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Determination of Alkaline Process Parameters in Kraft Paper Mills Using the UPA® Universal Process Analyzer

Challenges

- Optimum control of Kraft causticizing process
- Enhancing product quality and reducing process variability
- Fast results by simultaneous analysis sequences
- Fully automatic multi-stream sampling and preconditioning system with auto-cleaning

Executive summary

Kraft paper mills use large amounts of strong alkaline pulping solutions that are continuously spent and recovered during manufacturing. Efficient operation and consistent quality specifications depend largely on tight control of the mill's recovery lines and causticizing degree. The existing "ABC" laboratory test on the pulping solutions involves time-consuming analysis procedures and does not fully enable operators to control the (re)causticizing process, resulting in loss of productivity and energy losses. Process transparency was introduced in a paper mill by means of an UPA® automatic (on-line) titration system monitoring simultaneously all critical alkaline parameters. The system can be used as an important tool in debottlenecking and stabilizing the causticizing process, while keeping conformity with industry-standard tests.

Causticizing and process control

The Kraft pulping process (often shortened as the "Kraft process") is the predominant production process used in industrial pulp and paper facilities. It requires large amounts of strong alkaline cooking solutions or *liquors* of caustic soda ($NaOH$) and sodium sulphide (Na_2S) to convert wood chips to pulp. Efficient operation is of concern to any Kraft mill and depends largely on a carefully controlled chemical balance, determined by (1) the recovery of the spent cooking liquor and (2) the causticizing efficiency.

The chemical recovery operates with relatively low losses, at typical recovery rates of 96–98%, although part of the recovered pulping chemicals is considered as *deadload*, inert chemicals. Green liquor is the intermediate pulping solution resulting from the recovery process and causticized with lime (calcium hydroxide) to obtain fresh white liquor. This is expressed by the following equilibrium reaction:

$$Na_2S + Na_2CO_3 + Ca(OH)_2 \leftrightharpoons Na_2S + 2\ NaOH + CaCO_3(\downarrow)$$

Table 1. Process parameters in Kraft causticizing and the typical measuring ranges used.

	$NaOH$	Na_2S	Na_2CO_3
Causticizer	90 g/l	30 g/l	30 g/l
Slaker	70 g/l	30 g/l	50 g/l
Green liquor	10 g/l	30 g/l	110 g/l
White liquor	100 g/l	30 g/l	20 g/l

The goal of (re)causticizing is to produce, as efficiently as possible, white liquor with the highest possible concentrations of hydroxide (OH^-) and sulfide (S^{2-}), called the causticizing efficiency or degree (as %CE). Since the causticizing reaction is characterized by incomplete conversion, as described by Goodwin's curve, Kraft mill operators need to take measures to overcome the equilibrium limit. Over-liming is one option but shows to have adverse consequences due to lime filtration issues.

Experience has shown that Kraft mill operators can reach a net CE of around 84%, on the condition that a proper control strategy is outlined. A positive side-effect of such a strategy would also strongly influence the environmental impact on the whole production process by the direct effect on the recovery boiler. While the heat recovery from this process unit allows a paper mill to be self-sufficient, it is also the main source of sulphur emissions and inorganic solid waste. *Deadload* significantly increases emissions of inorganic material entrained in vent gases and decreases overall efficiency. End-of-pipe solutions such as biological water treatment and vent scrubbers may well be one way to meet environmental regulation, they have little process relevance.

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Solution - System description

Conform with the paper industry's practices, AppliTek's UPA® Universal Process Analyzer uses wet-chemical titrimetry based on the widely used ABC method, but carried out by a fully automatic (on-line) analyzer mainframe, in conjunction with a rugged sampling/ preconditioning system. The UPA® Universal Process Analyzer can carry out two titrations at the same moment by using a double analysis train with separate analysis vessels, allowing two results (as OH^-, CO_3^{2-} and S^{2-}) each 15 minutes. At all times the analyzer can be supervised and controlled from a remote location through a Local Area Network using commonly available VNC software.

The UPA® Universal Process Analyzer was equipped with a special valve panel for measuring 4 streams, with settler systems specifically for the slaker and causticizer streams. Since the controller software of the analyzer controls the loop valves of the sampling system, it is perfectly possible to adjust the sequence of the streams. In this particular application, the mill operator choose to simultaneously monitor the white liquor and causticizer streams and have an occasional check at every x cycles of the slaker and green liquor streams.

Liquid handling and analysis

The hydroxide (OH^-), carbonate (CO_3^{2-}) and sulfide (S^{2-}) concentrations are determined by an acid-base titration using a pH electrode. Before the sample is analyzed, a small sample volume is taken by the sampling loop system and diluted with demineralized water. The sample loop is flushed with fresh sample and after activating the external loop valves, sample and dilution water are injected in the analysis vessel by the carrier pump and the titration with

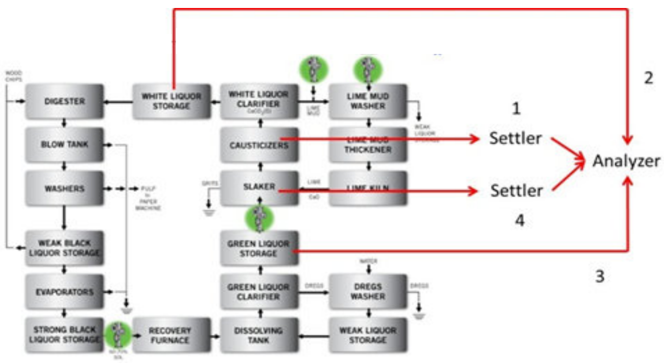

Fig. 1. Schematic layout of the Kraft process and the sample take-off points for the on-line titration system. Settler systems are used for the causticizer and slaker.

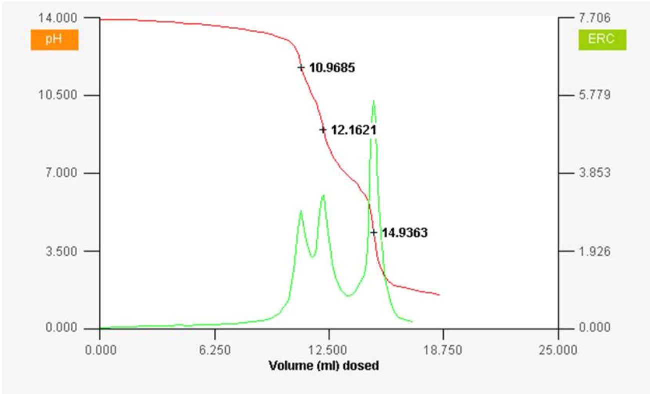

Fig. 2. Titration curve showing the inflection points for NaOH / Na_2CO_3 / Na_2S, obtained after exporting the analysis data to spreadsheet. This curve can also be visualized in real-time on the analyzer screen.

hydrochloric acid is started. Once the actual titration is finished, the NaOH, Na_2CO_3 and Na_2S concentrations are calculated. After each analysis cycle an automatic cleaning with demineralized water takes place to prevent cross-contamination between the individual samples. The causticizer and slaker streams are sampled and preconditioned by small precipitation clarifiers or settlers. When the solids have precipitated, only the top layer is used for analysis. In addition to a regular automatic cleaning, an acid cleaning cycle in the complete sample pathway of these streams is run every three days to prevent fouling.

Results

The notion that on-line monitoring is an important tool in debottlenecking and stabilizing the causticizing process became evident with the UPA® Universal Process Analyzer. Operators can implement a proper liquid control strategy based on the analyzer data, taking advantage of the immediate effects of an improved causticizing efficiency on the different process units:

- Stabilizing the alkali content of the green liquor
- Prevention of under– or over-liming
- Maximizing white liquor strength
- Better recovery boiler operation by reduced deadload
- Eliminate shift to shift variability

Interestingly, no structural changes to the process were necessary and operator intervention was minimized. The embedded software of the analyzer calculates automatically the Effective, Active and Total alkali, Sulphidity, Degree of causticizing and Degree of reduction (conform with SCAN-N 30:85 standard), all communicated by analogue or digital signals to the mill DCS.

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