Pirssonite deposits in green liquor processing

W. J. Frederick, Jr.* and Rajeev Krishnan

Associate professor and graduate student, Dept. of Chemical Engineering, Oregon State University, Corvallis, Ore. 97331

Russell J. Ayers

Senior process engineer, Weyerhaeuser Paper Co., Springfield, Ore. 97477

ABSTRACT *Pirssonite deposits are a persistent problem in green liquor processing. The extent of this problem is related to the solubility behavior of pirssonite, but it also depends on the design of the green liquor process equipment and control system. Pirssonite deposits form at total titratable alkali (TTA) concentrations that correspond to the solubility limit for Na_2CO_3 in sodium salt solutions when $CaCO_3$ is present. Ineffective mixing in the dissolving tank also can contribute to the problem. Pirssonite deposits can be minimized by keeping the average TTA below 90% of the TTA at pirssonite saturation, controlling TTA variability, allowing some lime mud to be carried over with the weak wash, minimizing the calcium input to the soda cycle, providing adequate mixing for the dissolving tank, maintaining a high green liquor temperature throughout the process, and providing positive flow in green liquor lines where stagnation or low flow can otherwise occur.*

KEYWORDS
Calcium carbonate
Deposits
Green liquors
Smelt
Sodium carbonate

Pirssonite, a double salt of sodium and calcium carbonates, often deposits in smelt dissolving tanks and in green liquor lines, clarifiers, and storage tanks. At the Weyerhaeuser Paper Co. mill in Springfield, Ore., severe pirssonite scale problems began in 1984. Deposits were found on the dissolving tank agitator blades, in the raw green liquor lines to the green liquor clarifiers, and in equalization lines between the clarifiers. Six-inch ball valves in the raw green liquor lines sometimes were reduced to 1-in. openings by the deposits. The scale always showed a layered appearance, with alternating lighter and darker bands, suggesting that the deposits formed intermittently rather than continuously. The fact that pirssonite forms with a layered appearance suggests that total titratable alkali (TTA) or temperature variability causes the scaling.

The deposition problem at first was blamed on cloudy weak wash, and steps were taken to improve the clarity. The pirssonite problems did not improve but instead became worse. A program was begun to identify the causes of pirssonite deposits and to find a suitable solution to the problem. This effort included a solubility study to determine under what conditions pirssonite would be expected to form, discussions with other mills to identify factors that influence pirssonite deposition, and various improvements in the green liquor area. As a result of this effort, we were able to formulate guidelines for dealing with pirssonite deposits.

How pirssonite deposits form

Pirssonite is a double salt that contains both sodium carbonate and calcium carbonate. It is a chemical compound, not just a mixture of Na_2CO_3 and $CaCO_3$, and it has the chemical formula $Na_2CO_3 \cdot CaCO_3 \cdot 2H_2O$. Pirssonite forms at temperatures above 35°C in solutions that contain high concentrations of Na_2CO_3, other sodium salts, and $CaCO_3$ or a source of calcium ions.

Pirssonite deposits can form when kraft smelt is dissolved, with smelt containing sodium, calcium, and carbonate ions. Pirssonite deposits also can form at the surface of lime

*Frederick currently works in the Department of Chemical Engineering at Abo Akademi, SF-20520, Turku, Finland.

I. Typical green liquor composition data during pirssonite deposition problems

		Corrected values	
		lb/ft³	g/L
Liquor parameters			
Total titratable alkali	...	7.8	125
Sulfidity (TTA basis)	26	...	...
Sulfate reduction, %	80	...	...
Sodium salt concentrations			
Na_2CO_3	...	4.90	78.5
NaOH	...	0.87	13.8
Na_2S	...	2.03	32.4
Na_2SO_4	...	0.51	8.1
Total	...	8.31	133
Na_2CO_3 and other sodium salts	1.44	...	...

Conversion factor: lb/ft³ × 16.02 = g/L.

II. Conversion of the solubility limit data from Fig. 4 to TTA_{sat}

	lb Na_2O/ft³	g Na_2O/L
Na_2CO_3	5.11	81.8
Other Na salts	3.55	56.7
Total Na salts	8.66	139
Less Na_2SO_4*	0.53	8.5
TTA_{sat}	8.13	130

* 0.48 lb Na_2O/ft³ (7.7 g Na_2O/L) from Table I, adjusted by the ratio of total Na salts in green liquor at the solubility limit vs. the total in Table I.

mud particles that are carried into the dissolving tank. Cooling green liquor below its solubility limit, as may occur in a green liquor line with low flow, also can result in pirssonite deposits.

Solubility of pirssonite in green liquor

In solving pirssonite deposition problems, it is important to know the solubility limit for pirssonite and how the solubility limit changes with temperature, Na_2CO_3 concentration, and the concentration of other sodium salts. Prior to our study, there were only two sets of pirssonite solubility data available. Data from one of these, on the solubility of pirssonite in NaOH solutions by Littman and Gaspari (*1*), are shown in **Fig. 1**, along with experimental data from our study. The other available data were for solutions that contained Na_2CO_3 and $CaCO_3$ but no other sodium salts (*2*).

The pirssonite data in Fig. 1 define the solubility limit for pirssonite at 95°C. In the region above the data, pirssonite deposits form; below it, they do not. Pirssonite is the least soluble sodium salt in green liquor. Na_2SO_4, Na_2CO_3, and burkeite ($2Na_2SO_4 \cdot Na_2CO_3$) are all more soluble under green liquor processing conditions.

The solubility of pirssonite decreases as the NaOH concentration increases. Other sodium salts have the same effect on the solubility of pirssonite as does NaOH. The data in **Fig. 2** are for solutions that contain Na_2CO_3 and either NaOH, Na_2S, or NaOH and Na_2SO_4. All points lie on the same solubility curve.

The solubility of pirssonite decreases as green liquor cools. **Figure 3** shows the solubility curves at 55°, 75°, and 95°C. The change in Na_2CO_3 solubility is about 0.5 lb/ft³ (8 g/L) as Na_2O per 10°C change in temperature.

Estimating the maximum TTA for green liquor

The data in Fig. 3 can be used to estimate at what total titratable alkali content (TTA) pirssonite will precipitate (TTA_{sat}) in green liquor processing. TTA_{sat} will differ from one mill to the next because of differences in the Na_2CO_3, Na_2SO_4, and NaCl concentrations in the green liquor.

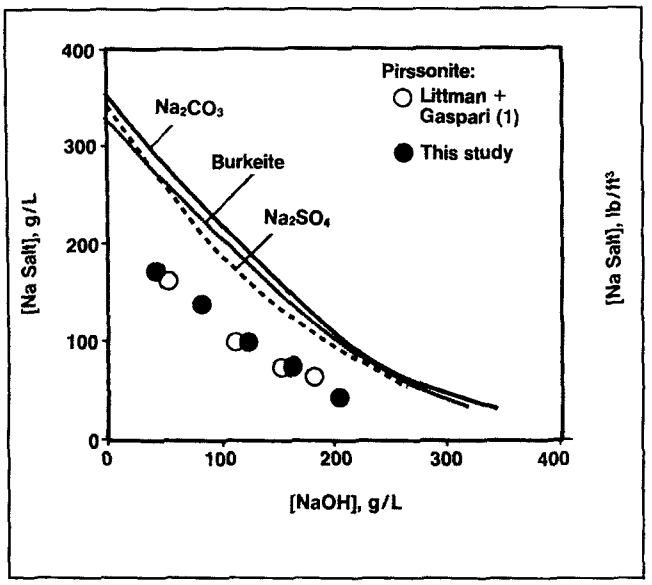
The data for green liquor composition in **Table I** were typical of the conditions at the Springfield mill when pirssonite deposits were a problem. Originally, the mill testers reported an average TTA of 7.3 lb Na_2O/ft³ (117 g Na_2O/L). Later, it was discovered that the test procedure used was in error, and the reported TTA values were low by about 0.5 lb Na_2O/ft³ (8 g Na_2O/L). This error was an important contributor to the pirssonite deposition problem.

Figure 4 shows how to use the mill green liquor composition data to determine TTA_{sat}. The diagonal line is the line along which the mill can operate by raising or lowering the green liquor TTA. Its slope is 1.44 and does not change with TTA for a given mill unless the ratio of the concentration of Na_2CO_3 to the concentration of other sodium salts changes. The intersection of the operating line with the solubility curve locates the upper limit for green liquor concentration without pirssonite deposition. The location of this point depends only on the slope of the mill operating line and on the green liquor temperature. The corresponding TTA_{sat} for the Springfield mill data is 8.13 lb Na_2O/ft³. The calculations to convert the data from Fig. 4 to TTA_{sat} are shown in **Table II**.

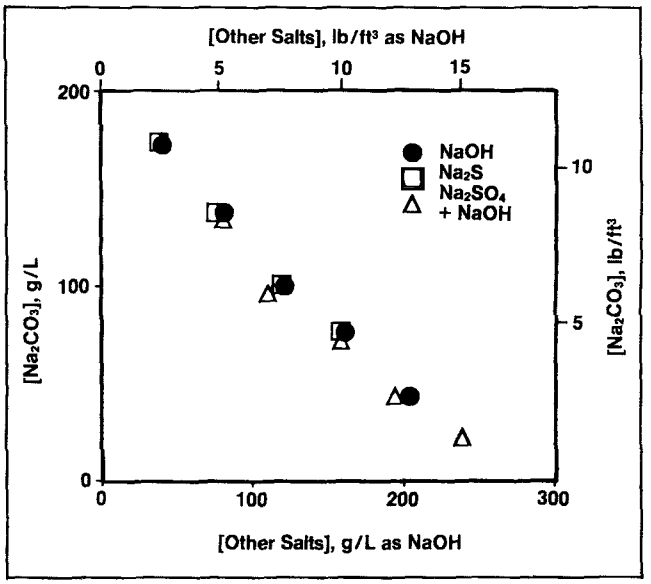
According to these calculations, the Springfield mill was operating, on average, near and sometimes above the solubility limit for pirssonite. In addition, the concentrations in Table I are *average* concentrations for a two-year period. The actual TTA varied (2σ value) by about 0.6 lb Na_2O/ft³, and the corrected maximums often exceeded 8.5 lb Na_2O/ft³. Another factor is that these measurements are not the *local* concentrations in the dissolving tank. Smelt particles do not dissolve instantaneously, and the concentrations near them are higher than the concentrations indicated by liquor samples. Both of these factors result in green liquor concentrations that exceed the pirssonite solubility limit and contribute to pirssonite precipitation.

Figure 4 also provides some guidance in estimating a safe maximum

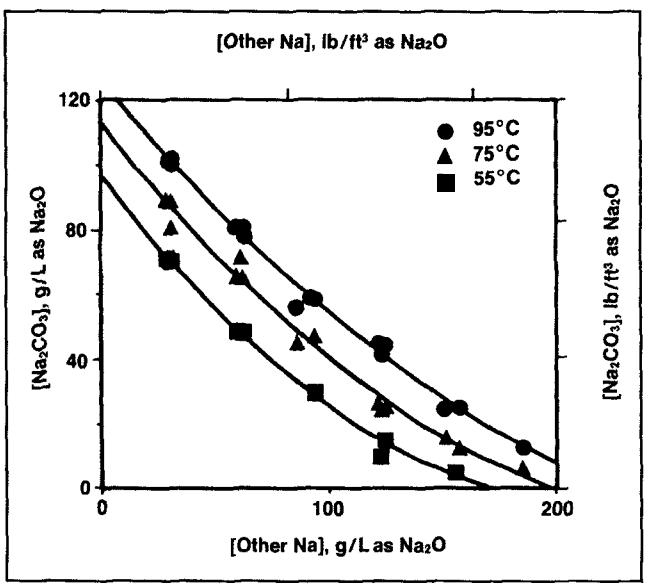
1. The solubility of sodium salts in NaOH solutions at 95°C



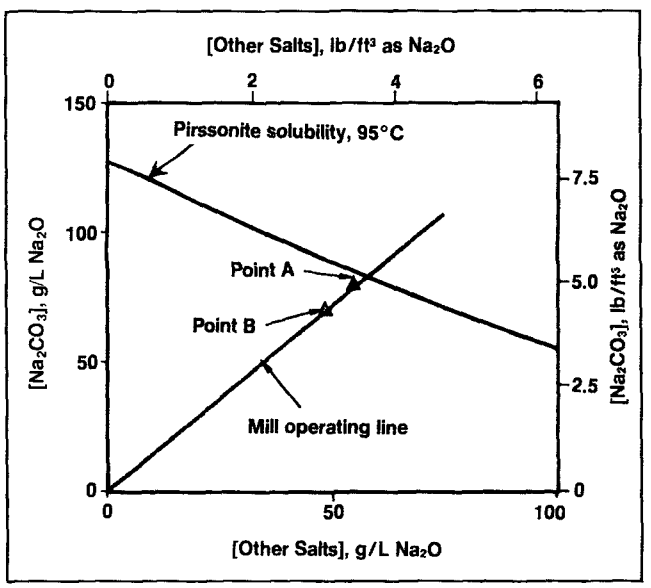
2. The effect of different sodium salts on pirssonite solubility at 95°C



3. The effect of temperature on pirssonite solubility



4. The intersection of the mill operating line for green liquor with the pirssonite solubility curve



TTA (TTA_{max}) for green liquor. At the mill's average operating point, Point A in Fig. 4, pirssonite deposition problems were severe. At a lower TTA, Point B (7.1 lb Na_2O/ft^3), almost no deposits formed. As a percentage of TTA_{sat}, the two mill operating points are as given in **Table III.**

These data suggest that operating TTA_{max} below 96% of TTA_{sat} is advisable to avoid pirssonite deposition problems.

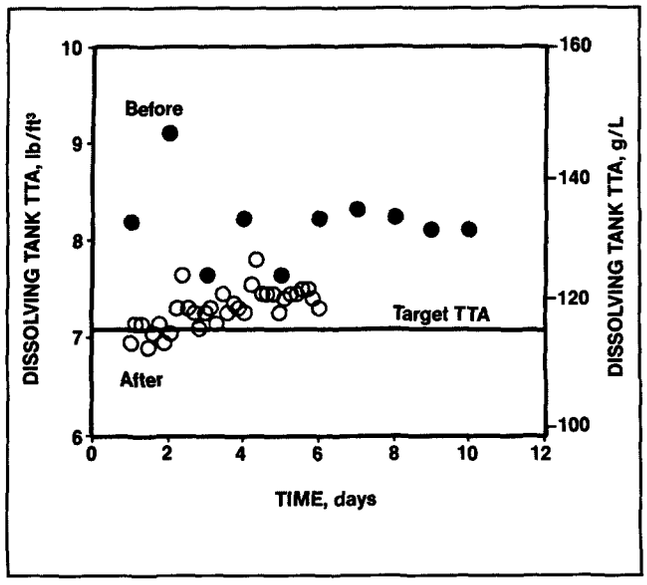
Green liquor TTA control

Good control of green liquor TTA means minimizing the peak values as well as keeping the average TTA on target. **Figure 5** shows how the green liquor TTA in one of the dissolving tanks at the Springfield mill compared with the target value before and after new green liquor TTA sensors and controllers were installed. During the earlier period, the TTA was usually above 8.0 lb Na_2O/ft^3, as compared with a target value of 7.1 lb/ft^3, and it once exceeded 9.0 lb Na_2O/ft^3. A TTA value of 8.0 lb Na_2O/ft^3 is high enough to cause pirssonite deposition, according to our method of estimating the maximum TTA. During the more recent period, the TTA was usually between 6.9 and 7.5 lb Na_2O/ft^3, where pirssonite is much less likely to form.

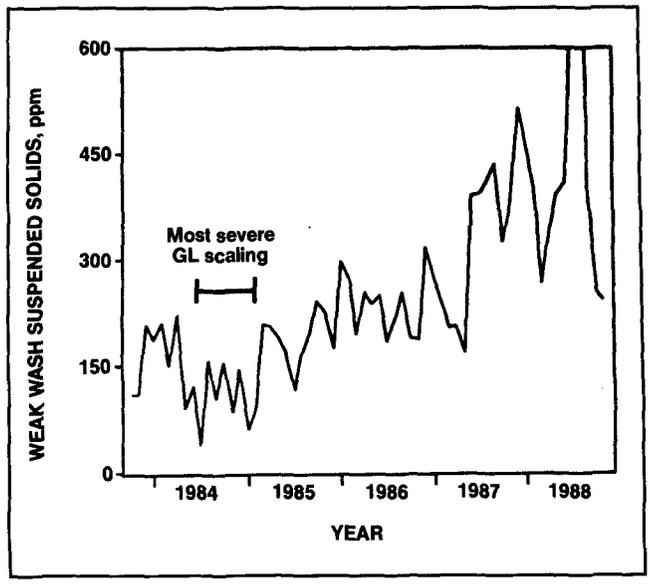
Lime mud carry-over

The pirssonite deposition problem was initially thought to be caused by lime mud carry-over from the mud washers. Weak wash was found to be

5. TTA in the dissolving tank before and after TTA control improvements were made



6. Solids content of the weak wash from October 1983 through November 1988



the largest input of calcium to the dissolving tank (**Table IV**). The weak wash clarity was improved when the recycling of slurry from the kiln precipitator was switched from the mud washers to the slaker. The first severe pirssonite deposits were observed three months after this modification. The most severe scaling problems in the past five years corresponded with the period of clearest weak wash (**Fig. 6**). Clear weak wash has been associated with pirssonite deposition problems in at least three other kraft mills (*3-4*). In all of these cases, the problems began after weak wash pressure filters were installed or mud filters were upgraded.

The reason that clear weak wash can result in pirssonite deposit problems is that the suspended lime mud particles provide a surface for pirssonite to grow on. Seed crystals are effective in preventing or reducing the rate of scaling by inorganic salts on heat transfer surfaces (*5*). The mechanism is one of competing surfaces. If sufficient surface area is present as suspended solids, then deposition is reduced or eliminated on heat transfer surfaces. The same mechanism applies in pirssonite deposition. Suspended lime mud particles act as sites for deposition in competition with impeller blades or pipe walls. This argument is supported by the observation of small particles, quarter-inch pebbles, in the green liquor dregs at the Springfield mill. These particles contain 74% pirssonite. They have a layered structure centered in the middle of the particle, suggesting that pirssonite grows around a single particle.

The current practice at the mill is to allow the weak wash suspended solids to be above the 150-300 ppm range.

Controlling other calcium inputs

The calcium in pirssonite deposits enters the dissolving tank as smelt, not as suspended solids in the weak wash. Since calcium is almost completely insoluble in green liquor, the calcium that enters as smelt can all end up as pirssonite. The source of this calcium is the pulped wood (*6*) and makeup chemicals. The calcium content of wood varies a great deal, but it is not usually practical to change wood supplies to reduce the calcium input. It is possible, and often practical, to change makeup chemicals, however.

The data in Table IV are for the period when pirssonite deposition at the mill was severe. Later, the saltcake makeup was changed to a saltcake that contained almost no calcium (12 lb/day calcium input). This change cut the amount of pirssonite that could form by about half.

III. TTA and TTA_{sat} for Points A and B in Fig. 4

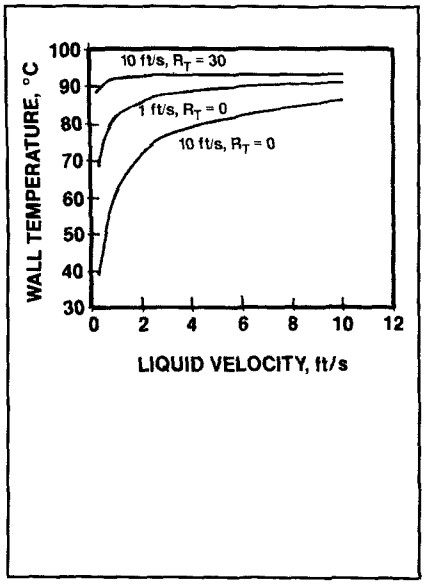
Point in Fig. 4	TTA, lb Na_2O/ft^3	TTA, g Na_2O/L	TTA_{sat}, %
A	7.8	125	96
B	7.10	114	87

Dissolving tank mixing

A well-mixed dissolving tank is important for two reasons. First, poor mixing can result in regions of high TTA. Second, good mixing minimizes local fluctuations in sodium carbonate concentration. When a hot smelt droplet dissolves, the Na_2CO_3 concentration at its surface can be much higher than the equilibrium concentration. If this concentrated solution moves near an impeller or tank wall, pirssonite is more likely to form.

The design and maintenance of the agitators are the keys to a well-mixed dissolving tank. Rohr *et al.* (*3*) found that poor mixing in a dissolving tank resulted in short circuiting or bypassing of some of the fluid, while the rest was well mixed. When short circuiting occurs, the bypassing fluid dissolves little smelt, so the TTA in the rest of the dissolving tank is higher than the target value. A new impeller, designed to provide high-turbulent eddy

7. Wall temperature vs. liquid velocity for an 8-in. green liquor line with a bulk liquid temperature of 93°C and an air temperature of 0°C



IV. Calcium inputs to the dissolving tanks

Source	*Calcium input, lb/day as Ca*
Black liquor	280
Saltcake makeup	300
Weak wash (100-200 ppm suspended solids)	600-1400

strength at 300-350 rpm, eliminated the short circuiting problem (*3*).

Green liquor temperature

The solubility limit for pirssonite decreases by about 0.5 lb as Na_2O per 10°C drop in green liquor temperature. For this reason, the dissolving tank should be run hot, at not less than 95°C. If colder temperatures are used, the TTA limit will have to be lower to avoid pirssonite deposits. Hot water, rather than cold mill water, should be used for smelt dissolving when weak wash is unavailable.

Insulating green liquor tanks and lines (or steam tracing the lines) also is important in minimizing pirssonite deposits. This effort is particularly important in equalizing lines between green liquor clarifiers, where flow is usually low. **Figure 7** shows how the wall temperature varies with liquor velocity for an 8-in. (0.20-m) pipe that contains green liquor at 95°C. The three curves are labeled for air velocity (ft/s) and amount of insulation (R_T is the thermal resistance of the insulation in $ft^2h°F/Btu$. For an uninsulated pipe, the wall is always cool enough so that pirssonite will precipitate if the liquor is nearly stagnant. A reasonable amount of insulation will solve the problem as long as the liquor is not stagnant in the line.

Other operational factors

A number of day-to-day operating practices can help minimize pirssonite deposition problems. The following are guidelines that have evolved from our experience at the Springfield mill.

1. Dissolving tank density controllers should not be set on manual instead of automatic control. It is too easy for the operators to forget that they are on manual control, and TTA swings while they are can result in pirssonite deposition.
2. The HCl solution used for TTA titrations should be checked against an accurate standard. An occasional check of the TTA by an outside laboratory should be used to verify the accuracy of the TTA measurements.
3. The tank-to-tank variability in a multi-tank dissolving system should not be ignored simply because the combined TTA is on target. TTA levels should be measured for each dissolving tank.
4. Dissolving-tank agitators should be kept operating at all times and should receive a high priority for maintenance.
5. Green liquor piping should be cleaned frequently enough to ensure that the dilution water (weak wash) supply to the dissolving tank is not limited. If it is, excessively high levels of TTA in green liquor are difficult to avoid.

Current status at the Springfield mill

Over the past four years, the mill staff has lowered the TTA target, improved the TTA control at the dissolving tank, maintained a moderate level of suspended solids in the weak wash, and changed to a saltcake makeup of low calcium content. The reduction in pirssonite deposition has been evident. During an October 1988 shutdown, the pirssonite deposits in the green liquor piping were so insignificant that many scheduled cleaning jobs using high pressure were cancelled.

Conclusions

Pirssonite deposits will form in green liquor process equipment when the sodium carbonate concentration exceeds the pirssonite solubility limit. The solubility limit depends on temperature and the total concentration of other sodium salts. There is always enough calcium available in the smelt to form pirssonite.

The following guidelines should be followed to minimize pirssonite deposition:

1. Operate with a green liquor TTA target 5-10% below TTA_{sat}.
2. Keep the weak wash suspended solids above 150-300 ppm.
3. Provide adequate mixing to prevent any weak wash from short circuiting the dissolving tank.
4. Use makeup chemicals with low calcium content (saltcake, etc.).
5. Insulate green liquor tanks and lines.
6. Use hot water to dissolve smelt when weak wash is unavailable.
7. Switch the raw green liquor and weak wash lines to and from the dissolving tank regularly.
8. Follow the other guidelines recommended in the section "Other Operational Factors."

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Conversion factor: $lb/ft^3 \times 16.02 = g/L$.

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Appendix: Calculation of TTA_{sat}

Causticizing conversion *CE* is defined as

$$CE = 100\,[NaOH]/[NaOH]+[Na_2CO_3] = 100\,[NaOH]/TTA-[Na_2S] \quad (1)$$

where

NaOH = sodium hydroxide concentration as Na_2O

From the definition of sulfidity *S*,

$$[Na_2S] = TTA\,(S/100) \quad (2)$$

and

$$[NaOH] = TTA - [Na_2S] - [Na_2CO_3] \quad (3)$$

Combining Eqs. 1–3 yields

$$[Na_2CO_3] = (1 - CE/100)\,TTA\,(1 - S/100) \quad (4)$$

The total sodium content in green liquor is

$$[Na]_{total} = TTA + [Na_2SO_4] \quad (5)$$

$[Na_2SO_4]$ and $[Na_2S]$ are related by sulfate reduction efficiency *R* as

$$[Na_2SO_4] = [Na_2S]\,(100/R - 1) \quad (6)$$

Combining Eqs. 2, 5, and 6 yields

$$[Na]_{total} = TTA\,[1 + (S/100)\,(100/R) - 1] \quad (7)$$

Dividing Eq. 4 by Eq. 7 yields

$$[Na_2CO_3]/[Na]_{total} = [(1 - CE/100)\,TTA\,(1 - (S/100)/1 + (S/100)\,(100/R - 1)] \quad (8)$$

Equation 8 can be solved simultaneously with one of the regression equations for pirssonite solubility. This solution gives both $[Na_2CO_3]$ and $[Na]_{total}$ at TTA_{sat} for the temperature chosen. TTA_{sat} is then found by solving Eq. 7 for TTA at $[Na]_{total}$.

The regression equations for pirssonite solubility at three temperatures, expressed in terms of $[Na]_{total}$ and $[Na_2CO_3]$, are as follows.

For 95°C

$$[Na]_{total} = 212.79 - 1.397\,[Na_2CO_3] + 0.00598\,[Na_2CO_3]^2 \quad (9A)$$

For 75°C

$$[Na]_{total} = 189.13 - 1.588\,[Na_2CO_3] + 0.00909\,[Na_2CO_3]^2 \quad (9B)$$

For 55°C

$$[Na]_{total} = 162.26 - 1.604\,[Na_2CO_3] + 0.01038\,[Na_2CO_3]^2 \quad (9C)$$