Improved energy efficiency, safety, and emissions in smelt dissolving through smelt solidification

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ABSTRACT

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 emission 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 flow 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. Research is planned to address these issues.

THE CURRENT 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 noncondensible 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 by transferring sensible and latent heat in the smelt to the fluidizing gas. By feeding only solidified smelt to the dissolving tank, the need for shatter jets and the possibility of molten smelt-water contact is 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 steam 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 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. For a recovery boiler processing 1350 metric tons/day of black liquor solids, the estimated vessel size is ≈ 28 m^3, which for a 3-m-diameter bed yields a total vessel height of 4 m, including the freeboard zone.

Fluidized-bed solidification has been reported for several salts, including $(NH_4)_2SO_4$, $CaCl_2$, and NaCN *(2)*. That a fluidized bed can continuously and controllably solidify smelt is also based in concept upon fluidized-bed black liquor combustion technology in both conventional bubbling-bed *(3, 4)* and entrained-bed *(5–8)* combustors. Even though black liquor is combusted at bed temperatures below the melting point of the inorganic salts present, the bed particles are known to slowly grow with time, necessitating a purge at a fixed rate to maintain steady-state operation. The mechanism for particle growth 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 comes in contact with 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.

Figure 1 shows a flow diagram for a conceptual smelt solidification installation. The type of fluidizing gas for the smelt solidifier must be chosen prudently. Air is not permissible because it will reoxidize Na_2S and lower reduction efficiency. If low-pressure steam is used as the fluidizing gas, heat would be recovered in the form of superheated steam for

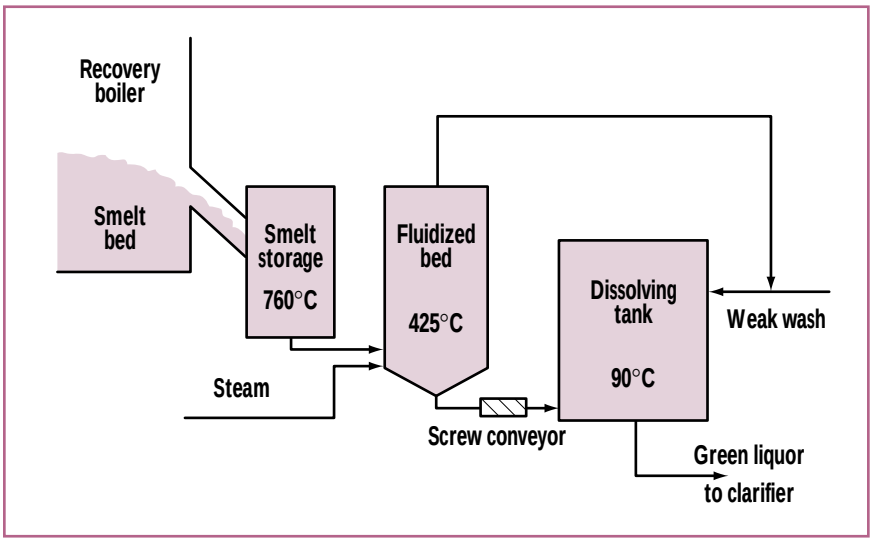
use elsewhere in the mill. Bed solids that are withdrawn can be fed to the dissolving tank at a controlled rate using a screw feeder. Having a steady carbonate concentration in the green liquor would help improve causticizing efficiency and decrease dead load in the white liquor.

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 had 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 existing 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 continuously feeding molten smelt to the bed
- Materials of construction.

Current 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 ton/day mill, cooling smelt to 400°C (needed to maintain green liquor temperature at 90°C) would recover about 500 million kJ/day. Over half of this total is presently recovered by the vent scrubber, leaving the energy recovery benefits offered by the proposed process as relatively minor.



1. Conceptual smelt solidification process

Elimination of the dissolving-tank vent scrubber is possible 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. Limited laboratory data by Reeves *(9)* strongly support this claim.

If steam is used as the fluidizing gas, there is potential for gasification of the carbon contained in the dregs. Recently obtained data on carbon content of dregs samples from five U.S. kraft mills show a range of 5% to 30%, on a solids basis. Hence, removing this would decrease the dregs solids flow by approximately 10–20% on average, proportionately reducing landfill costs. Carbon removal 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_2, H_2, and H_2S generated by the gasification and water gas shift reactions would become minor contaminants in the superheated fluidizing steam and would have to be reclaimed.

The fact that the superheated steam product contains small amounts of these gases suggests that possibly the best place to use it is as direct heating steam for recycled weak wash or green liquor to the slaker. In this way, both the energy and chemical values in the steam could be recovered.

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 heated 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 I.D. ¥ 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,

	SMELT			
Component	Before, g	After, g	Change, g	%Δ
Cl	3.56	3.67	0.11	3
$CO_3^=$	20.45	18.30	-2.15	-10
$S^=$	4.64	2.54	-2.09	-45
$SO_4^=$	1.15	4.23	3.08	268
$S_2O_3^=$	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	57.40	55.90	-1.5	-3

I. Mass balances for smelt steaming test

deionized water to a steam coil; the vapor was then fed to the bed. The offgas 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, then withdrawing it and quenching in nitrogen. This procedure was repeated a number of times until 1–2 g of solid smelt had accumulated. Dissolving rates for this material were then measured at 88°C (190°F).

Continuous feeding of molten smelt to a fluidized bed was not attempted due to significant handling issues, including corrosion, flow control of both smelt and fluidizing gas, maintaining a molten smelt feed, and continuous withdrawal of hot solid particles. Most of these issues will be studied in a laboratory-scale fluidized-bed installation using a model system featuring salt with a near-ambient melting temperature and air as a fluidizing gas. A mill-scale system would also have to engineer storage of molten smelt in a refractory lined tank to accommodate surges and process upsets characteristic of continuous operation.

RESULTS

Smelt chemistry

Ground smelt (57.4 g) was sparged with steam at 427°C for two hours. Analysis and weights of the bed salts yield mass balances, the results of which are summarized in Table I (Na + K values include contents of quench).

Results with smelt show several interesting changes. The organic carbon was totally gasified. Gas samples were taken and showed the presence of both CO_2 and CO at low levels. 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_2S; unfortunately, the gas was not analyzed for H_2S. 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. Since conversion of sulfide to sulfate represents a decrease in smelt reduction efficiency, the extent must be better quantified. Hence, improved data are needed.

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 II. 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_2, and H_2S. Carbonate and the sum of sodium and potassium showed sizeable decreases of 43% and 38%, respectively. Because we didn't analyze for bicarbonate and hydroxide, 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.

Salt entrainment

One potential problem with employing steam as the fluidizing gas in a smelt solidifier centers around the

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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 *(10, 11)* passed steam through a bed of sodium chloride in the 400°C to 540°C (750°F to 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_2O per 100 g of green liquor *(12)*. 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 g smelt per 1 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/s were obtained. Assuming a target green liquor concentration of 120 g Na_2O/L and a typical smelt composition of 25% Na_2S/75% Na_2CO_3, this dissolving rate would require a dissolving tank residence time of 3.1 minutes for complete dissolution. Since actual residence times are much longer, solidified smelt dissolving rates appear to be more than adequate.

	DREGS			
Component	**Before, g**	**After, g**	**Change, g**	**%Δ**
Cl	0.15	0.61	0.46	307
$CO_3^=$	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 $S^=$	...	...	...	...
S as $SO_4^=$	...	...	...	...
S as $S_2O_3^=$	...	...	...	...
Total S	2.12	1.39	–0.73	–34
Other	10.18	4.05	–6.13	–60
Total salt	46.0	24.60	–21.40	–47

II. Mass balances for dregs steaming test

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 III shows the height of the interface as a function of time for both untreated 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. Strikingly, the rates for the treated dregs are 2–3 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, effectively increasing the particle density.

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 Na_2S to H_2S. More data are needed to quantify the smelt-steam chemistry, especially with regard to sulfur and carbon.
- 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

Time, s	Interface height, cm		Rise rate, cm/s x 10^3		Rate treated/ Rate untreated at same height
	Untreated	Treated	Untreated	Treated	
0	0	0	...	...	...
90	4.01	9.59	...	...	...
120	5.35	11.0	44.7	47.0	...
150	6.71	11.50	45.3	26.7	...
180	7.90	12.14	39.7	11.3	...
240	9.82	12.55	32.0	6.8	...
300	10.96	12.80	19.0	4.2	2.5
360	11.62	13.14	11.0	5.7	...
390	11.87	...	8.3	...	3.2
420	12.10	13.34	7.7	3.3	1.5
540	12.59	...	4.1	...	1.7
600	12.75	13.67	2.7	1.8	...
660	12.84	...	1.5	...	2.8
720	13.03	13.80	3.2	1.1	...
780	13.14	...	1.8	...	3.2
900	13.33	13.93	1.6	0.7	2.1

III. Dregs settling rates

existing dissolving tanks.

- Settling rate of the dregs from steam-solidified smelt should be 2–3 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.
- Work should also be initiated to assemble a continuous pilot-scale fluidized-bed solidifier to prove the fluidized smelt solidification concept, including a feasible method for feeding molten smelt.
- How to recover the chemical and energy values in the product fluidizing steam is an unresolved issue. It will be low pressure, superheated steam, contaminated with low levels (<4%) of CO_2, CO, H_2, and H_2S. One possibility is to use it directly to heat weak wash or green liquor. This would not only use recovered energy, but also put gaseous chemical species back into the liquor cycle. TJ

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