

The effect of dead load chemicals in the kraft pulping and recovery system

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ABSTRACT: The primary dead load chemicals are sodium carbonate from incomplete conversion during causticizing, and sodium sulfate from low reduction efficiency in the recovery boiler, but thiosulfate and chloride also are potentially important. The difference between a low and high dead load operation might amount to as much as 125 kg/metric tons of pulp (mtp). A 1% increase in causticizing efficiency reduces dead load by 6-7 kg/mtp, and a 1% increase in reduction efficiency decreases dead load by 2-3 kg/mtp. Costs associated with dead load include increased internal energy use, greater chemical losses, reduced equipment capacity, and operating problems. The differences in energy use between a low and high dead load operation can be as much as 0.7 GJ/mtp. Evaporators are likely to be affected most, but the green and white liquor system and recovery boiler also could be affected. This paper provides some guidelines for minimizing the effects of dead load.

Application: Understanding the main benefit of dead load reduction could help kraft pulp mills devise strategies for improving their chemical recovery operations.

The kraft pulping process is based on the use of sodium hydroxide (NaOH) and sodium sulfide (Na_2S) to convert wood to pulp. Dissolved wood substances and spent inorganic chemicals are washed from the pulp to produce black liquor, which can be concentrated and burned in the recovery cycle. The recovered inorganic chemicals can be causticized and reused for pulping more wood. This kraft pulping and recovery cycle operates with very low losses (greater than 97% recovery is typical), but not all of the recovered inorganic chemical is available as sodium hydroxide and sodium sulfide, the active pulping chemicals. Around 20% of the recovered inorganic circulates through the cycle as inactive species. These are usually referred to as “dead load” chemicals.

Without question, process and economic consequences result from the dead load [1-5]. However, these effects often are not that straightforward and considerable misinformation has been presented over the years on the effects of dead load and the value of reducing the amount of dead load. This paper provides a basis for a quantitative assessment of dead load effects and identifies factors that can make this a difficult task.

CHARACTERISTICS AND SOURCES OF DEAD LOAD

Dead load chemicals are inorganic chemicals in the white liquor that do not participate in pulping reactions in the digester and are capable of circulating through the pulping and recovery cycle. The main dead load species are alkali carbonate, sulfate, thiosulfate, and chloride. Potassium, sodium hydroxide, and sodium sulfide are active pulping agents, so no differentiation is made between sodium and potassium in classifying compounds as dead loads. The determining factor is the anion. For simplicity, they will be referred to as the sodium compound.

Another term frequently used in discussions of the chem-

ical recovery cycle is “nonprocess elements.” This term usually refers to all of the chemical elements in the system other than sodium, sulfur, carbon, hydrogen, and oxygen. The main elements affecting the pulping and recovery process are chlorine, potassium, silicon, calcium, magnesium, and manganese. With the exception of chlorine and potassium, nonprocess elements have limited solubility in liquors and do not tend to build up in the system. Silicon can build up in the system with high silica input, such as with straw or bamboo pulping, but it is not an issue with most kraft mills. Nonprocess elements can significantly affect the process, but the effects are very element-specific and not primarily associated with the relatively large amount of inert material present. The concept of dead load and that of nonprocess elements overlap. This paper will focus only on the effects of four dead load species: sodium carbonate (Na_2CO_3), sodium sulfate (Na_2SO_4), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), and sodium chloride (NaCl).

Sodium carbonate

Sodium carbonate dead load is the result of incomplete conversion during causticizing with lime. The causticizing reaction ($\text{CaO} + \text{H}_2\text{O} + \text{Na}_2\text{CO}_3 = 2 \text{NaOH} + \text{CaCO}_3$) has an equilibrium limit, and it is not possible to get complete conversion of carbonate with conventional technology. Various schemes for overcoming the equilibrium limit have been proposed [5,6], but none have been implemented. This paper will deal only with the conventional process.

The extent of completion of the causticizing reaction is described by the causticity (often called causticizing efficiency [CE]), normally defined and measured as

$$\text{CE} = \frac{[\text{NaOH}]}{[\text{NaOH}] + [\text{Na}_2\text{CO}_3]} \times 100$$

where [] is the concentration of each species on a sodium oxide basis.

Because of the adverse consequences of over-liming (which increases the difficulty of separating solid phase from white liquor), it is extremely difficult to reach the equilibrium limit in a commercial operation and most mills try to operate some distance below it, typically 82%-84%. A causticizing efficiency of 85% would constitute a very high value.

The amount of dead load sodium carbonate from incomplete causticizing is given by

$$DLC = \frac{106}{62} \times \frac{1 - CE}{CE} \times \frac{2(1 - S)}{(2 - S)Y} \times EA \times 1000$$

where DLC = amount of sodium carbonate dead load, kg per metric ton unbleached pulp

S = sulfidity of cooking liquor, %/100

EA = effective alkali charge on wood, %/100

Y = pulp yield, %/100

Figure 1 shows the effect of an increase in causticizing efficiency on decreasing carbonate dead load for two different white liquor sulfidities. The EA charge was assumed to be 15% on the wood and the pulp yield was assumed to be 50%. The dead load at 85% CE is about 75 kg/metric tons of pulp (mtp) and increases rapidly as CE declines. Typically, sodium carbonate dead load increases by 6-7 kg/mtp for each 1% decline in CE. The dead load is less in higher sulfidity operations because less NaOH is needed in pulping for the same EA charge. The effect of sulfidity is small, however, compared with that of CE.

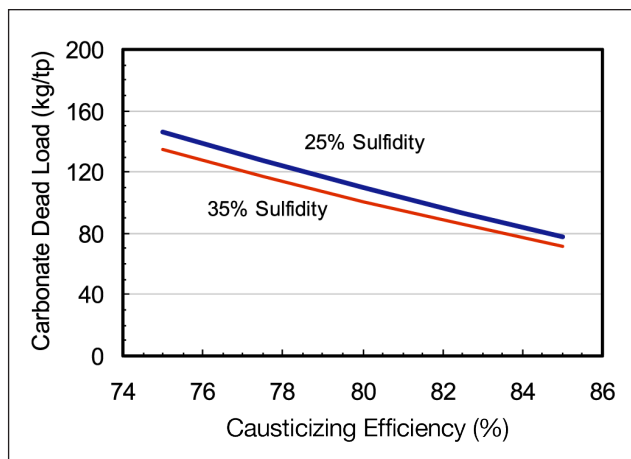
The dead load values in Fig. 1 are for a specific EA charge and pulp yield. The fraction of the black liquor solids that is dead load carbonate depends on the total amount of black liquor solids produced. Typically, high EA charges give lower pulp yields, so more dead load and more total black liquor solids are obtained with higher EA charges. Another way of characterizing the dead load is to look at the increase in sodium charged to the digester in the white liquor. For dead load carbonate, this is total titratable alkali divided by active alkali (TTA ÷ AA; all components on a sodium oxide basis). In terms of causticizing efficiency and sulfidity, this becomes

$$\% \text{ Na Increase} = (1 - S) \times \frac{1 - CE}{CE} \times 100$$

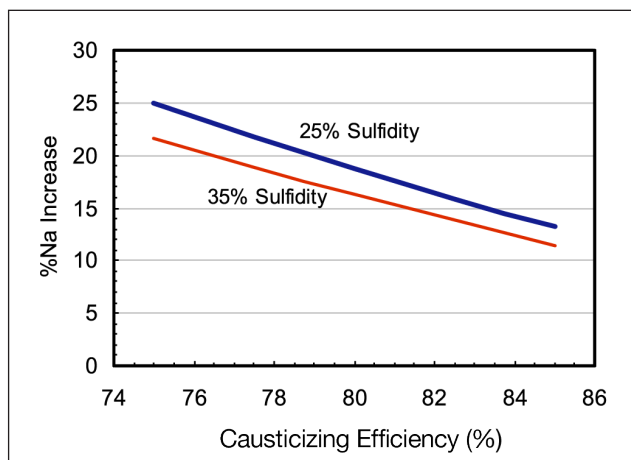
Figure 2 shows this relation for the same range of CEs and sulfidities as in Fig. 1. Again, dead load amounts are higher at lower sulfidities, but CE has the greatest effect. Each 1% increase in CE decreases the dead load sodium by 0.8% to 0.9%.

Sodium sulfate

The primary source of sodium sulfate dead load is incomplete reduction in the recovery furnace. The recovery boiler is the only place in the process where Na₂SO₄ and other oxidized



1. Effect of causticizing efficiency on carbonate dead load.



2. Increase in sodium in white liquor vs. causticizing efficiency.

sulfur compounds can be converted to Na₂S, the desired active pulping chemical. The effectiveness of the recovery boiler in producing sulfide is usually characterized by reduction efficiency, which is usually defined and measured as

$$RE = \frac{[Na_2S]}{[Na_2S] + [Na_2SO_4]} \times 100$$

where RE = reduction efficiency, and [] = concentration of each species on a sodium oxide basis.

The analysis for reduction efficiency is preferably based on a smelt sample rather than green liquor to avoid complications arising from sulfur compounds in weak wash used as a water source and air oxidation within the dissolving tank. The definition of reduction efficiency considers only sulfide and sulfate and ignores other sulfur compounds. This causes the amount of dead load sulfur compounds to be underestimated.

The amount of dead load sodium sulfate from incomplete reduction is given by the equation

$$DLS = \frac{142}{62} \times \frac{1 - RE}{RE} \times \frac{2S}{(2 - S)Y} \times EA \times 1000$$

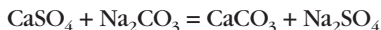
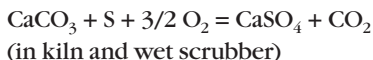
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where DLS = amount of Na_2SO_4 dead load in kilograms per metric ton unbleached pulp.

Figure 3 shows the amounts of sulfate dead load as a function of reduction efficiency for two different sulfidities and the same EA and Y values used in calculating carbonate dead load in Fig. 1. For the same reduction efficiency, the dead load increases as operating sulfidity increases. Sulfidity is more important for the amount of sulfate dead load than it is for carbonate dead load.

A comparison of Fig. 3 with Fig. 1 shows that sulfate dead load is much less than carbonate dead load, typically by a factor of about 4. This is a bit misleading, however, because a substantial amount of carbonate dead load is irreducible with conventional technology. A better comparison might be that a 1% change in causticizing efficiency represents a little more than twice the change in dead load amount as a 1% change in reduction efficiency.

Sulfate in white liquor also can result from calcium sulfate (CaSO_4) in the lime reacting with green liquor sodium carbonate to produce sodium sulfate. In this case, the source of the sulfur is either sulfur in the fuel used in the lime kiln or sulfur from noncondensable gas (NCG) or stripped off gas (SOG) incinerated in the lime kiln. The reaction sequence is

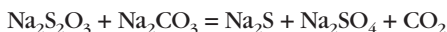


Any sodium sulfate produced in this way will add to the sulfate dead load in the system.

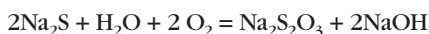
It is difficult to make general estimates of the magnitude of this source of sulfate dead load. Very limited data suggest that about half the sulfur introduced into the lime kiln might end up as sulfate dead load in the pulping and recovery system, but this is likely to be very system dependent. Careful white liquor system sulfur balances are needed to evaluate the extent to which this might be an issue at any given mill.

Sodium thiosulfate

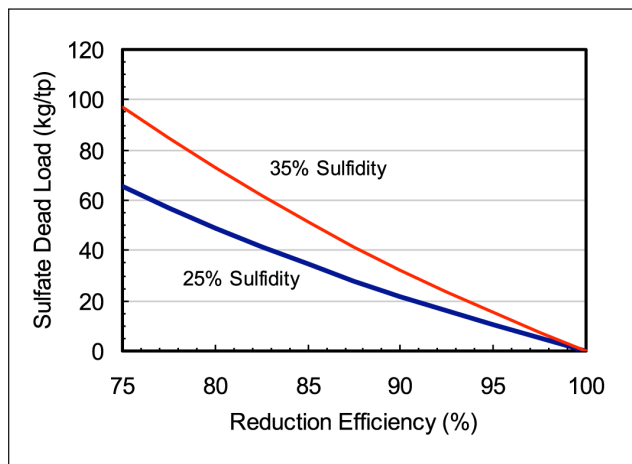
Sodium thiosulfate in white liquor arises mainly from air oxidation of sulfide in aqueous solution (i.e., in smelt dissolution) and in the green and white liquor systems. A small amount of the thiosulfate compound might be present in the smelt leaving the furnace, but this is minor in most operations. Sodium thiosulfate decomposes in molten carbonate according to the reaction



and this minimizes sodium thiosulfate in the smelt. The sodium thiosulfate-forming reaction can be represented as follows:



Aqueous oxidation of sulfide to thiosulfate can be catalyzed



3. Dead load sodium sulfate vs. reduction efficiency.

by carbonaceous material such as dregs and by entrained black liquor solids. Air entrainment in pumps and excessive exposure of green and white liquor to air can favor sodium thiosulfate formation.

Most mills do not routinely measure sodium thiosulfate in green or white liquor. The common definition and measurement of reduction efficiency ignores sodium thiosulfate and considers only sulfate and sulfide. This is not a big problem if based on a smelt sample in which sodium thiosulfate is expected to be low, but it can lead to problems if green liquor or white liquor is analyzed. The lost sulfide that ends up as sodium thiosulfate is not accounted for. The consequences of this are two-fold: the recovery boiler actually performed better than the measured reduction efficiency, and the true amount of dead load is underestimated.

Very little data have been published on the amount of sodium thiosulfate in the green liquor and the white liquor. A reasonable estimate is that 5% of the sulfide is being converted to sodium thiosulfate. If so, the amount of sodium thiosulfate dead load would amount to about 7-8 kg/mt.

Sodium chloride

The dead load of sodium chloride in the pulping and recovery system is the result of a balance between chloride inputs and losses from the system, and thus varies considerably from mill to mill. Chloride inputs include the wood, mill water, makeup chemicals, and chlorine dioxide generator effluent. Chloride losses include liquor losses, losses from the recovery stack, and deliberate purges. Because of the adverse effects of chloride on recovery boiler operation, many mills attempt to minimize it by a combination of careful control of chemical inputs and by periodic or continuous purging. The most common purge method is to dump precipitator dust, which is enriched in sodium chloride.

The amount of sodium chloride dead load ranges widely. Some mills target 1.5% sodium chloride in the precipitator dust, which corresponds to about 5-6 kg/mt. This would represent the low end of the range. In a few mills pulping logs that were transported or stored in salt water, the chloride dead load could range up to 100 kg/mt. For most mills it is probably <10 kg/mt.

Total dead load

Table 1 summarizes the amounts of dead load chemical that could be circulating in pulping and recovery systems. The first column shows what is attainable in a low dead load operation and the second gives the other extreme.

Chemical	Low dead load operation	High dead load operation
Na ₂ CO ₃	75	140
Na ₂ SO ₄	15	40
Na ₂ S ₂ O ₃	7	15
NaCl	5	20
Total	92	215

I. Amount of dead load (kg/mtp).

To put these numbers in perspective, they suggest the total dead load may range from 7% to 15% of the total black liquor solids, and that carbonate constitutes the largest amount of dead load. Because of the equilibrium causticizing limit, carbonate dead load cannot be completely eliminated. The best conceivable conventional recovery operation would still have a total dead load of about 75 kg/mtp.

EFFECTS OF DEAD LOAD

The main effects of dead load in the system include the following:

- Process energy is needed to heat the dead load and associated water as it moves around the system. Because no liquid water leaves the recovery boiler, all of the water associated with the dead load has to be evaporated.
- Greater chemical losses occur because more inorganic is circulating in the system.
- Equipment capacity is reduced and operating problems increase.
- Chemical inventory costs increase.

Energy use due to extra water load

Because of dead load, extra energy is needed to heat the dead load chemical and associated water to the desired cooking temperature. Because of the much larger specific heat of water and the much greater mass of water than chemical, the heat needed by the chemical might be neglected compared with that of the extra water load. The concentration of the white liquor is basically set at the dissolving tank and would normally be independent of the amount of dead load present. A typical value is about 15% by weight, and the amount of extra water needed is 5.67 kg/kg dead load. Assuming a temperature rise of 75°C, the extra heat at the digester is 1780 kJ/kg dead load. This amounts to about 0.16 GJ/mtp for low dead load operation and up to 0.39 GJ/mtp for a high dead load operation.

The heat load associated with the extra water is even higher for the evaporators, because latent heats are involved. The sensible heat effects can be ignored relative to the latent heat effects in the evaporators. Because the weak liquor concentra-

tion is primarily determined by the dilution factor used in pulp washing, which is likely to be little affected by the amount of dead load chemical present, the weak liquor solids should be about the same regardless of the amount of dead load.

The amount of steam required for evaporation is determined by the steam economy. For an evaporator set where the liquor is first concentrated to about 50% solids in a six-effect evaporator and then concentrated to about 72% solids in a three-effect concentrator, the evaporator steam requirement starting with weak liquor at 14% solids would be $(6.14 - 1)/5 + (1 - 0.39)/2 = 1.33$ kg steam per kilogram dead load. The energy requirement would be $1.33 \times 2160 = 2875$ kJ/kg dead load. Thus, the extra energy use in the evaporators is about 0.27 GJ/mtp for low dead load operation, and up to 0.62 GJ/mtp for a high dead load operation. The energy value for dead load reduction would be even higher in a system with a direct contact evaporator, because more water is evaporated at low steam economy.

An energy penalty also will be associated with the water carrying the dead load into the recovery boiler, because the heat needed to evaporate this water will not be available to generate steam. The magnitude of this cost is directly dependent on the solids content at which black liquor is fired in the boiler. For the case discussed above, this is 72%, and the energy associated with the evaporation of this water is $0.39 \times 2255 = 880$ kJ/kg dead load. The dead load totals for these three process components are 1780 kJ/kg for the digester, 2875 kJ/kg for the evaporators, and 880 kJ/kg for the recovery boiler, for a total of 5535 kJ/kg.

The difference between a low dead load and high dead load operation could be as much as 0.68 GJ/mtp. Actual values depend on specific mill conditions and evaporator arrangements, but the values given above are considered representative.

Greater chemical losses

Chemical losses would be expected to be higher as a result of dead load, simply because more chemical is circulating around the system. This is likely to be the case for losses from spills and leaks and to entrained wash liquor leaving with the washed pulp. However, some of the unwashed inorganic material is chemically adsorbed on the fibers, and so does not depend on the total amount of inorganic material in the system. Other losses are dependent on process conditions and not on overall inorganic loads.

The total amount of dead load could cause an increase of 15% to 20% in the sodium content in the sodium in the liquor solids (even more for a high dead load operation). One might expect that chemical makeup requirements may increase by some percentage less than the fractional increase in sodium associated with dead load. The effect of dead load is already involved in existing makeup requirements and about half of the dead load is irreducible (even more than half if starting with relatively little dead load). It is difficult to be precise about how much chemical savings to expect with dead load reduction, but it is unlikely to be more than 5%.

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Reduction in equipment capacity

Digester

The effects of dead load on digester capacity would be expected to be minimal, because the extra volume of white liquor required to carry the same amount of active chemical could be compensated for by reducing the amount of recycled black liquor needed to fill the void.

Evaporators

The capacity of the evaporators would be affected by dead load. Because the evaporators are essentially water removal devices, the water that enters the evaporators with the dead load is water that otherwise could be supporting more pulp production. Thus, the effective capacity of the evaporator is reduced by the ratio of the water carrying the dead load to the total water entering the evaporator. For a typical recovery operation with 1500 kg black liquor solids/mtp, 100 kg of dead load would reduce evaporator capacity relative to pulp production by about 7% as a result of the extra water load.

The dead load also increases the boiling point rise of the black liquor in direct proportion to the increase in the sodium content. Higher boiling point rises reduce the effective ΔT driving force for evaporation, directly reducing evaporator capacity. This effect becomes more important as the number of effects increases, because the boiling point rises for each effect are added together and then subtracted from the total available temperature driving force. All of the dead load chemicals contribute to boiling point rise up to the point where sodium carbonate and sodium sulfate begin to precipitate from the black liquor (about 50% solids). In commercial evaporators operating above this solids region, the effect of dead load on boiling point rise is difficult to predict. If the dead load precipitates, it does not affect the boiling point rise. If the liquor supersaturates and precipitation is delayed, boiling point rise increases with dead load. A 15% increase in boiling point rise can cause a 5% drop in capacity in a conventional six-effect evaporator producing 50% solids liquor. The loss of capacity would be significantly greater with more effects or if higher liquor solids contents and supersaturation are involved.

Finally, the dead load sodium carbonate and sodium sulfate are precipitable as the liquor solids increases, and so can contribute to evaporator scaling and fouling. As dead load increases, the amount of crystallized solids in the liquor will increase at solids levels above about 50%. Whether or not this will increase scaling rates and require more frequent boilouts or hydroblasting depends on the types of evaporators used and operating diligence, however, the potential is there. Scaling and plugging of evaporators can have a significant effect on overall capacity and certainly is not helped by higher inorganic loads.

Considering all three effects (extra water, boiling point rise, and scaling), high dead loads could conceivably reduce evaporator capacity by 15% to 20%. If evaporators are a production bottleneck, the incentive to minimize the amount of dead load in the system could be great.

Recovery boilers

It is difficult to quantify all of the effects of dead load on recovery boiler performance and capacity. The energy effects of the

water carried in with the dead load were already discussed. The smelt flow out of the boiler will increase in direct proportion to the amount of dead load. This has a relatively small effect on the overall heat balance because the sensible heat of smelt is only about 3.5% of the heat input. Thus, an increase in smelt flow by 15% would only amount to a 0.5% drop in steam efficiency or a 0.7% decrease in steam production.

Recovery boiler capacity is often determined by fouling and plugging rates, which can be affected by dead load. Superheater fouling is typically related to carryover of burning particles and the inorganic ash in the carryover particles would increase in direct proportion to the amount of dead load. In the worst case, the firing rate would have to be decreased in direct proportion to the amount of dead load to keep the inorganic deposition rate constant. This is unlikely to be the normal case. Superheater fouling is heavily influenced by the composition of the deposits, especially chloride, which affects the melting behavior and liquid content of deposits. In many cases it is much more important to reduce chloride dead load than the other dead load chemicals. Reducing dead load lowers the content of sodium in the black liquor, but the black liquor from even a very low dead load operation will still have a sodium content exceeding 15% on the black liquor solids. Combustion of this fuel will still produce a large amount of ash (sodium carbonate and sodium sulfate) with a relatively low melting temperature, and thus still have a high fouling potential.

Increased dead load will decrease the heating value of the liquor solids and tend to cause lower burning temperatures in the furnace. The effect of lower temperatures on capacity is very difficult to predict quantitatively. If combustion in the furnace is marginal, the reduced heating value could lead to frequent blackouts and unstable operation. If the furnace runs hot anyway, lower liquor heating value could well have little effect.

Some recovery boilers have permit limits on the amount of liquor solids they can burn. In this situation, the amount of dead load and the loss in recovery boiler capacity would be directly related and there would be considerable incentive to reduce dead load as much as possible.

Dissolving tank

The smelt flow out of the furnace will increase in direct proportion to the extra sodium associated with the dead load. This could be about 15% more than that of the best low dead load operation and about 25%-30% more than if there was no dead load at all. Smelt spouts should be able to handle that kind of load, but the shatter jets and dispersing equipment could be strained. The weak wash input and green liquor flow from the tank would increase in proportion to the dead load and the residence time available for dissolution would decrease. The heat input into the dissolving tank would increase in proportion to the dead load and so the amount of steam produced and the load on the dissolving tank vent would increase, possibly leading to increased emissions. It is unlikely that these problems would force a reduction in liquor firing rates, but it is likely that increased

dead loads increase operating problems and vice versa.

Green liquor/causticizing

The increased green liquor flow associated with the potential extra water to carry the dead load could result in some loss of capacity. Increased volumetric flows through clarifiers and settlers could result in poor separation of dregs and thus allow nonprocess element build up in the system. The effect of higher volumetric flows on filter performance is less predictable. In addition, residence times in the slaker and causticizers would decrease at the higher volumetric flows, which might affect conversion. Similarly, higher flow rates through the equipment could affect lime mud separation and residual sodium in lime mud. Although it is difficult to quantify how much the capacity of the green liquor and white liquor systems would be affected by dead load, some adverse effect of higher dead loads is almost certain.

Lime kiln

Dead load should have no direct effect on the capacity of the lime kiln, unless the dead load affects lime mud washing and dewatering. It is very difficult to predict the extent of this problem.

Chemical inventory costs

A kraft pulp mill has a large inventory of chemical tied up in weak and heavy black liquor storage, green and white liquor storage, and within different process components. Associated with this large amount of stored chemical is a considerable inventory of dead load chemicals. Acquisition of this inventory of dead load carries a cost, and a potential gain if the inventory is reduced by efficiency improvements that decrease the amount of dead load circulating in the system. The total value of the dead load inventory can be quite high, but depletion of the inventory does not constitute a significant economic benefit over the long haul. The reason is that once the inventory is built up it simply remains (unless the entire system is dumped for some reason). The cost of the chemical inventory is a "one-time cost" that is spread over all of the pulp production for the life of the mill (or until the system is dumped). Thus, the cost of the dead load inventory per unit amount of pulp becomes smaller and smaller and eventually becomes negligible.

Similarly, credit should not be taken on a continuing basis for "free chemical" obtained by increasing reduction efficiency or causticizing efficiency. This "one-time" gain can just as easily become an additional cost if the reduction efficiency or causticizing efficiency subsequently drops. This can be a confusing issue and it is responsible for much of the erroneous estimates of the value of dead load reduction. To be assessed properly, the costs and effects of dead load must be looked at on a steady state basis.

This issue arises most frequently in connection with reduction efficiency and sulfidity. Is there a real gain in sulfidity by increasing reduction efficiency? The answer is yes in the short term, no in the long term. In the long run, sulfidity is determined by a chemical balance between the amount of makeup sulfur chemicals added and sulfur losses from the

system. Reduction efficiency merely determines how much sulfate circulates in the system with the desired amount of sulfide. Increasing reduction efficiency to increase sulfidity can affect the sulfur flows around the whole cycle, including the amounts in NCGs and SOG. This in turn can affect makeup requirements. The economic benefits of improving reduction efficiency can only be assessed by comparison with other ways of increasing sulfidity that result in higher recirculating sulfate loads.

DEAD LOAD MINIMIZATION GUIDELINES

Concentrate first on reducing carbonate dead load. If causticizing efficiency is below 80%, considerable gains might be made by raising it to that level or even higher. However, attempts to maximize causticizing efficiency can lead to overliming and adverse process effects. Variations in TTA concentrations coming to the slaker/causticizer make it extremely difficult to accurately control lime addition stoichiometry. Thus, stabilizing the TTA concentration in the green liquor is a key factor in improving causticizing efficiency. If existing causticizing efficiency is already in the 82%-84% range, care should be taken in attempting to increase it further.

Chloride effects can be out of proportion to the amount of dead load present because it affects ash melting behavior. Reducing chlorides might be of real value if the recovery boiler is subject to fouling and plugging. Some mills use a target value as low as 1.5% sodium chloride in the precipitator dust (or 0.2% chlorine) in the as-fired black liquor dry solids for controlling chloride. Chloride might be controllable solely by reducing chloride inputs. If not, deliberate chloride purges can be used. The most commonly used purge is discarding part of the precipitator dust (which is enriched in chloride).

Most recovery boilers operate with reduction efficiencies of 90% or more and many can reach 95% without too much difficulty. Relatively little is gained by improving reduction efficiency in these units. It is worthwhile to focus on improving reduction efficiency if it is below 90%. Operating conditions that result in a hot lower furnace are favorable for reduction.

An occasional study of the amount of sodium thiosulfate and other intermediate oxidized sulfur compounds in the green and white liquor system can be useful. The amounts of these substances can be compared with the amount of dead load sulfate to determine if actions to minimize their presence are warranted.

If a sulfur-containing fuel is used in the lime kiln or if NCG and SOG gases are incinerated in the kiln, a sulfur balance over the kiln and white liquor can determine how much of this ends up as sulfate dead load. The recovery boiler is the only place in the pulping and recovery cycle where incinerated sulfur gases can end up as sulfide.

CONCLUSIONS

Sodium carbonate is the dominant dead load chemical. Carbonate dead load can only be reduced by increased causticizing efficiency. Because of an inherent chemical equilib-

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rium limit, it is not possible to reach 100% causticizing efficiency, and a fairly sizable carbonate dead load is inevitable. As a practical matter, 85% causticizing efficiency is about the maximum possible. If typical causticizing efficiencies are 80% or less, carbonate should be the primary target of dead load reduction campaigns. However, serious consequences related to overliming can result in attempting to increase causticizing efficiency too much. Greater decreases in dead load are obtained by increasing causticizing efficiency than by increasing reduction efficiency. A 1% increase in causticizing efficiency decreases dead load by 6-7 kg/mtp, a 1% increase in reduction efficiency decreases dead load by 2-3 kg/mtp.

Sodium thiosulfate and other intermediate oxidized sulfur compounds can constitute a hidden dead load because they are not usually measured. The same is true for sulfate formed in the lime kiln if sulfur is introduced there. Chloride has an effect on recovery boiler processes far out of proportion to its fraction in the total dead load and needs separate attention.

The primary value of dead load reduction is in energy savings in the digester, evaporators and recovery boiler. This value is highly mill specific but is on the order of 5500KJ/kg dead load. The difference between a low dead load and high dead load operation could be as much as 0.7 GJ/mtp. The potential energy savings are even higher in a mill with direct contact evaporators.

Dead load affects evaporator capacity in several different ways. High amounts of dead load could result in an evaporator capacity reduction of 15%-20%. The payback for a dead load reduction program could be considerable for mills in which evaporators are a bottleneck. The effect of dead load on recovery boiler capacity is difficult to quantify, but clearly less dead load means more capacity. If the recovery boiler firing rate is permit limited, the relation between recovery boiler capacity and dead load is direct. Dead load can reduce the capacity of the green and white liquor process-

ing system because the increased volumetric flow due to the water used to carry the dead load lowers the residence time in all of the process components.

Economic benefits of dead load reduction must be based on a "steady-state" analysis of the system. This is particularly true in estimating the chemical savings from dead load reduction. **TJ**

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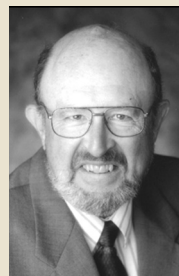
INSIGHTS FROM THE AUTHORS

We chose this research topic because dead load is an important operating issue in the chemical recovery area of a kraft pulp mill. It complements our research on chemical recovery, particularly the efficiency of ash treatment systems, the effect of chlorine and potassium on recovery boiler fouling, and alternative fuels for lime kilns.

The most challenging aspect of this research was to obtain sufficient operating data to evaluate the effect of dead load. We addressed it by discussing the issues with recovery staff at various mills.

The researched showed that dead load can affect many aspects of chemical recovery operation. Mills might use this information to devise appropriate strategies for improving their chemical recovery operations.

The next step in this research would be to examine the amount of sulfate deadload generated by burning high sulfur containing fuels in lime kilns.



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