Recovery of Silica from Black Liquor

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SUMMARY

The main raw material for pulping and papermaking being used in this country, is bamboo, which contains silica, to the extent of 2.7% to 3.5%. Most of this silica dissolves during the sulphate pulping of this raw material in the digester, and remain in the black liquor. The dissolved silica in black liquor has adverse effects at various places in the chemical plant of an integrated pulp and paper mill. This necessitates the removal of silica from the process. Based on extensive laboratory and pilot plant studies, a plant for the desilication of black liquor of 30% solids concentration has been designed at the West Coast Paper Mills. The silica in black liquor reacts wth lime to form calcium silicate. The reaction of lime with lignin, under the conditions adopted for desilication, is minimum. Thus, the sludge of desilication plant consists mainly of calcium silicate, with silica content of 25.5%. As silica has wide industrial applications, an attempt was made to recover silica in the form of a useful product from the sludge of black liquor desilication plant. The method adopted was, firstly removing from sludge the undesirable inorganics as soluble chlorides, and secondly the organics by incineration. The sludge was treated with conc. hydrochloric acid. For getting silica of 96% purity, and 87% brightness, it was found necessary to add conc. hydrochloric acid in the molar ratio, Ca : HCl :: 1:3. After evaporating the mixture, to about 50% solids, sufficient water was added and the whole mass was digested to faciliate the dissolution of chlorides. The residue was filtered hot and washed with hot water, till free from chlorides. This residue containing silica and some organic matter was incinerated in a furnace, to remove the latter. It was found that to get a product of high purity and brightness a temperature of about 900°C. was necessary. By adopting this procedure, about 98% silica could be recovered from the sludge. The product had silica content of 96% and brightness 87% (Elrepho).

INTRODUCTION

Bamboo, which is the principal fibrous raw material of the Indian pulp and paper industry, contains silica to the extent of 2.5% to 3.5%. Most of this silica dissolved during the sulphate pulping of this raw material in the digester and thus ramains in black liquor. The dissolves silica in black liquor has adverse effects at various places in the chemical plant of an integrated pulp and paper mill. This necessitates the the removal of silica from the process. The various sources of introduction of silica in the process of pulping have been discussed in the literature ([1,2]).

In a review article, various patents and methods of the removal of silica from black and green liquors of sulphate mills were discussed([3]). Exhaustive work was carried out at the West Coast Paper Mills, Dandeli, on the removal of silica from black liquor, green liquor, etc. It was observed that the green liquor containing silica, consumes extra lime during causticizing, due to the formation of calcium silicate. This insoluble calcium silicate goes out of the system along with lime sludge. The amount of silica in the lime sludge is about 11–15% on dry solids([4]). It is obvious that, silica must be removed from the system, before the lime sludge is sent to the reburning kiln.

Detailed experimental work was carried out at the West Coast Paper Mills, to study the desilication of sulphate black liquor of bamboo, employing different methods([5]). It was found that of all the chemicals available, for desilication of black liquor, the use of lime was characterised by its simplicity of operation, effective action and cheaper cost. The desilication reaction by the use of lime was observed to complete in 15 minutes at 90°–95°C. A counter-current method of treatment of black liquor of re-using the lime in the first stage and adding fresh lime in the second stage was found more effective. It was found possible to remove silica to the extent of 90%. For this, silica to lime ratio of 1:1.8 was found desirable. The resultant black liquor was found to be higher in active alkali content, and useful for processing([6]).

At the West Coast Paper Mills, a desilication

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plant has been installed, designed on the basis of the findings of the pilot plant. In this plant, partially concentrated black liquor of about 30% solids is treated with pulverised lime (-40 mesh) at 90°–96°C. The dissolved silica in black liquor which is mainly present as sodium silicate reacts with lime to form insoluble calcium silicate, which can be represented as follows :

$$Na_2SiO_2 + CaO + H_2O \longrightarrow CaSiO_3 + 2NaOH$$

In actual practice, for the efficient and maximum removal of silica, the lime requirement is about twice the stochiometric quantity of silica present in the black liquor. This may probably be due to the formation of some di-and tri-calcium silicate. The reaction of lime with lignin in black liquor is also found to be minimum when total solids in black liquor were 30% and under the reaction conditions. Some lime is observed to react with sodium carbonate for conversion into sodium hydroxide. Thus, the sludge of the black liquor desilication plant consists of mainly calcium silicate. Calcium silicate contains about 52% silica. This product has wide use in large number of industries. In the desilication plant of the West Coast Paper Mills, 16–18 tonnes of this sludge is produced per day. The chemical analysis shows that, the sludge contains 25.5% silica. Thus, if silica is recovered from the sludge of the desilication plant, it would be possible to recover about 4 tonnes of silica per day. Hence, a project was undertaken on laboratory scale to prepare silica of high purity marketable grade from the sludge of black liquor desilication plant.

EXPERIMENTAL

CHEMICAL ANALYSIS OF THE SLUDGE

Sufficient quantity of the sludge was collected from the desilication plant. The sludge was found to contain about 60% moisture. It was air dried to about 10% moisture and was powdered. This powder was analysed for itt various constituent like SiO_2, CaO, MgO, R_2O_3, Na_2O and sulphur. The silica was determined by oxidation of the sludge with nitric acid and perchloric acid and then ignition.

The CaO was determined by the oxalate method. MgO was determined by the 8–hydroxy quinoline method. Na_2O was determined by the zinc uranyl acetate method. The sulphur was determined as sulphate by precipitating with barium chloride. The results are recorded in Table—I. The loss on ignition of the sludge was determined by igniting it at 900°C.

PREPARATION OF SILICA—It was found that the sludge consists of mainly calcuum silicate. Some lignin is also precipitated during the desilication process and comes in the sludge. Thus for preparing pure silica from this sludge, both the unwanted inorganics and organics are to be removed. The inorganic can be removed by converting them into soluble salts and the organics by oxidation or by burning. It has been found advantageous to remove the inorganics first and then the organics.

TABLE—I

CHEMICAL ANALYSIS OF THE SLUDGE

Calcium as CaO, %	34.6
Silica (SiO_2), %	25.5
Magnesium as MgO, %	3.4
Mixed oxides as R_2O_3, %	1.8
Sodium as Na_2O, %	1.2
Sulphur as such, %	0.8
Loss on ignition (at 900°C), % ..	30.4

The above results are on the basis of oven dry solids.

REMOVAL OF INORGANICS— As mentioned above, the inorganics can be removed by converting then into soluble salts. From the analytical data of the sludge, it can be seen that the chlorides of all the constituents are soluble in water. Moreover, hydrochloric acid is cheap and is easily available. So it was found better to remove the inorganics as soluble chlorides by treating the sludge with hydrochloric acid.

OPTIMISATION OF REACTION CONDITIONS

The sludge containing 60% moisture was treated with various amounts of commercial grade concentrated hydrochloric acid. The doses of HCl were fixed on the basis of the amount of calcium present in the sludge. After the complete evolution of caıbon dioxide, the mixture was heated on a sand bath. In some experiments it was heated to complete dryness while in others, to a paste of about 50% solids (as shown in Table—II). This facilitates the conversion of the undesired inorganics into chlorides. Where the mixture was evaporated to complete dryness, it was moistened with HCl after the reaction. Water was added to the mixture and the whole mass was digested to facilitate the dissolution of all the chlorides formed. The whole mass was filtered hot and the residue was washed with hot water until free from chlorides. The washed residue was then air dried.

REMOVAL OF ORGANICS—The residue obtained above was brown in colour, consisting of silica along with the organic material. It was found that the organics could be removed at this stage without much difficulty. Different methods like oxidation, bleaching and burning were tried to remove the organics. Out of these the last one was found to)be the most efficient. In some cases, the residue was burnat at 650°C. and in some others at 900°C (as shown in Table—II). After the ignition the material was cooled and powdered. The brightness of the powder and the percentage of silica in the product were determined. The results are included in Table—II.

The silica in the final product was determined by fusing Rith fusion mixture, destroying the excess carbonate and precipitating the silica with hydrochloric acid. This was followed by washing the silica precipitate with water, free from chlorides and igniting it at 900°C and weighing as SiO_2.

RESULT AND DISCUSSION

CHEMICAL ANALYSIS OF THE SLUDGE The chemical analysis of the sludge indicates that it contains 34.6% CaO and 25.5% SiO_2. The silica is present mainly as calcium silicate. However, calcium may be present as $CaCO_3$, lignin salt and as free lime along with calcium silicate, depending upon the amount of the lime added for the desilication of the black liquor. Some lignin is also precipitated during the desilication process. The loss on ignition of the sludge is 30.4%. This includes carbon dioxide, organics, water of crystallisation of calcium silicate and any other volatile matter that may be present. The sludge was also found to contain 3.4% MgO which mainly originates from the lime. Presence of sodium and sulphur was also found in the sludge which may be because of the inefficient washing of the sludge.

PREPARATION OF SILICA— The sludge was found to contain 25.5% silica which can be separated as a useful product. It was found most convenient to remove the inorganics first and then the organics. Hydrochloric acid was found to be suitable for converting the inorganics into soluble chlorides.

$$CaSiO_3 + 2HCl \longrightarrow SiO_2 + CaCl_2 + H_2O$$

Stoichiometrically each mole of calcium requires two moles of hydrochloric acid. However, in practice, it was observed that when hydrochloric acid was used in this molar ratio, the silica obtained was only of 68% purity and brightness was 71% (Elrepho). This showed that more hydrochloric acid was required for the efficient removal of the inorganic salts. The purity of the product increased to 92.5%, when hydrochloric acid was used in the molar ratio, Ca:HCl:: 1:2.5 and the brightness of the product was 79.8% (Elrepho). However, when hydrochloric acid was used in the ratio Ca : HCl : : 1:3, a product of 96% purity was obtained with 87–89% brightness. This indicated that dose of hydrochloric acid is to be fixed depending upon the required purity and brightness of the final product.

It was observed that, it is sufficient to evaporate the reaction mixture to a paste of about 50% solids, rather than going for complete dryness. But it was very essential to digest the reaction mixture properly to convert the maximum amount of inorganics into the chlorides. The washing to remove chlorides could be done quickly without any difficulty, when wash water of about 75–80°C. was used.

The temperature of burning the residue, obtained after the acid treatment, was observed to influence the brightness and purity of the final product. If a product of higher purity is required, higher temperature for burning is recommended. Since the residue after the acid treatment contains some organics, it is advantageous to use a suitable, fuel based furnace for its burning. The burning of the residue after the acid treatment would help in getting higher brightness of the final product. The final product was amorphous in nature and could be powdered to the required mesh size.

The following stepwise procedure is recommended for recovering silica from the sludge on a commercial scale.

1. Addition of hydrochloric acid to the sludge containing about 60% moisture should be done in the ratio Ca:HCl::1:3.
2. Boiling of the reaction mixture, and evaporation to a paste of about 50% solids.
3. Addition of water to the mixture and digestion is to be carried out at 90–95°C.
4. Filtration and washing of the residue free from chlorides.
5. Drying of the residue.
6. Burning of the residue at 900°C. in a suitable furnace.
7. Powdering the product to the required mesh size.

From these experiments, it has been found that the following materials are required for preparing one tonne of silica of 87% brightness and 96% SiO_2 content.

1. Sludge required 3.85 tonnes (25.5% SiO_2 content)
2. Concentrated hydrochloric acid (commercial grade) — 7.65 tonnes
3. Water — 5.8 m^3
4. Heat.

i) To evaporate to a paste
ii) To boil and digest
iii) To burn the organics

USES OF SILICA—Precipitated silicas are widely used in the rubber industry as fillers and reinforcing pigments. Other applications include, use as a carrier and a dilient for high concentration insecticides and agricultural chemicals, anticoking substances, absorbing liquids, and sticky solids, as well as for viscosity control purposes in plastics, inks, textiles coating and pharmaceuticals. These reacive forms of silica are also used in manufacturing molecular sieve catalysts(7).

APPLICATIONS OF SILICA IN PAPER INDUSTRY

Amorphous silica is well known in the paper industry as a high quality synthetic pigment for use in paper filling(8). Its use for replacing 20% to 50% of TiO_2 without any drop in opacity or brightness has been discussed in literature(9). The out-

TABLE—II

PREPARATION AND PROPERTIES OF SILICA

Experiment No.	I	II	III	IV	V
Ratio of Ca : HCl	1 : 2	1 : 2.5	1 : 3	1 : 3	1 : 3
Condition after evaporation	Dryness	Paste	Dryness	Paste	Paste
Yield after acid treatment and washing (% on original sludge)	46.0	37.0	36.0	36.0	36.0
Burning temperature, °C	900	650	900	900	650
Yield of final product (% on original sludge) ..	33.0	27.0	26.0	26.0	26.6
Brightness, % (Elrepho)	71.1	79.8	88.7	87.3	87.0
SiO_2, % (in the final product)	67.9	92.5	96.2	95.8	94.0
% SiO_2 recovered (on the basis of SiO_2 present in the original sludge)	87.7	97.9	98.1	97.8	97.9

standing property developed by amorphous silica pigment, with respect to its printing characteristics, is a marked improvement in show through resistance. This is attributable to the large surface area, and the affinity of the pigment for ink. The great oil absorbancy of this pigment, enables it to immobilise the ink and prevents it from penetrating the sheet, thereby reducing the showthrough(10). Minor applications of silica in paper industry have been mentioned in the literature, like filler retention aid, and as a flocculating agent etc. (11 & 12).

CONCLUSIONS

It is possible to produce pure commercial grade silica from the sludge of the black liquor desilication plant. By treating the sludge with hydrochloric acid (Ca : HCl : : 1 : 3) and then burning the residue at 900°C a product of 87% brightness and SiO_2 content of 95.8% can be obtained. Silica of this purity has wide applications in numerous industries.

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