

Predicting Non-Process Element Behavior in Modern Pulp Mills

Vettenranta, A., Karlemo, C., and Wimby, M.

Valmet, Lentokentänkatu 11, PO Box 109, 33101, Tampere, Finland

Penttilä, K., and Pajarre, R.

VTT Technical Research Centre, Tietotie 4 E, Espoo, FI-02044 VTT, Finland

ABSTRACT

These days, many pulp mills are moving away from using fossil fuels, and changing the lime kiln fuel is often the first step. However, many renewable fuel alternatives, such as gasified bark, may cause operational problems by introducing non-process elements (NPEs) into the pulping cycle. Understanding and predicting the behavior of these elements is necessary to ensure the operational efficiency of the mill and to minimize the dead load in the mill.

This work presents a model for the simulation of the NPEs in the chemical and aqueous streams of the pulp mill. The applied methodology combines calculating mass balances of the mill and evaluating the thermodynamic equilibrium of multi-phase systems in selected process units. Empirical data is used to validate the modeling results.

In the case of adapting to non-fossil fuels, the developed model can be used to plan purge strategies for the NPEs. Furthermore, the NPE model can help to utilize the waste and side streams of the pulp mill, decrease the use of fresh water in the mills (e.g., by recycling bleach plant filtrates, which is the second example in the paper), and develop new innovative technologies.

INTRODUCTION

The need for more efficient use of water, natural resources, and chemicals is increasing in all areas of industry, including pulp mills. This requires new technologies and operational solutions. Pulp mills are complex units with several interconnected unit processes and aqueous streams. Adding a new piece of technology to the mill or changing the operations of one affects the whole mill.

These days, many pulp mills are moving away from using fossil fuels, and changing the lime kiln fuel is often the first step. However, many renewable fuel alternatives, such as gasified bark, may cause operational problems by introducing non-process elements (NPEs) to the pulp mill. Non-process elements mainly originate from the wood raw material. They are defined as elements that do not participate in the pulping cycle as process elements, examples being K, Cl, Mg, Si, P, Mn, Al, S, and Fe [1]. If they are left to accumulate in the fiber line or recovery cycle, they may cause problems through scaling, corrosion, plugging of filters, forming dead load, and increasing bleaching chemical consumption, for example. Figure 1 summarizes the locations where some elements typically accumulate and which problems they may cause.

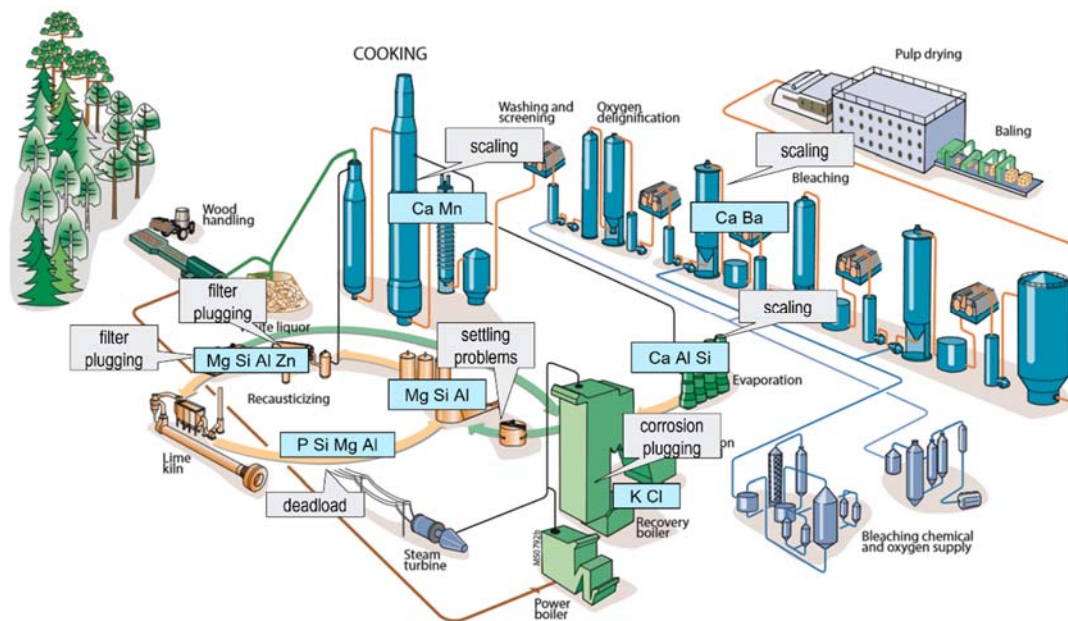


Figure 1. Example pulp mill with some NPEs and the operational problems they may cause.

Understanding and predicting the behavior of the NPEs is necessary to ensure the mill's operational efficiency and minimize the dead load in the mill. This paper presents a simulation model for the NPEs, which has been developed in cooperation with Valmet and VTT Technical Research Centre. The model covers almost the entire pulp mill, including the recovery and causticizing cycles and the fiber line. The applied methodology combines calculating mass balances of the mill and evaluating the thermodynamic equilibrium of multi-phase systems in selected process units. The model is similar to the so-called FUPU reference model [2], with the addition of chemical equilibrium calculations.

One of the objectives of the NPE model is to help the pulp mills in technology selection, for example, when decarbonizing the pulp mill. In a modern pulp mill, the lime kiln in the chemical recovery cycle is the only major consumer of fossil fuel, and in recent years, there has been an increased interest in replacing this fuel with a renewable option. The two main alternatives are wood powder firing and biomass gasification, and the NPE balance is one aspect to be studied in deciding between these fuels.

A typical energy source for gasification is wood bark, which is often readily available in pulp mills. Biomass gasification is a combined system of a biomass dryer, a gasifier (often a circulating fluidized bed gasifier), and a lime kiln optimized for burning the product gas. The biomass gasifier captures many non-process elements that originate from bark, but some NPEs enter the lime kiln. The NPE model can be used to study these elements' enrichment and to plan for efficient purge strategies. A case example of a lime kiln with a biomass gasifier is presented in this paper.

Another case example is given on the possibility to recycle one filtrate of the pulp bleaching sequence back to the process, instead of taking it to effluent. The objective of this process change is to decrease the environmental load in terms of COD (chemical oxygen demand) and inorganics by reducing the effluent amount. However, there may be negative consequences of NPE enrichment when an alkaline process stream is recycled, and these can be investigated with the NPE model.

As shown by the second case example, one objective of the NPE model development is to predict the level of NPEs and their compounds entering the pulp mill effluents. This is important from an environmental point of view. Furthermore, the NPE model can help to utilize the waste and side streams of the pulp mill, decrease the use of fresh water in the mills (e.g., by recycling bleach plant filtrates), and develop new innovative technologies for NPE removal. It is essential to control the non-process element behavior in these cases to prevent the accumulation of NPEs in the pulp cycle and the distribution of possibly harmful elements in the environment.

MODELING METHODS

The applied methodology combines the calculation of mass balances of pulp mills and the evaluation of the thermodynamic equilibrium of multi-phase systems in selected process units. The simulations are for steady-state situations so that the accumulation of non-process elements at equilibrium can be studied. The Balas process simulator [3] is used for assessing mass balances, and the ChemApp solver [4] is used to compute the thermodynamic equilibrium of chemical systems through the Gibbs free energy minimization method. A similar approach has been applied to model a paper mill's calcium chemistry [5] and other pulp mill processes [6].

For the fiber line, the presence of water inside the fibers must be considered, and this is done by calculating the Donnan equilibrium. It describes the pulp-water system where the ions in the water are distributed between the free water and the water inside the fibers. The combination of Gibbs energy minimization calculations and the Donnan equilibrium-based models has been presented in [7].

The NPE model's scope is presented in Figure 2, which shows the main equipment covered by the model and the main input and output streams. The NPE model can be used to simulate the whole cycle presented by the figure, or only some smaller part of the process, such as the recausticizing cycle.

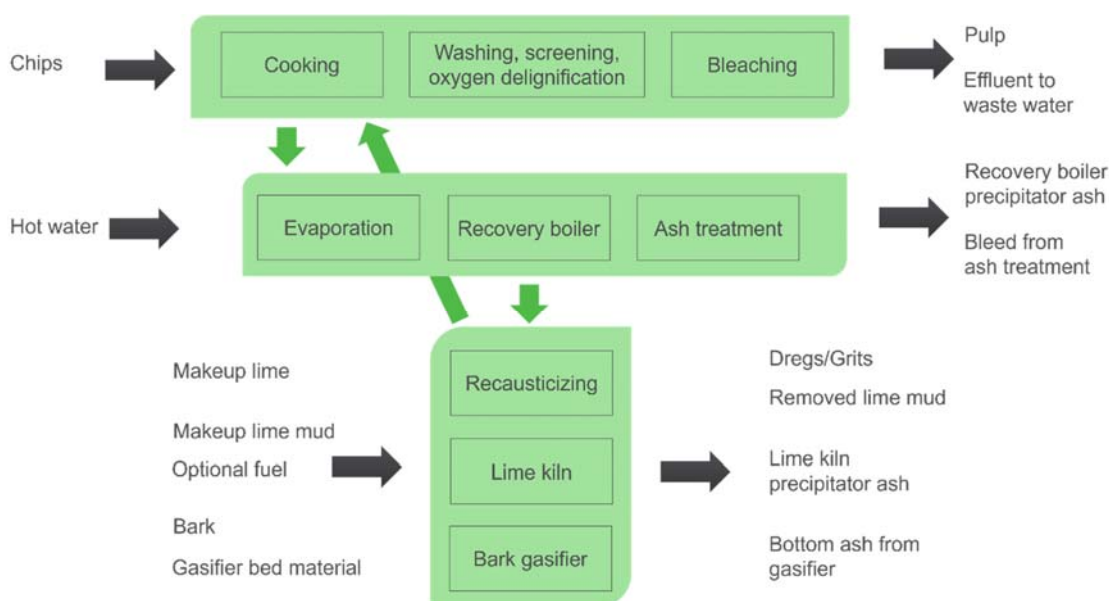


Figure 2. Scope of the NPE model with modeled unit processes and input and output streams.

The thermodynamic equilibrium model requires a thermodynamic database, which is tailor-made for this model, but based on the work conducted at VTT [8]. The thermodynamic system comprises the following elementary components: Ba, Sr, Zn, Cu, Fe, Mn, Ca, K, Cl, S, P, Si, Al, Mg, Na, O, N, C, and H. The system has a gaseous phase, an aqueous phase, several solid stoichiometric phases, and a second aqueous phase representing the fiber-bound aqueous phase, as discussed earlier. The gaseous phase is modeled as an ideal gas phase. The Pitzer activity coefficient model [9] is applied for the aqueous phase. In addition, some oxides (such as Fe_2O_3 , MnO , and ZnO) are removed from the system as these stable phases are not assumed to form in industrial processes, and they would dominate the calculation if included in the chemical system.

The thermodynamic database is built for a typical process temperature range from 25 - 105 °C [8]. It is worth mentioning, that processes operating close to the evaporation point of water may cause difficulties for the thermodynamic data regarding the temperature dependence of the solubility and its possible extrapolation close to the boiling point. Generally, however, the thermodynamical functions work well below and slightly above the boiling point.

There are limitations when applying the thermodynamic equilibrium approach to the modeling of the chemical streams in pulp mills. First, limitations with mixing or other mass transfer phenomena cannot be considered, and therefore, the extent of some reactions might be overestimated. Also, as the size of the thermodynamic database must be restricted, some important chemical compounds might be missing. There are also some compounds that are very difficult to predict by thermodynamic calculations, one example being the compounds of the K_2O - CaO -

SiO₂ subsystem [10]. Reaction constraints can be used to cover the deficiencies in the thermodynamical data, but empirical data is needed to adjust these constraints.

The model validation has been conducted against experimental data obtained from different pulp mills. A list of the most important samples collected and analyzed in external laboratories is presented in Table I. Typically, the NPEs are analyzed using ICP-OES (inductively coupled plasma optical electron spectroscopy) and following SCAN-N 38:10 (Acid-soluble metals).

Table I. Most important samples collected and analyzed from different pulp mills.

Evaporation and recovery boiler	Weak black liquor Strong black liquor As-fired black liquor Electrostatic precipitator ash from recovery boiler Treated ash
Recausticizing	Raw green liquor Clear green liquor Green liquor dregs Make-up lime/quick lime Lime mud Burnt lime Electrostatic precipitator ash from lime kiln White liquor
Gasification	Bark Gasifier bed material Bottom ash from gasifier
Fiber line	Wood chips Pulp after different washers Filtrates after different washers

In the validation, it has been noticed that some elements and compounds do not follow the predicted equilibrium behavior, and the reactions of these elements have been constrained based on empirical data. Silicon, already mentioned, is one example of these elements that must be manually restricted. More empirical data would be needed to confirm whether the same constraints apply to all mills or the ones where validation data has been available. Moreover, the model cannot predict whether the solids that form contribute to scaling, or how the organics in the process streams affect the solubility of metals.

RESULTS

This paper presents two case examples, which show the capabilities of the NPE model. They are calculated with imaginary but realistic mill data representing modern pulp mills. The model simulations are iterated until they reach convergence, so the accumulation of the NPEs in the different process streams can be predicted. It is worth noting that the presented results are mill-specific and cannot be generalized to all mills.

Changing the Lime Kiln Fuel

The first case example studies a lime kiln, where the fuel is changed from natural gas to gasified bark. This is nowadays a typical case when the mills are decarbonized. Several small changes should be made in the kiln operation when changing the fuel, but this paper only focuses on the changes in the NPE levels as predicted by the NPE model.

This case example is calculated in a large-scale imaginary mill that burns natural gas as the lime kiln fuel, dumps part of the lime mud to control the balance of different elements, and adds make-up lime and lime mud to the process. To simplify the simulation, these make-up flows have been modeled as consisting only of water with CaO and CaCO₃, respectively. The bark used in the example is a mixture of softwood and hardwood bark, with the NPE concentration being approximately average compared to references of Scandinavian bark.

The NPEs in the gasified bark (also known as product gas) originate both from the bark itself, as well as the bed material used in the gasifier. The bed material used in this example consists mainly of CaCO₃ and is enriched with Si and Mg. Some NPEs in the bark and bed material are captured in the gasifier bottom ash and with the cyclones after the gasifier, but some enter the lime kiln with the product gas. Table II shows example

concentrations of selected NPEs that enter the lime kiln with the product gas. This composition is based on mass balance calculations across the process.

Table II. Example concentrations of some NPEs in the product gas.

Product gas content	mg/Nm ³
K	700
Al	200
Mg	700
Si	1 100
P	200
Mn	100
Fe	100

When this product gas enters the lime kiln, the NPEs mix and react with the lime and lime mud. Some can be removed with the electrostatic precipitator ash, but some NPEs are enriched in the burned lime. Table III shows how much the levels of some NPEs increase in the burned lime when comparing the case of gasified bark with the original case of natural gas as the lime kiln fuel. In this case, the purging level of lime mud is kept the same.

Table III. Increase of NPE content when natural gas is changed to gasified bark.

NPE content in burned lime	Increase (%)
K	900
Mg	300
Si	80
P	20
Mn	300
Fe	300

It is worth noticing, that although the increase in many of the NPEs is high, this is mainly because natural gas is such a pure fuel. For example, the potassium level of the original burned lime was very low, which makes the percentage increase high. Consequently, the change in the K levels of green and white liquor is negligible.

Nevertheless, the increases of some elements in the burned lime are significant. In this paper, we have focused on phosphorus because it forms a dead load in the recausticizing cycle by forming a compound with calcium [11], decreasing the amount of Ca available for causticizing reactions. Purging of lime mud is a typical way of removing NPEs, such as phosphorus, from the recovery cycle. In this case, the specific question is: how much more purging of lime mud would be needed to maintain the same phosphorus level in burned lime when changing the fuel from natural gas to gasified bark?

According to the simulations, maintaining the phosphorus level in the burned lime would mean 8 kg_{dry}/Adt (air-dried ton of pulp) of more lime mud purging, and 7 kg_{dry}/Adt of more make-up lime mud (23% increase). Since the lime mud coming from the process also contains NPEs, more lime mud must be purged than make-up used. The mill might also look at the residual carbonate in the burned lime and plan the purging of lime mud based on changes in that number, but this is not considered in the modeling.

If the mill would be changing the lime kiln fuel from heavy fuel oil (HFO) to renewable fuels, the required amount of make-up lime might even decrease. This is because the sulfur in HFO also creates a dead load in the cycle by forming CaSO₄, whereas renewable fuels typically contain very little sulfur.

These presented values can be used to estimate the profitability of the fuel change when the price of the make-up chemicals and the different fuels is known. In addition to the economics of the process, sustainability factors will also play a significant role in fuel selection.

Reusing Bleaching Filtrate

In the second case example, the reuse of OP (oxygen peroxide stage in bleaching) filtrate in the washer after oxygen delignification is investigated. Traditionally, the OP filtrate is taken to effluent, but this reuse of the OP filtrate (also called alkaline filtrate) can be done to decrease water usage and the amount of effluent created. The two process options for a medium-scale imaginary example mill are shown in Figure 3.

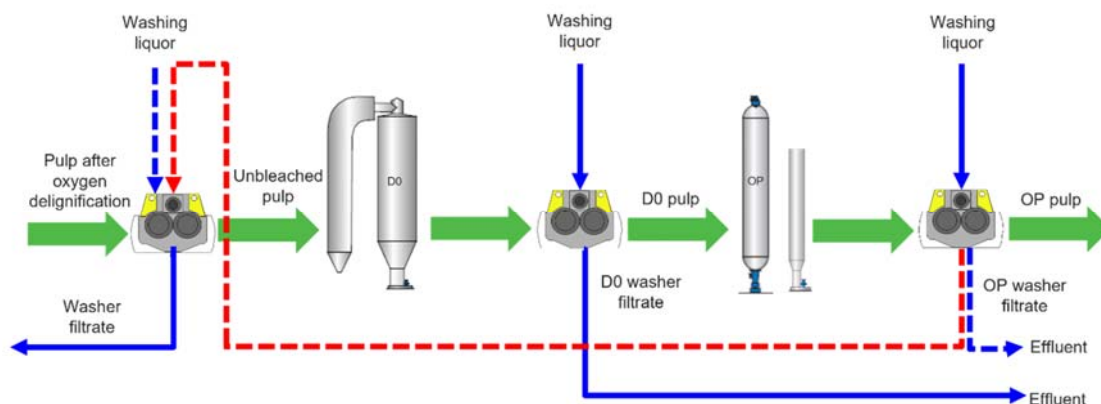


Figure 3. Part of the bleaching sequence with the option of recycling the OP filtrate with red (OP = oxygen peroxide stage, D0 = chlorine dioxide stage).

Recycling the OP filtrate will increase the levels of some NPEs in the streams after oxygen delignification because the OP filtrate contains NPEs. The composition of the D0 stage is of particular interest. Table IV shows the composition of OP filtrate in the case when it is not recycled. On the other hand, Table V shows the effect on some key process streams due to the OP filtrate recycling.

Table IV. Concentration of some elements in OP (oxygen peroxide stage) filtrate before it is recycled.

	Concentration (mg/l)
Na	2 000
K	20
S	400
Cl	400
Ca	30
Mg	30

Table V. Effect of OP filtrate recycling to some selected process streams, increase in percentages compared to the case where the OP filtrate is taken to effluent.

Increase (%)	Oxygen-delignified pulp after wash press (30% ds) (mg/kg _{ds})	Wash filtrate from unbleached pulp (mg/l)	D0 filtrate (mg/l)	Weak black liquor (mg/kg _{ds})	Bleached pulp (mg/kg _{ds})
Na	68	100	29	1	1
K	-5	13	-6	0	0
S	86	66	9	0	1
Cl	2 500	2 200	11	33	0
Ca	13	21	5	-1	69
Mg	37	25	14	5	25

As shown by Table V, the direct effect on the unbleached pulp after the oxygen delignification is significant in terms of sodium, sulfur, and chlorine concentration (first column). These elements also increase significantly in the washer filtrate from the unbleached pulp because they are water-soluble. Consequently, the concentration of these elements could increase in the product of the process, the bleached pulp. An increase is also expected to be seen in weak black liquor since the washer filtrate is taken to pulp cooking where black liquor is generated. However, these elements are diluted along the process, and only the chlorine level is significantly elevated in weak black liquor. Advanced recovery boiler ash treatment systems must remove the significantly increased chlorine (33%) in weak black liquor to avoid the accumulation of chlorine in the recovery cycle.

When looking at the other elements present in lower concentrations, there is a significant increase in the calcium and magnesium levels of the bleached pulp. This may benefit the process since calcium compounds are often

needed in papermaking, and magnesium is needed in pulp bleaching (often as MgSO_4). Recycling these elements from the OP filtrate into the process may reduce the need for purchased makeup chemicals.

The main objective for recycling the OP filtrate is to reduce the amount of effluent created in the pulp mill and to decrease the total amount of COD (chemical oxygen demand) and inorganics in the effluent. Traditionally, both the D0 and OP filtrate are taken directly to the effluent and wastewater treatment. But in the case of the recycled OP filtrate in this example mill, the total amount of effluent is reduced by $4 \text{ m}^3/\text{Adt}$, which is half of the total amount of effluent coming from the bleaching plant. On the other hand, the COD (in kg/Adt) is approximated to be reduced by at least 20%.

The composition of the D0 filtrate, which goes to the effluent in both process options, does not change significantly according to the modeling results, as shown in the third column of Table V. However, the total amount of cooking chemicals Na and S lost from the cycle decreases, and this reduces the amount of make-up chemicals needed (ca $5 \text{ kg}/\text{Adt}$ for Na and $1 \text{ kg}/\text{Adt}$ for S). According to the model, the pH of the D0 filtrate increases from 2.7 to 3.4 when the OP filtrate is recycled. This means that some additional acid or ClO_2 might have to be added at the beginning of bleaching to prevent the increase in pH. However, this is not considered in the modeling.

DISCUSSION

Traditionally in pulp mills, the problems caused by the non-process elements have been controlled by increased purging of different process streams, such as lime mud or fiber line effluent. But if this purging is not done effectively, excess waste can be created and too much make-up chemicals used. There is a need to optimize the methods of NPE control, and the NPE model presented in this paper can be utilized to achieve this.

As shown by the examples in the previous section, the NPE model can predict the levels of different non-process elements after a change has been made. When changing the lime kiln fuel, the pulp mill might set limits for certain elements in burned lime (e.g., P, Mg, and Si) and use the NPE model to plan purge strategies to achieve these. Moreover, the purchased make-up lime could be chosen based on its effect on the mill's NPE balance.

The main goal of the NPE model development has been the simulation of mill-wide chemical balances, and the possibility of modeling complex interactions between different chemical elements and compounds. This is achieved by the thermodynamic and mass-balance calculations considering the pH, temperature, and composition of different process streams. However, there are challenges with the accuracy of the NPE model.

For example, the thermodynamic equilibrium approach does not work with all elements and their chemistry must be constrained based on empirical data. The mismatch between the modeled and actual behavior can be either due to inaccuracy in the applied model system or because the actual process is not close to equilibrium. Close to modeled equilibrium behavior is expected when the equilibrium concentrations are determined by relatively fast precipitating or dissolving phases that are well characterized and the thermodynamics of the corresponding dissolved species are well known. Poor correspondence is obtained when or more of these conditions are not met.

Moreover, the model cannot predict whether the solids that form contribute to scaling, because a formed solid may either follow a liquid as a colloidal solid, follow a solid process material such as pulp or lime mud, or stick to the process equipment. Furthermore, it cannot predict how the organics in the process streams affect the solubility of metals. More empirical data is needed to reduce these uncertainties in the model.

In addition to the examples presented in this paper, some possible ideas for the use of the NPE model include the following: studying how new raw materials for pulp affect the whole pulp mill, finding new possibilities for reducing the freshwater use of mills, and figuring how to eliminate the land-filled waste generated by the pulp mills.

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