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Improved Energy Efficiency, Safety, and Emissions  
in Smelt Dissolving Through Smelt Solidification

H.J. Empie

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**IMPROVED ENERGY EFFICIENCY, SAFETY, AND EMISSIONS  
IN SMELT DISSOLVING  
THROUGH SMELT SOLIDIFICATION**

H. Jeff Empie  
Professor of Engineering  
Institute of Paper Science and Technology  
Atlanta, GA 30318

**ABSTRACT**

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Solidification of kraft smelt prior to dissolving to make green liquor represents a modification of the conventional recovery process that can improve energy efficiency, while eliminating the potential for smelt-water explosions in the dissolving tank and reducing TRS emissions levels in the dissolving tank vent stack. Use of a steam-fluidized bed concept may provide an economic means for achieving these benefits. Technical issues have been identified for this proposed process modification, and results of preliminary laboratory experiments are presented which address several of these issues, while showing additional process benefits in decreased dregs flows and enhanced dregs settling rates in the green liquor clarifier. Several unanswered process concerns still remain, including ultimate use of the superheated steam product and disposition of smelt sulfur.

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**INTRODUCTION**

The present configuration of the green liquor formation step in the kraft recovery process involves the direct contact of molten smelt with aqueous weak wash and green liquor in the dissolving tank. Several drawbacks result from this mode of operation, including a significant energy loss in the form of atmospheric steam escaping, the possibility of a smelt-water explosion, poor control of green liquor concentration, and emissions of TRS and other non condensible gases out the vent stack.

Each of these negative factors can be remedied wholly or in part by cooling and solidifying the smelt before it is fed to the dissolving tank. Energy can be recovered and smelt-water contact avoided. Also, a controlled, steady flow of solid smelt particles can then be conveyed to the dissolving tank, giving a uniform green liquor concentration. Feeding these particles at a point below the surface of the green liquor in the tank should virtually eliminate the TRS-laden vapor stream that presently leaves the vent.

Heat transfer calculations have shown that a conventional rotary drum crystallizer would not be a suitable equipment choice because of the extremely large size required for a commercial-scale mill, the controlling factors being a low heat transfer coefficient (based on fluid flow normal to a cylinder, [1]) and a low heat transfer surface area per mass of smelt. A more suitable equipment choice would be a fluidized bed which is characterized as having a higher heat transfer coefficient and a much greater interfacial area per unit mass, the combination of which shrinks the vessel down to a reasonable size.

That a fluidized bed can continuously and controllably solidify smelt is based upon fluidized bed black liquor combustion technology in both conventional bubbling bed [2,3] and entrained bed [4-7] combustors. In these cases, black liquor is combusted at bed temperatures below the melting point of the inorganic salts present. The bed particles slowly grow with time and have to be purged at a fixed rate to maintain steady-state operation. The mechanism for this behavior is that at the local point of combustion the temperature exceeds the salt melting point, leaving the salt in a momentary molten state. This liquid "sees" a relatively cool bed particle, coats it, and solidifies by giving up its latent heat and some of its sensible heat to the particle and fluidizing gas. Periodically purging the larger particles at the bottom of the bed provides a steady particle size distribution in the bed. Heat transfer from the bed particles to the fluidizing gas yields a constant bed temperature and energy recovery via a hot fluidizing gas.

The type of fluidizing gas for the smelt solidifier must be chosen prudently. Air is not permissible because it will reoxidize  $\text{Na}_2\text{S}$  and lower reduction efficiency. If waste steam is used as the fluidizing gas, heat would be recovered in the form of superheated steam for use elsewhere in the mill. Bed solids that are withdrawn can be fed to the dissolving tank at a controlled rate. Having a steady carbonate concentration in the green liquor would help improve causticizing efficiency and decrease deadload in the white liquor.

The goals of this project were to determine the technical feasibility of solidifying kraft smelt in a fluidized bed operating continuously at a temperature several hundred degrees below the melting point of the smelt, and to quantify the major impacts on the process of preparing clarified green liquor.

Prior to carrying out actual continuous fluidization tests, there were a number of engineering issues that needed to be addressed, including:

- \* Choice of fluidizing gas
- \* Nature and extent of smelt reactions with the fluidizing gas

- \* TRS and sodium salt content of the exiting hot fluidizing gas
- \* Physical characteristics of the solid smelt particles
- \* Dissolution rate of solidified smelt particles in green liquor
- \* Method of recovering energy contained in hot fluidizing gas
- \* Method of feeding molten smelt to the bed continuously
- \* Materials of construction

Present dissolving tank operation does recover some energy from the vent gas via a scrubber. The proposed smelt solidification process would recover a calculable amount of energy and possibly eliminate the need for a gas scrubber. For a 900 metric tons/day mill, cooling smelt to 400°C (needed to maintain green liquor temperature at 90°C) would recover about 500 million kJ/day. Of this total, about 385 million are recovered by the scrubber, while 120 million are lost out the vent. At \$3 per million kJs, this amounts to a net \$120,000/yr for such a mill.

Elimination of the present dissolving tank vent scrubber can be claimed for a smelt solidification process if the solid particles are fed well below the surface of the green liquor in the tank. Any localized generation of vapor and TRS should be recondensed and reabsorbed before the gas bubbles reach the surface and escape out the vent.

If steam is used as the fluidizing gas, there is potential for gasification of the carbon contained in the dregs. This would decrease the dregs flow by as much as 20%, thus reducing landfill costs. This could also increase dregs settling rate in the green liquor clarifier due to an increase in dregs density, effectively debottlenecking any mill limited by green liquor clarification rate. The CO, CO<sub>2</sub>, and H<sub>2</sub> generated by the gasification and water gas shift reactions would become minor contaminants in the superheated fluidizing steam and would have to be accommodated.

In the scrubber, H<sub>2</sub>S can compete for Na<sub>2</sub>CO<sub>3</sub> with the CO<sub>2</sub> that is also present (due to gasification) because H<sub>2</sub>S is absorbed at a rate many times that of CO<sub>2</sub>. This is due to the slow rate of reaction between dissolved molecular CO<sub>2</sub> and OH<sup>-</sup> ion. Hydrogen sulfide gas does not require hydration to form an acid, and hence, H<sub>2</sub>S absorption in alkaline solutions is more rapid.

An important operational benefit of a smelt solidification process is, of course, the elimination of the possibility for a smelt-water explosion. Only solidified smelt would be fed to the dissolving tank. This solids flow also eliminates the need for shatter jets and should improve control of green liquor concentration. Better control should allow the caustic plant to

operate closer to the equilibrium causticizing efficiency and result in a decrease in deadload in the liquor cycle; the dollar benefit of which has not yet been calculated.

## **EXPERIMENTAL**

A limited set of laboratory experiments was run to address the first five issues listed above. The basic idea was to run a flow of steam through a packed bed of smelt particles, chemically analyze the products, and calculate mass balances. Samples of solidified smelt and settled dregs were obtained from a Georgia mill recovery system for these tests.

A packed bed reactor (2.5 cm ID x 15.2 cm long) was fabricated such that test solids could be charged manually and contained by a quartz wool packing at each end. The bed was heated to 427°C (800°F), after which steam was made by pumping 3 g/min of distilled/deionized water to a steam coil; the vapor was then fed to the bed. The exhaust from the bed was directed to a receiving flask which contained distilled/deionized water as a quench fluid, kept cool by being placed in an ice water bath. Bed and quench water weights were taken before and after the run.

As received, the smelt was in large, irregular chunks, having a pinkish hue with black/gray specks distributed throughout. It had a reduced sulfur odor, was quite brittle, and was easily crushed by hand using a nitrogen-purged glove bag. The dregs, received as a black slurry, were vacuum filtered, and the resulting cake was dried in a vacuum oven at 200°C (392°F). The dried dregs were very friable.

Settling tests were carried out in a graduated cylinder by noting the height of the interface between the settled solids and the supernatant liquid as a function of time.

To measure solidified smelt dissolving rates, particles were needed that would have a density and porosity representative of fluidized bed operation. Short of running a fluidized bed solidifier, these particles were simulated by dipping a stainless steel rod into a pool of 525°C (978°F) smelt, followed by withdrawing it and quenching in nitrogen. This procedure was repeated a number of times until 1-2 grams of solid smelt had accumulated. Dissolving rates were then measured at 88°C (190°F).

## **RESULTS**

### **Smelt Chemistry**

Ground smelt (57.4 g) was sparged with steam at 427°C for

2 hours. Analysis and weights of the bed salts yield mass balances; the results of which are summarized in Table 1 (Note: Na+K values include contents of quench).

**Table 1. Mass Balances for Smelt Steaming Test**

Component	Smelt			
	Before (g)	After (g)	Change (g)	%Δ
Cl <sup>-</sup>	3.56	3.67	0.11	3
CO <sub>3</sub> <sup>=</sup>	20.45	18.30	-2.15	- 10
S <sup>=</sup>	4.64	2.54	-2.09	- 45
SO <sub>4</sub> <sup>=</sup>	1.15	4.23	3.08	268
S <sub>2</sub> O <sub>3</sub> <sup>=</sup>	1.21	1.39	0.18	15
Anions	31.00	30.13	-0.87	- 3
Total S	5.71	4.75	-0.96	- 17
Org C	0.40	0	-0.40	-100
Na + K	24.44	24.67	0.23	1
Other	1.56	1.09	-0.47	- 30
Total Smelt	57.4	55.9	-1.5	- 3

Results with smelt show several interesting changes. The organic carbon was totally gasified. Gas samples were taken and showed the presence of both CO<sub>2</sub> and CO, but evidence of significant contamination prevented results from being quantitative. Almost half of the sulfide sulfur disappeared, with 49% of this showing up as sulfate and 5% as thiosulfate; the remainder was unaccounted for. Most likely, this remaining sulfur left with the product gas stream as H<sub>2</sub>S; unfortunately, the gas was not analyzed for H<sub>2</sub>S. There was a 10% decrease in carbonate which may have been due to reaction with steam. The reaction(s) to form sulfate is(are) not known, although some oxidation could have resulted from oxygen entering the system with the supply water (i.e., steam).

More limited results are available for the run using dried dregs as bed material. As with the smelt, steam was sparged through the bed at 427°C, but only for 30 minutes. Results are shown in Table 2. Organic carbon decreased by 59%, and total sulfur decreased by 34% in this shorter run. Both decreases can be explained by the formation of CO, CO<sub>2</sub>, and H<sub>2</sub>S. Carbonate and the sum of sodium and potassium showed sizeable decreases of 43% and 38%, respectively. Because bicarbonate and hydroxide were not analyzed for, the potential reaction of steam with carbonate could not be quantified. Nonetheless, the change in carbonate was in the same direction as the run with smelt. The gain in chloride and the 47% loss in total mass underscore the difficulty in chemical analysis and sample preparation for this system.

**Table 2. Mass Balances for Dregs Steaming Test**

Component	Dregs			
	Before (g)	After (g)	Change (g)	%Δ
Cl <sup>-</sup>	0.15	0.61	0.46	307
CO <sub>3</sub> <sup>=</sup>	13.71	7.77	-5.94	-43
Org C	7.06	2.91	-4.15	-59
Na + K	9.26	5.70	-3.56	-38
Ca + Si	3.52	2.18	-1.34	-38
S as S <sup>=</sup>				
S as SO <sub>4</sub> <sup>=</sup>				
S as S <sub>2</sub> O <sub>3</sub> <sup>=</sup>				
Total S	2.12	1.39	-0.73	-34
Other	10.18	4.05	-6.13	-60
Total Salt	46.0	24.61	-21.4	-47

**Salt Entrainment**

One potential problem with employing steam as the fluidizing gas in a smelt solidifier centers around the solubility of the sodium salts, leading to salt entrainment with the superheated vapor. This could severely limit the potential uses for the product steam. Two studies reported in the literature [8,9] passed steam through a bed of sodium chloride in the 400-540°C (750-1000°F) temperature range and measured sodium concentrations of about 1 ppm in the offgas. Theoretical calculations based upon the vapor pressure of salt at 540°C support this result.

By trapping the superheated steam emerging from the fixed bed smelt runs and analyzing the quench solution for sodium content, the sodium concentration in the product steam flow can be back calculated. A value of 4 ppm was obtained, showing excellent agreement with the reported literature value.

**Solid Smelt Dissolving Rate**

Smelt dissolving tanks in kraft mills operate at around 90°C (194°F) with a dissolved salt concentration of about 10-15 g (as Na<sub>2</sub>O) per 100 g of green liquor [10]. In the laboratory, samples of solidified smelt collected on stainless steel rods, that had been repeatedly dipped into a molten smelt pool, were dissolved in water at 88°C. The final salt concentration was 0.52 grams smelt per ml of water, about three times greater than commercial operation. This should give a conservative estimate, since the lab conditions are closer to saturation. Rates of about 1 g/l/sec were obtained. Assuming a target green liquor concentration of 120 g Na<sub>2</sub>O/l and a typical smelt composition of 25% Na<sub>2</sub>S/75% Na<sub>2</sub>CO<sub>3</sub>, this dissolving rate would require a dissolving tank residence time of 3.1 minutes for complete dissolution. Since actual residence times are much larger, solidified smelt dissolving rates appear more than adequate.

## Dregs Settling Rate

The run using dried dregs as the bed material provided a unique opportunity to compare the settling rate for steam-treated dregs with the rate for untreated dregs. For a batch process, noting the rate of rise of the interface between the settled solids and the supernatant liquid, at the same approximate amount of settling (hence same location of the interface in the graduated cylinder), allows for equitable comparison of the settling rates. Table 3 shows the height of the interface as a function of time for both vacuum-dried dregs and steam-sparged dregs. Also shown is the change in interface height over successive time intervals, which, when divided by the length of the interval, is then a measure of the average settling rate over that time interval. The table also shows the ratio of the settling rate for the treated dregs to the rate for untreated at the same interface height. Almost without exception, the rates for the treated dregs are 2-4 times those for the untreated dregs. One possible explanation for this is that removal of more than half the carbon in the dregs by steam sparging created open spaces in the particles, allowing them to absorb water into the voids and effectively increase the particle density.

**Table 3. Dregs Settling Rates**

Time (sec)	Interface Height (cm)		Rise Rate <sub>3</sub> (cm/sec x10 <sup>3</sup> )		<u>Rate Treated</u> Rate Untreated @ same height
	<u>Untreated</u>	<u>Treated</u>	<u>Untreated</u>	<u>Treated</u>	
0	0	0	-	-	
60		6.15			
90	4.01	9.59		114.6	
120	5.35	11.0	44.7	50.0	
150	6.71	11.80	45.5	23.6	
180	7.90	12.14	39.6	11.2	
210	9.01	-	37.1	-	
240	9.82	12.55	27.2	6.9	4.2
270	10.53	-	23.6	-	
300	10.96	12.80	14.2	4.3	3.5
330	11.25	-	9.9	-	
360	11.62	13.14	12.2	5.6	
390	11.87	-	8.4	-	2.8
420	12.10	13.34	7.6	3.3	1.5
480	12.37	-	4.6	-	
540	12.59	-	3.6	-	1.9
600	12.75	13.67	2.8	2.8	
660	12.84	-	1.5	-	2.0
720	13.03	13.80	3.3	1.3	
780	13.14	-	1.8	-	3.1
900	13.33	13.93	1.5	0.8	2.2

## CONCLUSIONS

- \* Using steam as the fluidizing gas for smelt solidification should gasify all of the organic carbon left in the smelt, as well as convert a portion of the  $\text{Na}_2\text{S}$  to  $\text{H}_2\text{S}$ . More data are needed to quantify these reactions.
- \* Sodium entrainment by the steam flow will be on the order of a few parts per million in the product steam. This will need to be considered when deciding on how the superheated product steam is used in the mill.
- \* Dissolving rates for solidified smelt are more than adequate for existing dissolving tanks to handle the solid feed. A fluid bed operating temperature of 370-425°C should accommodate the heat balance around existing dissolving tanks.
- \* Settling rate of the dregs from steam-solidified smelt should be 2-4 times the rate for conventional dregs. This would improve the clarity of green liquor at existing production rates, or, alternatively, could enable an increase in the capacity of an existing green liquor clarifier.
- \* More data are needed to quantify the smelt-steam chemistry, especially with regard to sulfur and carbon. Work should also be initiated to assemble a continuous pilot-scale fluidized bed to prove out the workability of the fluidized smelt solidification concept.
- \* How to recover the energy contained in the product fluidizing steam is an unresolved issue. It will be low pressure, superheated steam, contaminated with low levels (<4%) of  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2$ , and  $\text{H}_2\text{S}$ . One possibility is to use it to deaerate and preheat boiler feedwater. Ultimately, how it will be used will be mill specific.

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