RECOVERY BOILER CHEMICAL PRINCIPLES

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1. INTRODUCTION

A black liquor recovery boiler has two main functions. On one hand, it generates steam from the heat energy liberated upon combustion of the organic constituents of black liquor burned in the boiler, whereby the recovery boiler serves as a steam boiler. On the other hand, the chemicals from pulp digesting - sulphur and sodium - are recovered from the black liquor, the recovery boiler then serving as a chemical reactor. This double function makes the design of a recovery boiler rather complex and the operation of such a boiler much more complicated than that of, for instance, a power plant boiler burning conventional fuels.

When viewing the recovery boiler as a chemical reactor, its construction is quite unique. In the recovery boiler furnace, to a great extent in the same space and at the same time, a number of entirely separate physiochemical processes take place:

- feeding of air and mixing it with the furnace gases
- feeding of black liquor and dispersing it into droplets
- drying of the black liquor droplets
- pyrolysis of the black liquor and combustion of the pyrolysis gases
- gasification and combustion of the char residue
- reduction of the liquor sulphur compounds to sulphide
- tapping the molten salt consisting of sodium sulphide and sodium carbonate from the furnace bottom

Further, as a more or less undesired side effect:

- vaporization or "fuming" of sodium and sulphur compounds (and to a lesser extent of chlorine and potassium compounds) and the vapours and fume escaping to the top of the furnace in the flue gases.

Traditionally, recovery furnaces have been designed and operated based on practical and empirical experience from full scale recovery furnaces rather than based on detailed information of the physicochemical phenomena involved in the process. However, this situation is about to change. Large amounts of completely new, fundamental information about the recovery furnace processes have very recently been produced in several research laboratories.

Åbo Akademi University in Turku, Finland, has during the past years had several major research programs concerning the high temperature chemistry in recovery furnaces and the physicochemical behaviour of black liquor during combustion or gasification. This research together with recent work elsewhere, particularly at the Oregon State University, at the Institute of Paper Science and Technology, and at the University of Toronto, in Canada, has considerably sharpened our picture of the chemistry in a recovery furnace.

This information is already clearly affecting and changing the recovery boiler operation and design.

This paper gives a short overview of the picture evolving from the recent research. Various schemes and diagrams are made use of to summarize the chemistry of sulphur and sodium, the main chemicals of the process. Also, the most important foreign elements in black liquor and their behaviour in the boiler is shortly discussed.

Research continues to be lively, and the latest results may quite soon further clarify our ideas of some of the key processes, e.g. those which govern the release of sodium and sulphur into the gas phase in the furnace.

2. SODIUM AND SULPHUR BALANCE IN A KRAFT RECOVERY BOILER

Table 1 shows the black liquor elemental composition for a typical open cycle kraft process. The contents of sodium and sulphur in black liquor vary considerably from one process to another. From the point of view of the recovery boiler chemistry, the molar ratio between total sulphur and sodium in the black liquor, S/Na_2, is a useful parameter. As will become evident later on, this relation largely governs the chemistry of the sulphur and sodium in the recovery boiler.

Table 1. An example of kraft black liquor elemental composition. Sample before the mixing tank.

	Wt% dry solids
C	38.2
H	3.4
O	31.1
N	0.1
S	5.2
Na	19.8
K	1.9
Cl	0.10
Others (Ca,Si,Fe,Mg,Al,Mn)	0.2
S/Na_2 = 0.38 mol/mol	

There is a considerable variation in the sulphur-sodium ratio between different processes. High sulphidity in pulping and the oxidized sulphur-sodium salts (Na_2SO_4, Na_2SO_3) in the recovery cycle increase the S/Na_2 ratio. The sulphidity of the processes of Scandinavian pulp mills as well as the S/Na_2 ratios of their black liquors are, in general, notably higher than those found in North America. In Scandinavia, the S/Na_2 range is typically 0.35 to 0.5, whereas the corresponding variation at mills in North America is typically 0.2 to 0.3. Table 2 gives an example of the various sulphur compounds in kraft black liquor.

Table 2. An example of distribution of sulphur compounds in kraft black liquor /1/.

	% sulphur of total sulphur
Sulphide, S^{2-}	11
Thiosulphate, $S_2O_3^{2-}$	36
Sulphite, SO_3^{2-}	13
Sulphate, SO_4^{2-}	5
Organic sulphur (balance)	35
Total	100

In an ideal recovery boiler process, all the diverse sulphur and sodium compounds would be transformed to sodium sulphide (Na_2S) and sodium carbonate (Na_2CO_3) and be contained in the smelt on the furnace bottom.

In a real recovery boiler, however, the process is more complicated. Figure shows an example of sulphur and sodium balances in a typical recovery boiler. This example could describe a process operated at nominal load and where the S/Na_2 ratio is about 0.4 and the dry substance of the black liquor at the sprays is about 70 %. It is to be noted here that Fig. 1 represents only a single case and certain conditions. The flow rates of sodium and sulphur vary greatly from one process to another, or even in the same process, depending on the operation strategy of the boiler.

The figure shows clearly a deviation from the ideal process referred to above. For one thing, the sulphur does not occur in the molten salt bound only in sulphide but also in sulphate. The reduction, or molar ratio (Na_2S)/(total S) in the smelt of actual processes is typically about 90 - 95 %.

A substantial part of the sulphur and the sodium is carried by the combustion gases into the boiler flue, mainly in the form of sodium sulphate dust and sulphur-containing gases. These compounds are the cause of most fireside problems, such as fouling of heat transfer surfaces and corrosion.

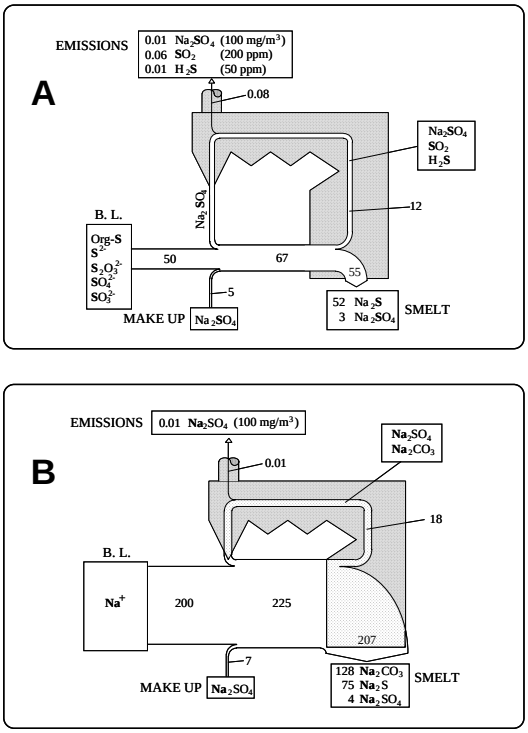


Figure 1. A) (upper) Sulphur, and B) (lower) Sodium balance in a typical kraft recovery process. Numbers refer to grams of S or Na per kilogram of black liquor solids.

Most of the dust falls out of the flue gases into dust hoppers or is captured by electrostatic precipitators. From these the dust is fed back into the boiler by mixing the dust with the infeed black liquor. Roughly 10 % of the sodium contained in the black liquor is typically in this circulation. Correspondingly, the part of the sulphur carried away by the combustion gases ranges from 20 to 40 %, depending on circumstances.

Finally, a small portion of both sodium and sulphur leaves the process as flue gas emissions. The main emission components are glauber salt dust (Na_2SO_4), sulphur dioxide gas (SO_2), and reduced sulphur gases, hydrogen sulphide (H_2S), methyl mercaptan (CH_3SH), etc. The emissions depend strongly on the process conditions and, of course, the performance of the flue gas purification equipment.

3. FURNACE BOTTOM AND CHAR BED

The lower furnace and the char bed are crucial for the entire recovery boiler process. The conditions in the lower furnace determine almost exclusively the performance of the process, that is, how the flows of sulphur and sodium as shown in Figure 1 are distributed in each case. The conditions in the furnace are chiefly influenced by the technique of

liquor spraying and the introduction of combustion air into the furnace. Also the black liquor properties, particularly its dry solids content, of course, affect the conditions in the furnace.

3.1 Equilibrium Composition in the Lower Furnace

Figures 2 and 3 by Pejryd and Hupa /2/ show the composition at the bottom of the furnace, on one hand, as a function of the lower furnace air factor (Fig. 2) and, on the other hand, as a function of temperature (Fig. 3). The bottom parts of the figures describe the smelt bed composition as mole fractions. The top part of the figures gives the composition of the gas phase near the bed. The figures are based on theoretical thermodynamic equilibrium calculations. Such calculations assume an isothermal process with perfect mixing, where all chemical reactions reach equilibrium. Although these conditions are not actually achieved in the bottom part of any actual recovery boiler furnace, some useful conclusions may be drawn from above figures.

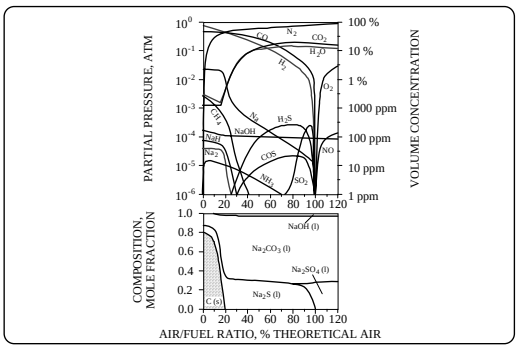


Figure 2. Equilibrium composition of smelt (mole fraction, lower graph) and lower furnace gas (partial pressure, upper graph) as function of air/fuel ratio. Temperature 1000 °C, molar ratio S/Na_2 in black liquor 0.30 /2/.

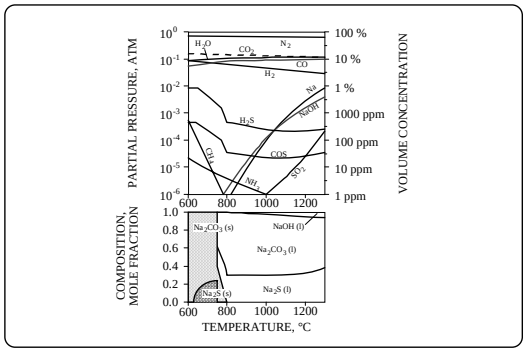


Figure 3. Equilibrium composition of smelt (mole fraction, lower graph) and lower fumace gas (partial pressure, upper graph) as function of temperature. Molar ratio S/Na_2 in black liquor 0.70, air/fuel ratio 0.70 /2/.

Firstly, the figures show all the significant chemical compounds which may occur in the lower furnace. In addition to the aforesaid sodium sulphide, sodium carbonate, and sulphate, also solid elemental carbon (C) may be present in the bed under extreme conditions. Figure 3 also shows that solid compounds begin to form in the bed, i.e. the bed starts "freezing" when the temperature drops below approximately 800 degrees C.

The main components of the flue gases are natural products of air-deficient combustion, i.e. nitrogen (N_2), carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2), and water (H_2O).

In the gas phase, sulphur occurs as hydrogen sulphide (H_2S), carbonyl sulphide (COS), and, at high air factors, as sulphur dioxide (SO_2). The most important gaseous sodium compounds are sodium hydroxide (NaOH) and metallic sodium (Na).

3.2 Reduction of the Smelt

Figure 2 further shows that, in principle, under equilibrium conditions, complete smelt reduction may be obtained when the (local) air factor remains below approximately 0.8. In the actual process, however, the limited rate of the reduction reactions, i.e. kinetics, prevents complete reduction.

Some information is available on the char bed reduction reaction rate /3-6/. In principle, the sulphate contained in a partly burned black liquor droplet entering the bed may be reduced either by means of (l) reducing gases (CO or H_2) or (2) the solid carbon (char) in the bed. A comparison by Adams and Frederick of laboratory test results found in the literature /6/ shows that the reduction of sulphate by means of char is about two orders of magnitude faster than a corresponding reduction with reducing gases. These authors concluded that the gas reactions become dominant in the reduction process only after 99 % of the char in the smelt bed has been consumed. At that stage, however, the whole reduction process is apparently very slow, and insignificant for any practical purposes.

Consequently, a prerequisite for efficient smelt reduction is a sufficient amount of char continuously on the bed surface. This means in practice that the spraying of black liquor should be arranged in such a way that a significant fraction of the droplets hit the bed surface at the stage when the char burning is still incomplete. The limit here will naturally be the capacity of the bed to burn char. An excessive flow of char onto the bed would result in an unwanted growth of the bed.

Another important factor with respect to efficient smelt reduction is the bed temperature. The rate of

the reduction reaction is strongly dependent on temperature (the process activation energy ranges from 120 to 170 kJ/mol /5/). The reduction rate roughly doubles each time the temperature is increased 50 - 60 degrees C. There are many ways to control the bed temperature /6/, but they are not to be dealt with here.

The reduction of the smelt is to some extent counteracted by reoxidation of the smelt near the furnace walls and smelt spouts. In normal practice, however, such reoxidation is of little significance.

3.3 Vaporization of Sulphur and Sodium Compounds

In the lower furnace, part of the sodium and sulphur is transferred into the flue gases and will not return to the char bed. Of the compounds so carried away by the combustion gases, the most important sulphur compounds are H_2S and COS, and, for sodium compounds, gaseous Na and NaOH. The main factor controlling the vaporization of the sulphur and sodium compounds is the temperature. In Figure 3, the equilibrium concentration of the gaseous compounds is given on the logarithmic axis. The figure shows how the concentration of gaseous sodium compounds steeply rises with rising temperature. The concentration of sulphur compounds decreases with rising temperature. These two trends have a great significance with respect to fireside chemistry, and they will be discussed in closer detail below.

The equilibrium curves for sulphur and sodium compounds as a function of temperature in Figure 3 have been transposed on the linear vertical axis in Figure 4. One reads from this illustration that the equilibrium content of sodium compounds in gaseous form doubles when the bed temperature increases approximately 50 degrees C. The opposite decreasing trend for sulphur is less steep, and it levels off at higher temperatures.

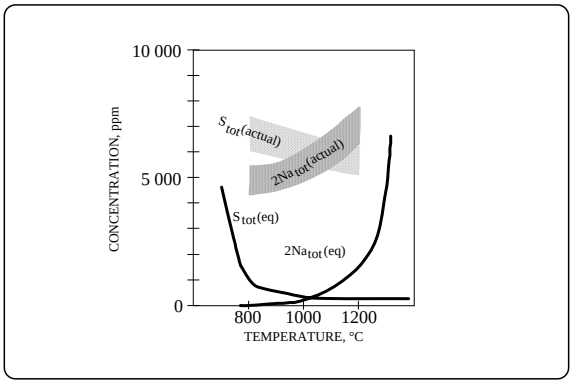


Figure 4. Sulphur and sodium release in recovery furnaces as function of temperature. Equilibrium values and typical actual boiler data.

The increasing and decreasing trends of vaporizing sodium and sulphur, respectively, with rising temperature has been observed also in operating boilers. It is generally known that when operating a boiler at a low temperature because of low heat value of black liquor or some other reason, flue gases of considerably high sulphur content are produced. It is also known that increasing the furnace temperature, e.g. by increasing the dry substance content of the black liquor, increases the rate of sodium vaporization and thereby the rate of dust circulation in the combustion gases.

In Figure 4, typical sulphur and sodium trends have been given for an operating boiler. These trends are based on the results of numerous flue gas surveys conducted on boilers of different types and sizes. Field observations deviate markedly from the results of the equilibrium calculations in two important respects:

(1) The concentration of fine sulphate dust condensed from the vapour state and collected in the electrostatic precipitator is typically in the range of 5 to 15 g/m^3 of flue gas. This indicates clearly that the release of sodium and sulphur into vapour state is 3 or 4 times higher than the results of the equilibrium calculations show.

(2) Field experience also indicates that the concentration of sodium in the flue gas does nor respond to changes in temperature so sharply as could be expected when studying the equilibrium curves. In converting boilers to ultra high dry solids firing, the sodium concentration increase does usually not exceed some 30 - 40 % from the figure before the conversion even though the furnace temperature in such cases rises at least 100 degrees C, possibly more. According to equilibrium calculations this should result in a 400 % increase in sodium concentration.

One proposed explanation for these deviations is formation of dust due to oxidation of sulphite in the smelt /8,9/. This oxidative fume as a phenomenon has been verified under laboratory conditions but its significance in an actual furnace is unknown.

Recent laboratory work, however, suggest a different explanation. Measurements done on individual droplets indicate that already in the earlier phases of combustion, considerable amounts of sulphur and sodium are released from the black liquor droplets, especially during the pyrolysis stage /9/. This vaporization is controlled by kinetics only, and it takes place, as it were, before the black liquor droplet enters the vicinity of the bed surface.

Consequently, one could think that the sodium and sulphur in the flue gas originate in two distinctly different sources. On one hand, they are vaporized

in the lower furnace from the surface of the smelt, possibly much in accordance with the equilibrium calculations. On the other hand, significant amounts of sulphur and sodium are released from the black liquor spray in connection with the complex pyrolysis reactions. The latter source, pyrolysis, probably accounts for substantially larger amounts of released sulphur and sodium than the amounts vaporized from the surface of the smelt.

Investigations on the vaporization of sodium and sulphur in the furnace continue, and more light is expected to be shed on the matter quite soon.

From the viewpoint of practical applications, the following may be stated:

- Sulphur is vaporized in a furnace mainly as hydrogen sulphide, whereas sodium is vaporized as sodium hydroxide and metallic sodium.

- The concentration of sulphur in the flue gas increases with decreasing furnace temperature. The trend for the sodium is in the opposite direction.

- The ratio of concentrations of sulphur and sodium in the flue gas controls, to a great extent, the entire flue gas and dust chemistry. This ratio in terms of moles varies from one boiler or process to another, typically from 0.8 to 1.5. The ratio is lower at high furnace temperature and at low sulphidity in the black liquor.

The effect of the S/Na_2 ratio on the flue gas chemistry is studied to closer detail below in the section which follows.

4. CHEMISTRY OF FLUE GAS AND DUST

The formation of dust in a recovery boiler and the boiler flue gas emissions are discussed here. Part of the dust consists of fine particles condensed from vapour. The particle size of these particles is typically 0.2 to 1 m, and the dust captured by means of electrostatic precipitators consists almost entirely of this type of dust. In addition to this dust, coarser particles, in the size range of 10 to 100 m, occur in large amounts in the superheater area and in the first dust hoppers. This coarser dust consists of carry-over liquor particles, that is, inorganic residue of black liquor droplets which have escaped from the sprays. These are of special significance, especially with respect to fouling of superheaters. The fouling behaviour of carry-over particles is treated to more detail in a number of references /10-16/, but these are not to be discussed here.

4.1 Reactions in the Flue Gas and the S/Na_2 Ratio of the Flue Gas

Under the reducing conditions in the lower furnace, sulphur occurs in the form of hydrogen sulphide, and sodium mainly as metallic sodium and sodium hydroxide. When the lower furnace gases rise to the upper furnace and their combustion is completed, the sulphur and sodium compounds are transformed and they react with each other. The final flue gas dust compounds and the sulphur emission compounds are produced in these reactions which take place in the upper furnace and, partly, in the superheater zone.

Figures 5 A and B illustrate the principle reactions of sulphur and sodium in the flue gas, beginning with sodium vapours and hydrogen sulphide formed in the bottom part of the furnace. The figures are based partly on theoretical calculations, partly on results of field measurements /9,11,17,18/.

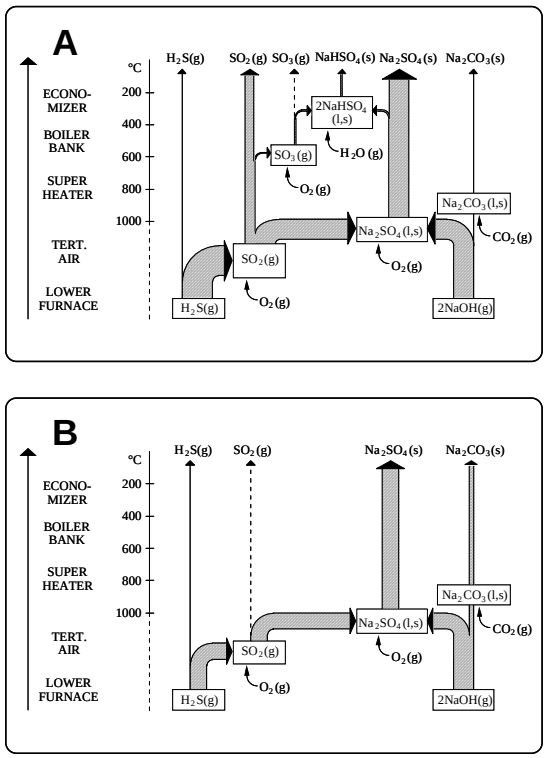


Figure 5. Reactions of sulphur and sodium in recovery furnace and flue gases.
A) (upper) Molar ratio in flue gases: $S/Na_2=1.5$ (Cool bed, high sulphidity).
B) (lower) Molar ratio in flue gases: $S/Na_2=0.8$ (Hot bed, low sulphidity).
Based on /17,10,19/.

Moving up on the diagram means moving up from the bottom part of the furnace, and further into the flue duct. The top of the diagram shows the final sulphur and sodium compounds in the flue gas at the

entrance to the dust collecting system. Each of the boxes in the diagram describe chemical reactions. The reactants participating in the reactions enter the boxes through the bottom or the sides. The reaction product is indicated as the label of the box. The product always leaves the box up through the top. The width of the line describing a material flow is proportional to the magnitude of the flow.

The reactions which take place in the flue gases are dependent on the molar ratio of total sulphur and total sodium entrained in these gases. Therefore, Figure 5 shows the reactions separately for two extreme conditions. Figure 5 A describes the reactions under conditions where the S/Na_2 ratio in the flue gases is very high, clearly exceeding unity. These conditions prevail in boilers where the furnace temperature is low and/or the black liquor sulphidity is high. Figure 5 B describes the opposite case, where the furnace temperature is high and/or the black liquor sulphidity is low. Actual boilers generally operate somewhere between these two extremes.

The first reaction in both diagrams is the oxidation of hydrogen sulphide into sulphur dioxide. This takes place by means of tertiary air in the top part of the furnace, and the completeness of this oxidation depends only on the efficiency of mixing the air with the combustion gases. Any hydrogen sulphide not oxidized at this point will not be oxidized later on in the cooling flue gases but will remain as a constituent of the flue gas and forms the main component of the TRS "total reduced sulphur" emissions of the boiler.

The sulphur dioxide produced as a result of oxidation of hydrogen sulphide reacts with the sodium compounds also in the oxidizing environment of the upper furnace and sodium sulphate is produced. In the furnace this sodium sulfate will be in molten state, but will solidify as the combustion gases cool down. After this reaction, the entire chemistry of the furnace gases depends on whether they originally contained a surplus of sulphur or sodium.

In the case of Figure 5 A, practically all of the sodium is bound in this reaction to sodium sulphate, and a surplus of sulphur dioxide remains. This sulphur dioxide is often a cause of trouble when the combustion gases cool down. A surplus of sulphur dioxide may change the sulphate dust into sticky, acidic sulphate (bisulphate). Acidic sulphates may in the worst case cause rapid fouling of the economizer, and boiler bank corrosion /19/. Moreover, this surplus of sulphur dioxide, as a rule, finally ends up in the atmosphere as flue gas emission.

In the case of Figure 5 B the reaction producing sodium sulphate consumes practically all of the sulphur dioxide and the surplus reacts with CO_2 to form sodium carbonate dust. In this case the sulphur dioxide emission of the flue gas will remain very low. Acidic sulphates cannot be produced in this case. The conditions involved in Figure 5 B correspond to those experienced with high dry solids firing. Under these, the content of SO_2 in flue gas may drop below the detection limit (< 1 ppm) and the carbonate content of the dust may rise to exceed 10 % /20/.

At actual boiler operation it would be advisable to aim at a low S/Na_2 molar ratio in the gases, below 1.0 if at all possible. Increasing the dry solids content above 70 %, even above 80 %, would be helpful in lowering the sulphur/sodium ratio. The favourable conditions as in Figure 5 B have been achieved with extremely high dry solids content in spite of the liquor having a high sulphidity /21/.

4.2 Dust pH

A simple and quick way to monitor the flue gas and the dust chemistry is to measure the pH-value of a water solution of a dust sample taken from the flue gas duct or the electrostatic precipitator.

The "dust pH" indicates readily on which side of the dust chemistry the boiler is operated, i.e. does the dust contain carbonate in addition to the sulphate, or does it contain acidic sulphate. The presence of carbonate produces alkaline pH water solution. Correspondingly, only a few percent of bisulphate drops the pH of the dust/water solution several units below neutral. If the dust would consist of pure sodium sulphate, water solution pH would be 7. Such a pH, however, is very unstable and uncommon. The relation between the dust composition and the pH-value of its water solution has been drawn in Figure 6. The pH-curve has been calculated for a 1 percent dust solution.

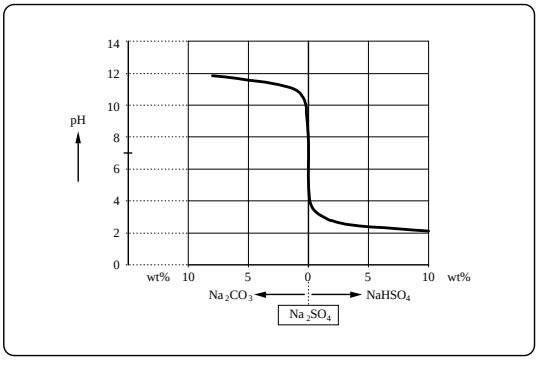


Figure 6. Dust pH as function of dust carbonate (Na_2CO_3) or bisulphate ($NaHSO_4$) content. (Water solution with 1% dust).

The dust sample may be taken at different locations using different sampling techniques. It is easy, of course, to take the samples from below the electrostatic precipitator or from the flue duct ash hoppers. The problem with such samples, however, is a long and poorly defined time of contact with the combustion gases before sampling. Prolonged contact with the combustion gases may substantially lower the dust/ water solution pH-value.

It is to recommend to take the sample from the flue gas flow directly using a suitable sampling device, for instance a suction probe.

The pH-value of the dust solution varies greatly between boilers and processes in the field. In kraft boilers, the pH typically varies between 7 and 12 (l% water solution).

It is impossible to give any generally applicable guide value for the pH of the dust. In most cases pH 10 to pH 11 (l% solution) should be optimal. Lower pH than this indicates that the process is not far from the point where acidic sulphate begins to appear, i.e. from the steep part of the pH-curve in Figure 6. The local conditions in some part of the flue duct may differ from the average conditions. This makes it possible that acidic sulphates may be produced somewhere locally (or at times) even though the pH of an average sample collected would still be slightly alkaline.

A very high pH-value (pH > 12, l% solution) may also indicate potential trouble. One reason for high alkalinity may be a high carry-over of black liquor droplets which escape the furnace and may be carried over all the way to the end of the flue duct. The content of carbonate is high in the carry-over particles and their high proportion in the dust sample raises the sample pH value markedly. Another potential reason for high alkalinity is an unusually high rate of vaporization of sodium in the furnace, which results in high dust concentrations in the flue gas and thereby, possibly, in precipitator problems.

5. FOREIGN COMPONENTS

In addition to the main chemicals, sodium and sulphur, many other elements participate in the recovery process. The chief foreign elements are chlorine and potassium. This section treats briefly the behaviour of chlorine and potassium in a recovery boiler. Other minor elements in the process are calcium, silicon, aluminum, iron, etc. However, these substances have seldom any significance in the recovery boiler process itself, and shall not be discussed any further here.

The chlorine is present in wood, but may also originate in wood floated in sea water, in make-up chemicals, or possibly in pulp bleaching process waters which have been brought into the recovery cycle. The concentration of chlorine in black liquor varies greatly from one process to another. The chlorine content in mills is usually quite low, typically 0.1 to 0.5 % of the liquor dry solids. In the mills on the west coast of North America, the chlorine content of the liquor dry solids has been found to be as high as to 3 - 5 %, and in closed cycle (that is bleach plant effluent recovery) processes it may rise even higher /22,23/.

Potassium enters the process mainly as a natural mineral component of the wood raw material. The potassium content in mills is typically 1 to 3 % of the liquor dry solids content. In more closed processes, the content of potassium easily rises substantially higher /22/.

5.1 Chloride Vapours

Chlorine occurs in the lower part of the furnace almost exclusively as alkali chlorides NaCl and KCl. The vapour pressure of these is markedly higher than those of other sodium and potassium compounds. The chlorine compounds are therefore enriched into gas phase in the furnace. A factor describing the enrichment is

$$\frac{\text{(Cl/Na) in gas}}{\text{(Cl/Na) in smelt}}$$

which according to field measurements typically ranges from 2 to 4 /6,8,22,24/.

The distribution of chlorine between smelt and furnace gas is strongly dependent on temperature. At high temperatures, the main part of the chlorine is vaporized, which is illustrated by Figure 7 based on the equilibrium calculation. Several indications have been obtained that the vaporization of chlorine in a recovery boiler conforms well to the equilibrium values /2,8/.

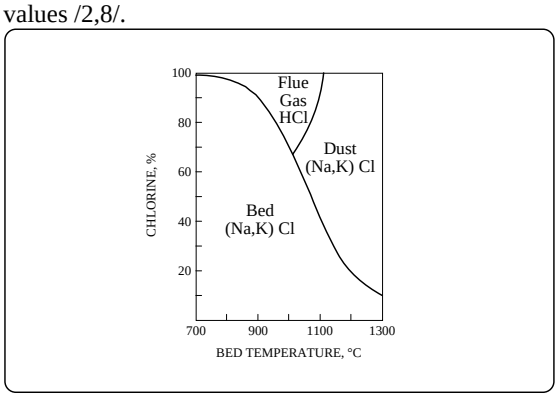


Figure 7. Distribution of chlorine between smelt bed, dust and flue gases. Based on an equilibrium model by /23/.

The chlorides being vaporized into the gas phase are condensed as the flue gases cool, thus forming dust.

Even small amounts of chloride in the dust substantially change the behaviour of the dust in the flue gas duct. Chloride, particularly in combination with potassium, lowers the melting temperature range of dust significantly and makes the dust more sticky and fouling /16,23/.

5.2 Hydrochloric Acid, HCI

If free sulphur dioxide remains in the boiler flue gas (see Section 3), the chloride dust resulting from condensation is partially transformed in the upper furnace and flue gas duct into sulphate:

$$2\ NaCl + SO_2 + 1/2\ O_2 + H_2O \rightarrow Na_2SO_4 + 2\ HCl$$

As a result of this reaction, gaseous hydrogen chloride is formed. This chlorine contained in the hydrogen chloride passes the dust removal devices and exits the process as flue gas emission. Through this reaction it is, in principle, actually possible to facilitate the removal of the chlorine from the recovery cycle /24/. The reaction is discussed more closely below.

The reaction referred to above requires - as mentioned - the presence of sulphur dioxide in the flue gases. The content of sulphur dioxide remaining free in the flue gases is in the end determined by the ratio of sulphur and sodium entrained in the combustion gases (see Section 3). Thus the S/Na_2 ratio in the flue gases turns out to be a significant parameter also from the viewpoint of the chlorine chemistry.

Figure 7 may also be used when examining the practical significance of the hydrochloric acid reaction. The figure is drawn based on equilibrium calculations and some additional assumptions /23/. At low furnace temperatures, the amount of chlorine released in gaseous form is quite small. On the other hand, this chlorine released mainly as alkali chloride later transforms practically completely into hydrochloric acid, through the sulphation reaction above. The amount of alkali chloride vaporized at high temperatures is, of course, large. Moreover, due to high bed temperatures, the S/Na_2 ratio in the combustion gases remains low. Thus little or no free sulphur dioxide is left in the flue gas after the reactions which take place in the furnace (see Section 3 and Fig. 5 B). Therefore, the alkali chloride vapour released in the lower furnace will not be sulphated but is condensed as such into alkali chloride dust.

5.3 Potassium

Potassium behaves in a recovery boiler process much like sodium. Potassium compounds, however, are more volatile than sodium compounds. Potassium is, therefore, also enriched in the dust. Values for the enrichment factor, defined as for chlorine above, range according to field measurements from 2 to 4, i.e. much the same as for chlorine /6,22/.

The chief potassium compounds in the lower furnace are K and KOH and, if the chlorine content of the liquor is even a little higher, also KCl.

As was established above, potassium - especially in combination with chlorine - tends to lower the melting temperature of the dust and thereby increases its fouling tendency.

6. CONCLUSIONS

The complicated chemistry of the recovery boiler has become much clearer in the past few years. Interesting further research is being done, and more information is expected to be available, particularly concerning the release of sulphur and sodium contained in black liquor.

The most important process in a recovery boiler, the reduction of sulphur compounds into molten sulphide, is mainly achieved by means of the char in the black liquor. To ensure an efficient reduction, the char content of the smelt bed must be maintained at a sufficient level.

The sulphur and sodium compounds in the flue gases are formed as the hydrogen sulphide and the sodium vapours released in the lower furnace react with each other. The reactions proceed in different ways depending on the ratio of sulphur to sodium in the combustion gases.

The S/Na_2 ratio in the flue gas is high at low furnace temperatures or high sulphidities of the black liquor. In cases like this, there will be a surplus of sulphur dioxide, which may turn the dust into acidic sulphate, with resulting fouling and corroding effects.

The S/Na_2 ratio in the furnace gases is low at high furnace temperatures or low sulphidities of the black liquor. Under these conditions the sodium compounds of the combustion gases bind virtually all the sulphur dioxide. Then, acidic sulphates will not be formed, and the sulphur dioxide emission with the flue gas will be completely eliminated.

The pH-value of dust is a sensitive indicator for the sulphur/sodium chemistry of the flue gases. The dust samples should be taken fresh, directly from the flue gas before the electrostatic precipitators. High pH (>10) indicates that the S/Na_2 ratio in the flue gases is less than unity. Low pH (<7), again, indicates that this ratio is high, with an increased tendency for formation of acidic sulphates.

Foreign elements potassium and chlorine are enriched into gaseous form in the lower furnace, mainly as alkali chlorides. If the S/Na_2 ratio of the combustion gases is sufficiently high, the alkali chlorides transform at a later stage into hydrochloric acid and alkaline sulphate.

The presence of potassium and chlorine in the dust - especially in combination - lowers the dust melting temperature range, which results in increased sticking and fouling tendencies.

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