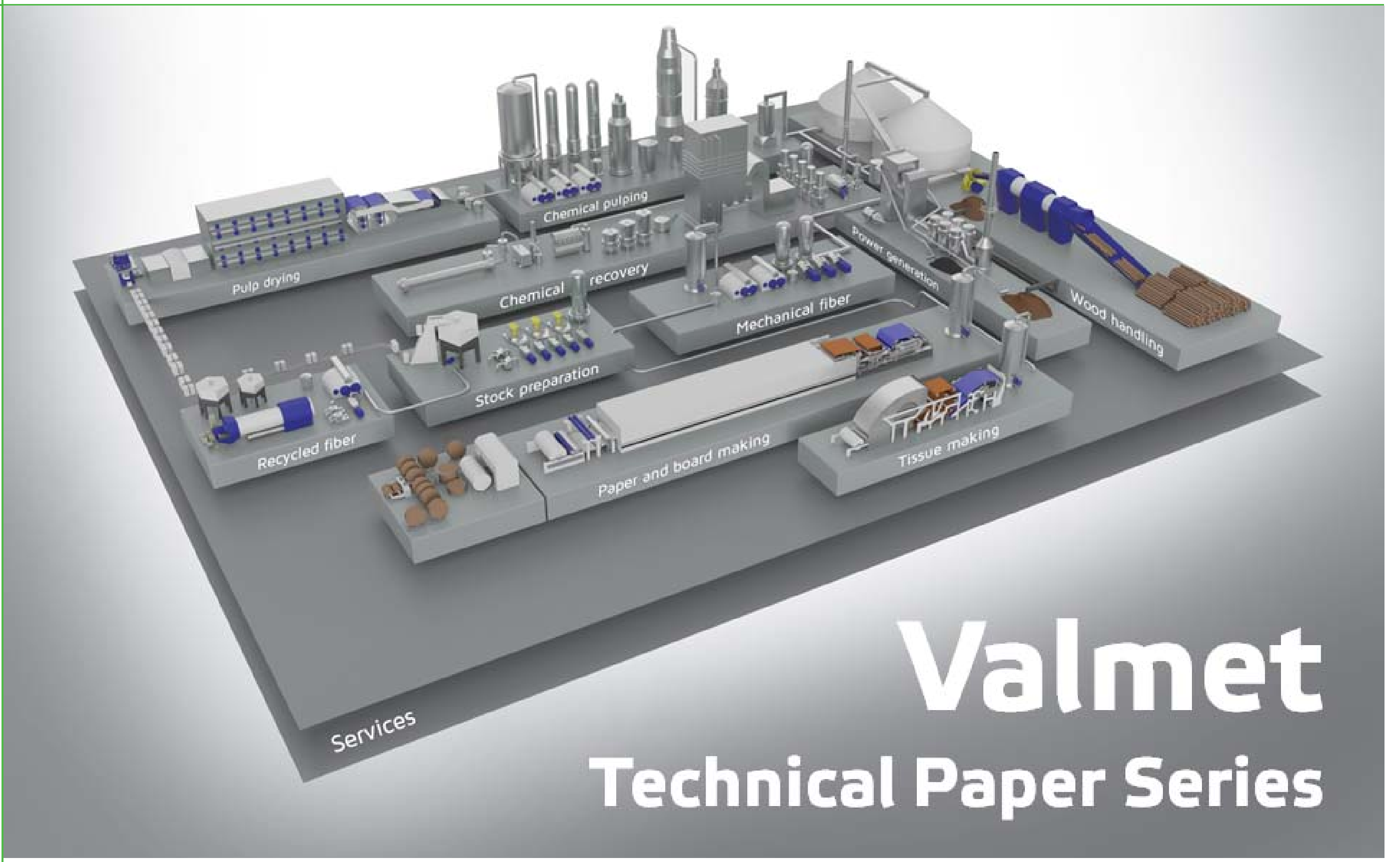

Control of sulfidity in a modern kraft pulp mill

Executive Summary

Many years ago, the kraft pulping liquor circuit used sodium sulfate salt as the main make-up source of cooking chemicals. The make-up chemical has given its name to the process in many languages. Back then, the sulfidity reached an equilibrium level that was dependent on the leakages.

Sulfur emissions impact the environment negatively. Reduced sulfur causes smell in the mill's surroundings and oxidized sulfur contributes to the large-scale acidification of soil, which negatively affects vegetation and biodiversity. Today, both environmental and economic forces have reduced the leakages and most modern mills have practically eliminated sulfur emissions to the atmosphere. In addition, improved pulp washing has reduced the loss of chemicals with the pulp leaving the washers. Reduction of sodium loss from the process is more difficult to achieve due to the fact that sodium is adsorbed on the fiber that leaves the closed liquor cycle. The result of this development is, for most mills, that the equilibrium sulfidity level is higher.

The methods used to control the chemical balance today include e.g. dumping of recovery boiler ash to reduce sulfur content, white liquor oxidation to the oxygen delignification to reduce sodium intake and dumping of chlorine dioxide brine. Although these methods are applied, some modern mills still have difficulties controlling sulfidity.

One development trend in kraft pulping is to create valuable side streams from the process. Such streams are in many cases created by primary acidification with sulfuric acid. Examples are tall oil production and lignin extraction. Introduction of processes like these further disturbs the sodium sulfur balance and the existing means of controlling it becomes insufficient.

Valmet has studied how to expand the sulfidity control toolbox. Our conclusion is that internal sulfuric acid production is the most efficient way to separate sodium and sulfur streams. Therefore, a process which oxidizes sulfur containing concentrated non-condensable gas (CNCG) to relatively concentrated sulfuric acid was developed. The first full-scale plant based on oxidation of CNCG [will be] started up late 2017. The intention is to avoid addition of external sulfur and replace it with internally produced acid. This paper describes the plant and scenarios for control of the chemical balance.

Introduction

The sulfur in the kraft mill system is essential for the pulp quality and yield. It is not only an effective chemical but also cheap. Since it is cheap, there are, in many cases, no reasons to minimize the sulfidity due to consumption cost. On the contrary, a modern mill running at stable conditions gets its sulfur supply through by-products of side processes such as chlorine dioxide generation and tall oil production, and therefore it is common that mills purge a sulfur rich stream e.g. recovery boiler ash and neutralized spent acid from the chlorine dioxide plant. If the sulfur purge flow contains sodium, the purge in many cases causes increased sodium consumption in the mill, either as sodium hydroxide or sodium carbonate.

This paper discusses the contributions to the sodium and sulfur balances of the liquor circulation. The effects of changed mill operating conditions on the balance and how the sulfidity can be controlled through conventional methods is also illustrated. Finally, a new way of controlling the sodium sulfur balance through mill internal production of sulfuric acid is presented, along with a new technology for sulfuric acid production, that [will be] started up in full scale at the end of 2017.

The chemical balance will be illustrated with a so-called vector diagram that was described in 1973 by Gösta Wiklander[1]. That paper also presents an opportunity to compare today's performance of the kraft pulping in terms of emissions and make-up consumption to the situation 44 years ago. In Wiklander's paper some mill cases were presented, of which one will be used for comparison. The modern reference mill will be a hypothetical bleached softwood mill balance with modern technology in all positions.

Contributions to the sodium and sulfur balances

The liquor cycle in the kraft pulping process is normally highly closed. Only a small fraction of the chemicals leak. Of course, this is a consequence of stricter environmental limits - but it also helps to reduce the cost of make-up chemicals. The fact that the purge and make-up is small in comparison to the circulation of chemicals makes the system very slow and it normally takes months to reach equilibrium conditions.

The main contributors to the sodium-sulfur balance in a kraft mill are listed in **Table 1** (**next page**). In the list oxygen delignification is included as a part of the closed liquor cycle definition. However, in 1973 oxygen delignification was not yet introduced.

Years ago, the kraft pulping liquor circuit used sodium sulfate salt as the main make-up source of cooking chemicals. The make-up chemical has given its name to the process in some languages. Depending on the leakages, the sulfidity reached an equilibrium level. Economical and mainly environmental forces have reduced the leakages which, in most cases, have increased the equilibrium sulfidity level. Sulfur emissions have a negative impact on the environment. Reduced sulfur causes smell in the mill's surroundings and oxidized sulfur contributes to the large-scale acidification of the environment, which affects vegetation

	Kg Na/ADT		kg S/Adt		Vector diagram balance point
	Mill 2017	Mill 1973	Mill 2017	Mill 1973	
Incoming flows					
Salt cake from ClO$_2$ plant	3.79	3	2.66	7	A
Spent acid from tall oil plant	0	0	2.31	0	B
Wood	0.47	0	0	0	C
Recirculated filtrate from bleaching	0	0	0	0	D
External fuel to lime kiln and recovery boiler	0	0	0	1	E
MgSO$_4$ to ox delignification	0	0	0.67	0	F
Sodium hydroxide to ox. delignification	7.04	0	0	0	G
Sodium sulfate make-up	0	9	0	6	H
Sum	**11.3**	**12**	**5.64**	**14**	
Outgoing flows					
Washing loss pulp	1.94	6	0.52	1	I
Liquor with dregs and grits	0.32	0.6	0.2	0.5	J
Liquor with digester rejects	0.06	0.6	0.3	0.5	K
Black liquor spills	0.32	4	0.06	1	L
Recovery boiler dust emission	0.06	0.8	0.03	0.6	M
Diffuse gas emissions	0	0	0.46	1.5	N
Lime kiln flue gas	0	0	0.01	0	O
Ash treatment loss	0.47	0	0.18	0	P
Oxidized white liquor to bleaching	0	0	0	0	Q
Gaseous emissions from recovery boiler	0	0	0.04	8.9	R
White liquor spill	0.32	0	0.06	0	S
Purge of recovery boiler ash	7.79	0	3.78	0	T
Sum	**11.3**	**12**	**5.64**	**14**	

Table 1: Na/S balances in mill from 1973 and reference.

and biodiversity negatively. This has led to sulfur emissions from pulp mills having been reduced, as seen in **Table 1**. The most modern mills have practically eliminated sulfur emissions to the atmosphere. In addition, improved pulp washing has reduced the loss of chemicals with the pulp leaving the washers. Reduction of sodium loss from the process is more difficult to eliminate due to the fact that sodium is adsorbed on the fiber that leaves the closed liquor cycle.

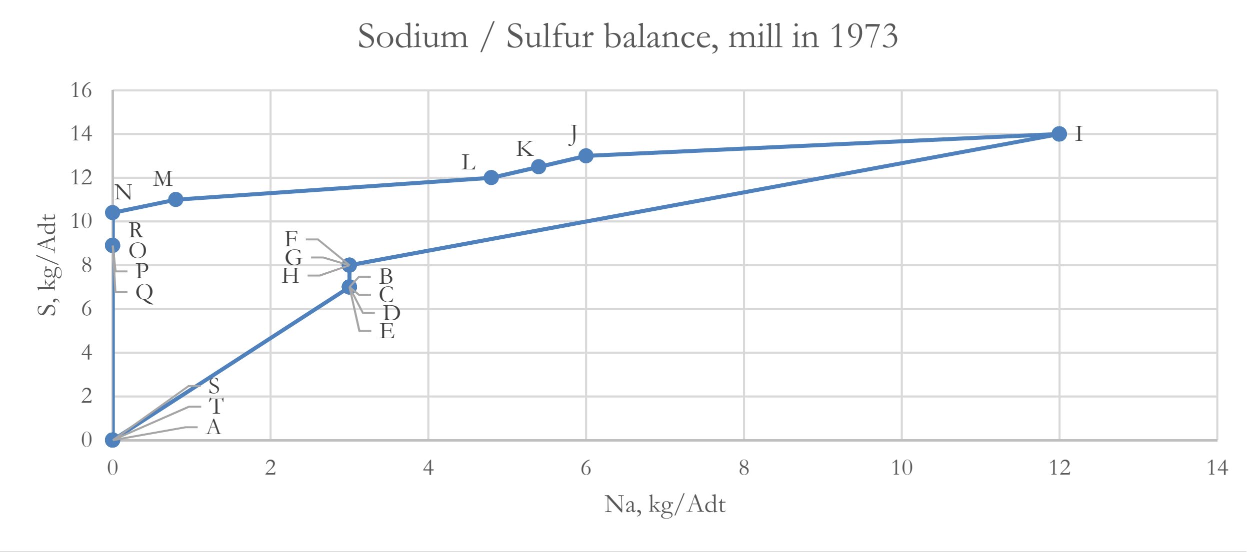

Figure 1: The sodium sulfur balance of one of the cases described in reference 1 (1973) illustrated in a vector diagram. The lower path from A to I represents intake while the upper path represents losses. Note the loss from the recovery boiler stack (R-S) and the sodium sulfate make up stream (H-I) which dominate both sodium and sulfur balance.

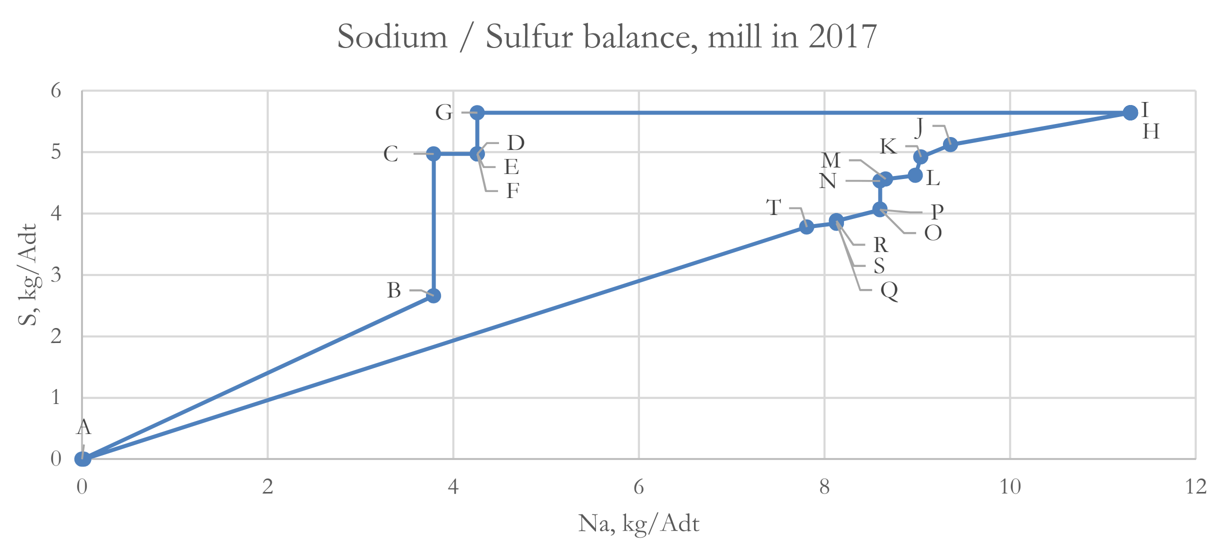

Figure 2: Balance of a modern mill (2017), where the lower path from A to I represents losses while the upper represents intake. Here, almost no sulfur is emitted to the atmosphere. Hence no sodium sulfate make-up is needed and all make-up is sodium hydroxide (G-H). The sulfur intake is from ClO_2-brine, tall oil spent acid and $MgSO_4$ which has to be taken out with purge of recovery boiler ash (T-A). Note that the slope of A-B is steeper than T-A which means that we would save some sodium hydroxide make-up by discharging the brine instead of the boiler ash.

There are methods to control the balance. They include e.g. recovery boiler ash dumping to reduce sulfur content, white liquor oxidation to the oxygen delignification to reduce intake of sodium, totally oxidized white liquor to the bleach plant to reduce sulfur content and dumping of chlorine dioxide brine. Although these methods are applied, some modern mills have difficulties controlling the sulfidity. One of the development trends in kraft pulping is to create valuable side streams from the process. Such streams are in many cases created by primary acidification with sulfuric acid. Examples are tall oil production and lignin extraction. The sulfur in those processes must be recycled to the closed liquor cycle. Therefore, the sodium sulfur balance will be even more disturbed and the existing means of controlling it will become insufficient. As seen in the vector diagrams, the main sodium loss in a modern process is due to dumped boiler ash in order to control sulfidity, as compared to 1973 when all sodium losses were caused by spills and various washing losses. Another very significant difference is that the mill of 1973 lost 10 kg of sulfur per ton of pulp to the atmosphere while the modern mill emits practically no sulfur at all to the atmosphere.

The means to expand the sulfidity control toolbox have been studied and the conclusion is that internal sulfuric acid production is the most efficient way to separate sodium and sulfur streams. Therefore, a process which oxidizes wet sulfurous gas to relatively concentrated sulfuric acid has been developed. In the process, we have concentrated non-condensable gas with high sulfur content. The first full-scale plant based on oxidation of CNCG [will be] started up late 2017. The intention is to avoid addition of external sulfur and replace it with internally produced acid. The plant is described in this paper. Depending on sulfidity and heat treatment in the evaporation and cooking, the sulfur release to NCG is between 3 and 7 kg/ADT as elemental sulfur. If more sulfur is needed, the best way is probably to acidify green liquor and make it release H_2S which can be used for sulfuric acid production.

Processing of side streams

In the 2017 mill mentioned previously, there are sulfur contributions from spent acids from chlorine dioxide and tall oil production. The tall oil spent acid has a high COD content and must therefore be recycled to the closed liquor circuit. However, the chlorine dioxide spent acid can in some cases be dumped if it is properly neutralized. In comparison with the above-mentioned processes, lignin extraction may disturb the sulfur balance to a much larger extent.

To minimize odorous emissions, non-condensable odorous gases are usually collected and incinerated. In some mills a bisulfite scrubber is used to recover sulfur after incineration, and sodium bisulfite is produced. Sodium can for example be used for pH control or in the bleaching plant where it is used to wash remaining chlorine components from bleach plant gases. A downside of sodium bisulfite is the fairly high pH (above 5), which prevents it from being used more in controlling pH. A new system for sulfur recovery has been designed and is currently being built [as of May 2017] in the Metsä Fibre Äänekoski mill in Finland. This is a sulfuric acid plant (**Figure 3 next page**), where sulfur from NCGs is used to produce H_2SO_4.

Concentrated non-condensable gases (CNCGs) are collected and lead to a collection tank, from which they are taken to a separate incinerator. In the separate incinerator, total reduced sulfur (TRS) compounds in the CNCGs are oxidized into SO_2. The burner and boiler are otherwise designed as for traditional CNCG incineration, but residual oxygen and flue gas exit temperature are adjusted to an optimum level. One limit is set by the catalyst process and another by the boiler heat surfaces which, in order to avoid corrosion, require a high enough temperature.

The flue gas from the boiler is led to a catalytic reaction vessel. The reaction vessel is a cylindrical tank with a special catalyst inside. The catalyst oxidizes SO_2 into SO_3 through an exothermic reaction, and therefore the flue gas temperature rises:

$$2\ SO_2 + O_2 = 2\ SO_3 + \text{heat} \qquad (1)$$

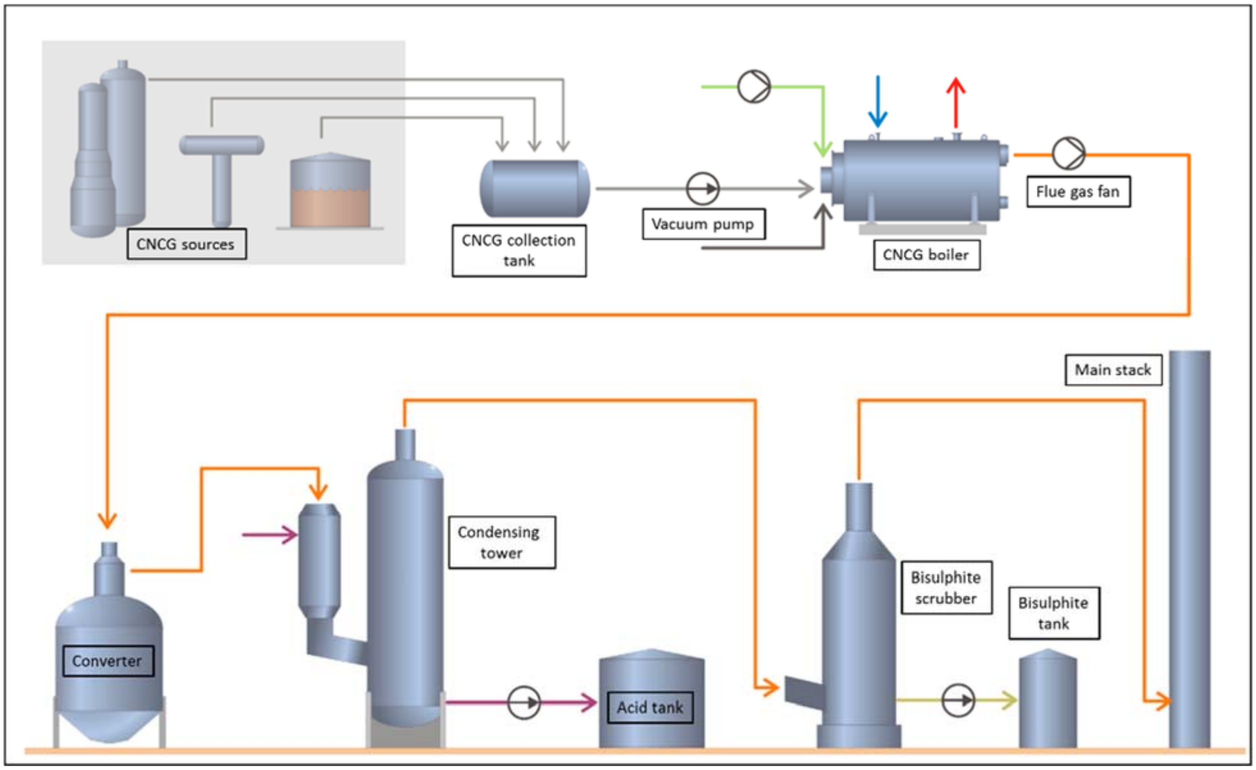

Figure 3: Process overview of the sulfuric acid plant.

When the gas has passed the converter, it enters a concentration tower. In order to protect the system from overheating, the gas temperature must to be adjusted to the proper level before the gases enter the tower. In the concentration tower, liquid is recirculated through a plate heat exchanger. The heat exchanger cools the liquid down, and the cooled liquid is pumped back to the tower. The gas flows upward and the SO_3 in the flue gases reacts with H_2O to produce sulfuric acid:

$$SO_3 + H_2O = H_2SO_4 + \text{heat} \qquad (2)$$

The acid concentration in the concentration tower depends on the partial pressures of SO_2 and H_2O in the flue gas. The gas cools down inside the tower, so water is also condensed from the flue gas. The final acid concentration depends on the sulfur amount in the CNCGs before incineration, but the expected concentration is 50-70 w-%. The produced acid is very aggressive; therefore, the concentration tower is made of acid resistant materials.

Acid is taken out of the concentration tower circulation after the heat exchanger and led to an acid storage tank.

After the concentration tower, the gases still contain SO_3 aerosols that must be removed before the gas can be treated further.

The biggest challenge in this kind of sulfuric acid production is the end concentration of the acid; 50-70 w-% is the most aggressive concentration, so all materials must be carefully chosen. After the converter, the gas contains SO_3 which will form sulfuric acid if the gas temperature drops below the sulfuric acid dew point. As long as the gas temperature is higher, normal carbon steel can be used. Since acid resistant materials do not tolerate high temperatures well, the system had to be designed to operate between these limiting temperatures. This was challenging, and in this case the solution was found by a thorough investigation to find the best materials and also by minimizing the area that operates under those conditions. Still it is clear that this area will corrode and need maintenance, so the system is designed to be easily maintained.

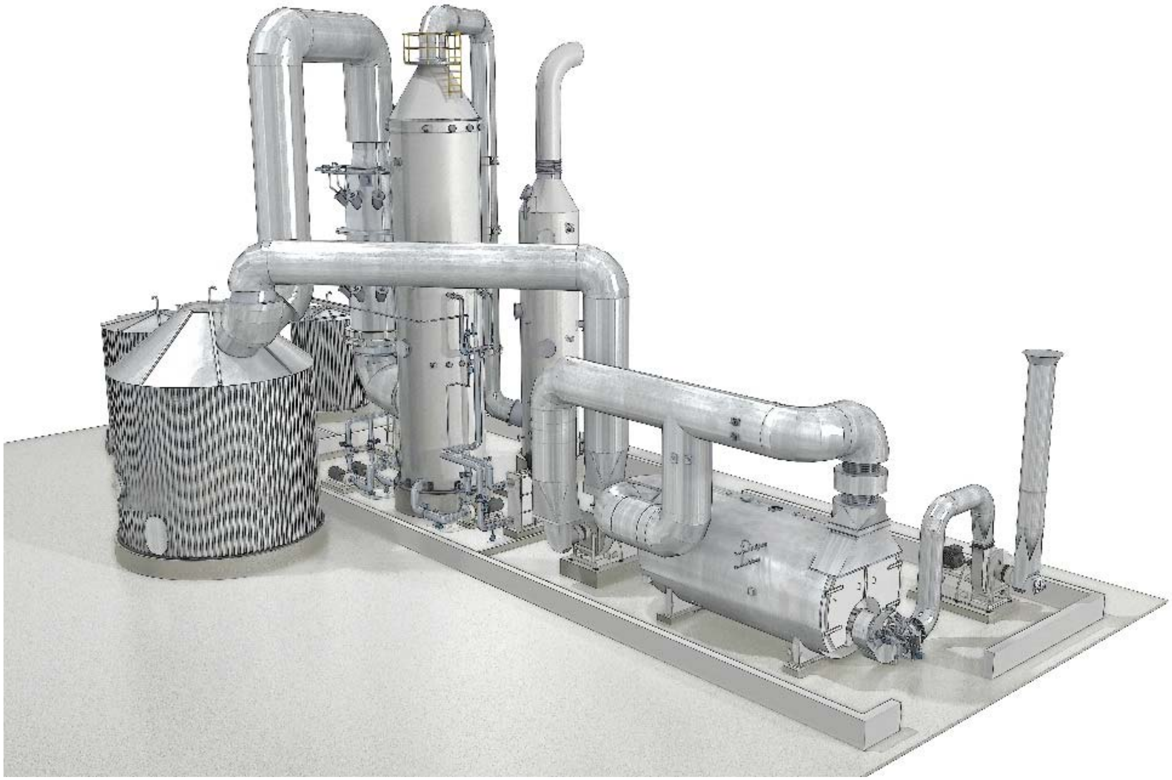

Figure 4: The sulfuric acid plant, based on the plant that is [being] built in the Metsä Fibre Äänekoski mill. The burner and boiler are located on the right, while the catalytic reaction vessel is located to the left in the image. The concentration tower and bisulfite scrubber are located to the right of the reaction vessel. The burner, boiler and the two towers are located inside a building (the lower part of the walls is seen in the image).

As stated before, the usage for sodium bisulfite is somewhat limited, but when it comes to sulfuric acid the pH is not a problem. Acid can be pumped to various end users in the pulp mill, and diluted on-site to the desired concentration. Examples of end users are the effluent treatment plant, the tall oil plant, LignoBoost or the bleaching plant, depending on the purity of the acid.

Conclusions

Although the kraft pulping process has been developed toward lower emissions to the atmosphere and to water, the amount of make-up sodium to the closed liquor cycle has not decreased significantly. The reason is that sulfurous emissions have been more or less eliminated, while at the same time the closed liquor cycle is to a larger extent receiving sulfur rich side streams. Together, this creates a need to purge sulfur from the process. With today's technology, the most harmless stream with a high content of sulfur is the recovery boiler ash. In a well-balanced, modern mill, dumping of recovery boiler ash is the most practical way to reduce sulfidity. A problem with that practice is that ash from a modern recovery boiler has a low content of sulfur due to the high carbonate content. All in all, the purge of sulfur in a 2017 mill requires as much sodium make-up as a 1973 mill used for make-up of sodium emissions.

In order to reduce sodium make-up and at the same time increase the capacity to receive sulfur rich side-streams, a new process for generation of sulfuric acid from non-condensable gases is introduced. The acid replaces intake of sulfur to the process and thereby creates a better balance which reduces the need for make-up sodium.

References

1. Gösta Wiklander Sulfatmakaren, miljövården och svavelbalansen (The pulpmaker, the environment and the sulfur balance) Sv. Papperstidning, nr 5 1973

This white paper combines technical information obtained from Valmet personnel and published Valmet articles and papers.

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