,036	1,236,564
Total Currents Defens Tours		4 040 000	7 704 005	7 007 704	0 400 040	0.000.000	0 500 074	0 750 050	0.004.044	0.040.000	0 500 504	0 770 707	40.000.000	40.004.400
Total Expenses Before Taxes		1,842,228	7,721,025	7,907,724	8,103,910	8,309,962	8,526,274	8,753,259	8,991,341	9,240,966	9,502,594	9,776,707	10,063,803	10,364,402
Income Taxes		(1,312,651)	299,226	450,649	600,670	748,888	895,666	1,041,370	1,177,917	1,281,456	1,388,330	1,498,671	1,612,491	1,730,315
Total Expenses After Taxes		529,577	8,020,251	8,358,373	8,704,579	9,058,849	9,421,940	9,794,629	10,169,258	10,522,422	10,890,924	11,275,378	11,676,294	12,094,716
Net Cash Flow from Operations		(529,577)	2,026,089	2,089,821	2,161,543	2,241,917	2,330,857	2,428,281	2,542,567	2,697,876	2,858,186	3,023,697	3,194,744	3,371,163
		(020,011)	2,020,000	2,000,02	2,101,010	2,2 ,0	2,000,001	2,120,201	2,012,007	2,001,010	2,000,100	0,020,000	0,101,111	0,01 1,100
Equity Capital Invested		(15,772,500)												
		(10,000,077)	0.000.000	0.000.004	0 404 540	0.044.047	0.000.057	0.400.004	0 5 40 507	0.007.070	0.050.400	0.000.007	0.404.744	0.074.400
Total Net Cash Flow		(16,302,077)	2,026,089	2,089,821	2,161,543	2,241,917	2,330,857	2,428,281	2,542,567	2,697,876	2,858,186	3,023,697	3,194,744	3,371,163
Discount Factor	40.0	1.0	1.1	1.2	1.3	1.5	1.6	1.8	1.9	2.1	2.3	2.6	2.8	3.1
NPV (\$ million)	10.6	(16,302,077)	1,843,575	1,730,269	1,628,436	1,536,841	1,453,875	1,378,202	1,313,072	1,267,770	1,222,113	1,176,417	1,130,997	1,085,944
IRR	15.9%													
Total Capital Invested	31,545,000													
Discount Rate	1.099													

#### Titanate Case

	Year	13	14	15	16	17	18	19	20	21	22	23	24	25
Avoided Cost Savings														
Avoided Lime Kiln Fuel Oil		15,397,791	16,013,703	16,654,251	17,320,421	18,013,238	18,733,767	19,483,118	20,262,443	21,072,941	21,915,858	22,792,493	23,704,192	24,652,360
Avoided Electricity Purchases		686,723	714,192	742,760	772,470	803,369	835,504	868,924	903,681	939,828	977,422	1,016,518	1,057,179	1,099,466
Subtotal - Avoided Cost Savings		16,084,515	16,727,895	17,397,011	18,092,892	18,816,607	19,569,271	20,352,042	21,166,124	22,012,769	22,893,280	23,809,011	24,761,371	25,751,826
Discret On continue Oceate														
Direct Operating Costs Titanium Dioxide		0.457.404	0.000 700	0 445 440	0 554 747	0.000 700	0.044.500	0.005.400	4 455 007	4 004 007	4 404 050	4 070 040	4 000 774	5 055 004
		3,157,464	3,283,762	3,415,113	3,551,717	3,693,786	3,841,538	3,995,199	4,155,007	4,321,207	4,494,056	4,673,818	4,860,771	5,055,201
Hydrochloric Acid		1,249,575	1,299,558	1,351,541	1,405,602	1,461,826	1,520,300	1,581,112	1,644,356	1,710,130	1,778,535	1,849,677	1,923,664	2,000,610
Sodium Hydroxide		2,410,044	2,506,445	2,606,703	2,710,971	2,819,410	2,932,187	3,049,474	3,171,453	3,298,311	3,430,244	3,567,453	3,710,151	3,858,557
Incremental Waste Treatment Costs		49,631	51,616	53,681	55,828	58,061	60,384	62,799	65,311	67,924	70,640	73,466	76,405	79,461
Operations & Maintenance		2,626,237	2,731,287	2,840,538	2,954,160	3,072,326	3,195,219	3,323,028	3,455,949	3,594,187	3,737,954	3,887,473	4,042,971	4,204,690
Subtotal - Operating Costs		9,492,951	9,872,669	10,267,576	10,678,279	11,105,410	11,549,627	12,011,612	12,492,076	12,991,759	13,511,429	14,051,887	14,613,962	15,198,521
Financing														
Interest		555,192	504,720	454,248	403,776	353,304	302,832	252,360	201,888	151,416	100,944	50,472	0	
Principal		630,900	630,900	630,900	630,900	630,900	630,900	630,900	630,900	630,900	630,900	630,900	630,900	
Cumulative Principal		8,832,600	9,463,500	10,094,400	10,725,300	11,356,200	11.987.100	12,618,000	13,248,900	13,879,800	14,510,700	15,141,600	15,772,500	
Subtotal - Financing		1,186,092	1,135,620	1,085,148	1,034,676	984,204	933,732	883,260	832,788	782,316	731,844	681,372	630,900	
		1,100,002	1,100,020	1,000,140	1,001,010	001,201	000,702	000,200	002,100	102,010	101,011	001,072	000,000	
Total Expenses Before Taxes		10,679,043	11,008,289	11,352,724	11,712,955	12,089,614	12,483,359	12,894,872	13,324,864	13,774,075	14,243,273	14,733,259	15,244,862	15,198,521
Income Taxes		1,851,786	1,977,566	2,107,312	2,241,698	2,380,394	2,524,089	2,672,465	3,318,582	3,547,838	3,712,363	3,882,661	4,058,964	4,221,322
Total Expenses After Taxes		12,530,829	12,985,855	13,460,036	13,954,653	14,470,009	15,007,447	15,567,337	16.643.446	17,321,913	17,955,636	18.615.920	19,303,826	19,419,843
Net Cash Flow from Operations		3,553,686	3,742,040	3,936,975	4,138,239	4,346,599	4,561,824	4,784,705	4,522,678	4,690,856	4,937,644	5,193,091	5,457,546	6,331,983
Equity Capital Invested														
Total Net Cash Flow		3,553,686	3,742,040	3,936,975	4,138,239	4,346,599	4,561,824	4,784,705	4,522,678	4,690,856	4,937,644	5,193,091	5,457,546	6,331,983
Discount Factor		3.4	3.7	4.1	4.5	5.0	5.5	6.0	6.6	7.3	8.0	8.8	9.6	10.6
NPV (\$ million)		1,041,619	998,023	955,426	913,803	873,351	834,027	795,974	684,608	646,101	618,829	592,215	566,308	597,857
IRR														

Total Capital Invested

Discount Rate