Bull. Univ. Osaka Pref., Ser. B, Vol. 19.
大阪府立大学紀要, 農学・生物学, Mar. 1967.

Removal of Silica from the Black liquor of Bamboo Sulphate Pulping

—Removal of Silica by lowering the pH value with sulphuric acid—

By

Kazuki ONO and Hisao TSUJI

Laboratory of Wood Chemistry, College of Agriculture

(Received September 1, 1966)

Introduction

It has been well-known since olden times that in the alkaline pulping of bamboo, bagasse and straw which contain high percentage of silica, the silica in the raw materials dissolves in the alkaline liquor (black liquor) and causes many troubles during the processes of chemical recovery. A. PANDA[1] (1962) has discribed the characteristics of various methods for the silica removal from the black liquor.

K.G. SCHWALBE[2] (1931) and A. PANDA[3] (1964) have reported on the method to remove the silica from the black liquor by passing carbon dioxide gas into it. A. PANDA has reported that the pH value of black liquor was lowered to 9.8 and the concentration of silica in it became 0.42 g/l, passing carbon dioxide gas into the black liquor of bamboo alkaline pulping (pH 11.6) which contained 3.80 g/l of silica.

K. ONO and Z. ISONO[4] have investigated on the desilicification of black liquor in this laboratory for many years, and have found the relation between the change of pH value of black liquor and the percentage of silica removed per the silica in the original black liquor (the rate of silica removal)[5]. It has been mentioned by K. ONO and Z. ISONO that the concentration of silica which dissolved in the black liquor of bamboo alkaline pulping depended on the pH value of it.

In the present paper, when sulphuric acid was used as the chemical lowering the pH value of black liquor, the relation between the amounts of sulphuric acid added and the pH value of black liquor, the relation between the pH value of black liquor and the effect of silica removal, and furthermore the organic matter content in the black liquor in each pH value are reported. There is no report in regard to the method of silica removal in which are used sulphuric acid as the chemical.

When the pH value of black liquor is adjusted to a weak alkalinity by the addition of acid into it, sodium silicate (Na_2SiO_3) dissolved in the black liquor liberates silicic acid ($xSiO_2 \cdot yH_2O$). The silicic acid makes hydrogel in existence of the electrolyte and can be precipitated as the colloidal form. It is difficult to separate only by sedimentating the colloidal product from the black liquor. By heating, however, the colloidal precipitate can be dehydrated and brought to a crystalline form which is easily filterable.

Therefore, in this investigation, the black liquor which was adjusted the pH value by the addition of sulphuric acid solution was heated before filtering.

Experiment and result

In the present experiment, the bamboo black liquor[6] which prepared in this laboratory was used for the removing test of silica from the black liquor. To produce the bamboo black liquor, Burmese bamboo was applied as the raw materials of sulphate pulping. The analytical values of the bamboo black liquor are shown in Table 1.

Table 1. Analytical data of Bamboo black liquor

pH value	12.3
Specific gravity	1.099
Total solid	188.7 g/l
Sulphated ash	64.3 g/l
Organic matter	119.4 g/l
Silica content	5.02 g/l

2N-Sulphuric acid solution was used as the chemical to lower the pH value of black liquor. The pH value of black liquor was measured with Hitachi-Horiba model M-III pH meter. After adding the variable volume of sulphuric acid solution into the black liquor, the mixture was boiled for 1 hour in a water bath, and then the precipitate was filtered off by Toyoroshi No. 5A filter paper in a Buchner's funnel.

In Table 2, the analytical values of the black liquor in each pH value which occured by

Table 2. Analytical data of black liquor treated with sulphuric acid

H_2SO_4 added	pH value	Specific gravity	Total solid	Sulphated ash	Organic matter	Organic matter removed	Silica content	Silica removed
g/l			g/l	g/l	g/l	%	g/l	%
9.5	11.0	1.097	186.2	64.7	116.8	2.2	4.74	5.6
12.7	10.6	1.091	178.3	63.4	111.4	6.7	3.26	35.1
15.8	10.1	1.090	175.7	64.5	110.1	7.8	1.11	77.9
19.0	9.8	1.087	174.7	63.9	109.7	9.1	0.99	80.3
22.2	9.3	1.083	171.3	64.1	107.0	10.4	0.50	90.0
25.3	8.9	1.079	159.4	64.5	94.6	20.8	0.38	92.8

All values were based on the original black liquor.

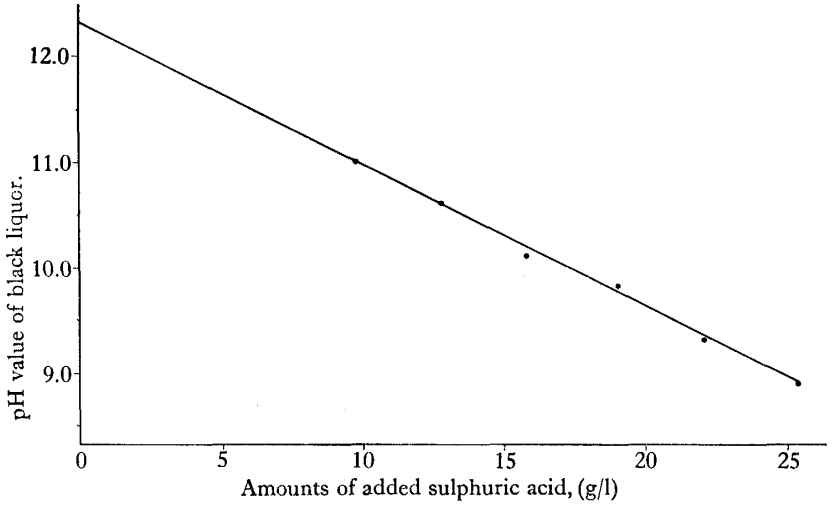

Fig. 1. Relation between pH value of black liquor and the amounts of added sulphuric acid.

addition of sulphuric acid solution and then heating are shown. The relation between the pH value of black liquor and the amounts of sulphuric acid added is shown in Figure 1.

The relation between the silica content (and the rate of silica removal) and the pH value of the black liquor treated with sulphuric acid is represented in Figure 2, and the change of the organic matter contents in the black liquor in each pH value which caused by the addition of sulphuric acid in Figure 3.

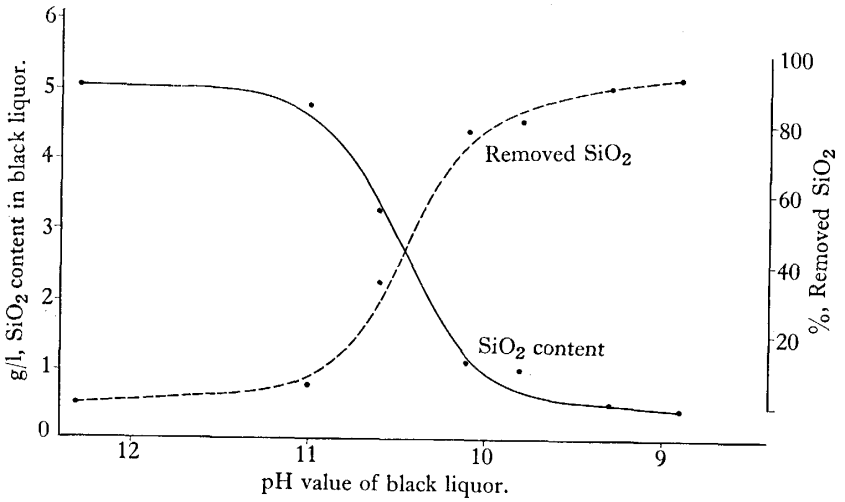

Fig. 2. Effect of pH value on silica content in black liquor.

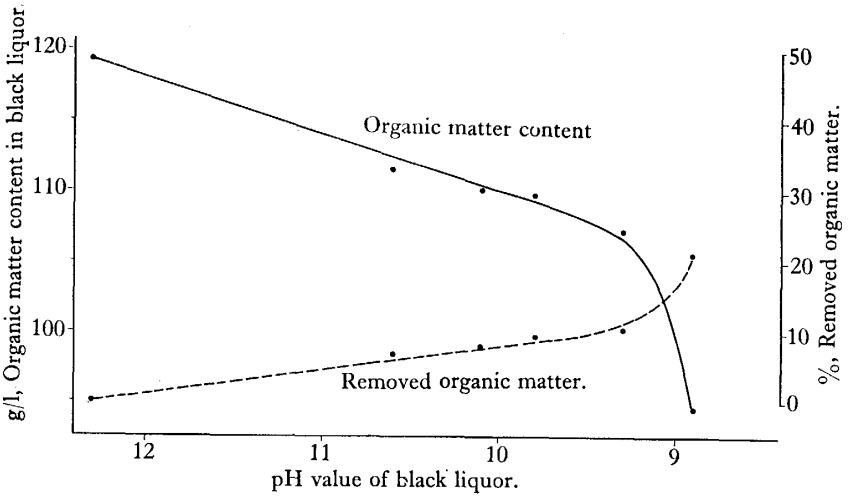

Fig. 3. Effect of pH value on organic matter content in black liquor.

The followings are evident from the results of this experiment.

(1) In the pH range which was examined in this experiment, the pH value of the black liquor was lowered in proportion to the amounts of sulphuric acid which was added in the black liquor. (Fig. 1) The amount of sulphuric acid which required to lower 1.0 in the pH value was approximately 7.3 g/l for the black liquor.

(2) The amounts of silica which precipitate from the black liquor after heating are noticeably effected by the pH value of black liquor. The silica in the black liquor was precipitated in a great quantity in pH value from 10.6 to 10.1. In pH 10.1, the silica content in the black liquor was lowered to 1.1 g/l, and 77.9 per cent of silica in the original black liquor was removed. In pH 9.3, the black liquor contained 0.5 g/l of silica, and 90.0 per

cent of silica was removed.

(3) The organic matter content in the black liquor was reduced in proportion to the pH value of it in the pH between the range of 12.3 to 9.3. In pH 9.8, approximately 9 per cent of organic matter in the original black liquor was precipitated. In pH 8.9, the precipitation of organic matter was remarkably produced, and 20 per cent of it in the original black liquor was lost.

(4) From the considerations of both silica removal and loss of organic matter in the black liquor, it seems most reasonable to conclude that the optimum pH value on the removal of silica by lowering the pH value with sulphuric acid was in the range of 10.1 to 9.3. In these pH ranges, 77.9~90.0 per cent of silica in the original black liquor was removed, and the concentration of silica was 1.1~0.5 g/l. And, 7.8~10.4 per cent of organic matter in the original black liquor was lost.

(5) The greater amounts of silica in the black liquor can be precipitated and removed by adjusting the pH value of black liquor to the optimum ranges as described above.

Summary

In this work, the desilicification of bamboo black liquor by the addition of sulphuric acid has been studied. The results are summarized as follows.

(1) In the pH ranges from 12.3 to 8.9 which investigated in this experiment, the pH value of black liquor was lowered in proportion to the amounts of sulphuric acid added.

(2) In pH 10.1, 77.9 per cent of silica in the original black liquor was removed, and the silica content in the black liquor was 1.1 g/l. In pH 9.3, 90.0 per cent of silica was removed and the silica content was 0.5 g/l.

(3) In pH 10.1, 7.8 per cent of organic matter was precipitated and lost, and in pH 9.3, 10.4 per cent was lost.

(4) The optimum pH value on the removal of silica by lowering the pH value with sulphuric acid was in the range of 10.1 to 9.3.

References

1) A. Panda; *Indian Pulp and Paper,* **16,** 701 (1962)
2) K.G. Schwalbe; *DRP* 522, 730 (1931)
3) A. Panda; *Das Papier,* **18,** 170 (1964)
4) K. Ono and Z. Isono; *Unpublished*
5) K. Ono and Z. Isono; *Application number for Japanese patent* S. 41-12572 (1966)
6) H. Tsuji and K. Ono; *Bull. Univ. Osaka Pref., Ser. B,* **18,** 37 (1966)