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# FIBER IN-SITU SYNTHESIS OF CALCIUM SILICATE FOR USAGE IN FINE PAPER

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## ABSTRACT

This paper researches fiber in-situ synthesis of calcium silicate that is made from sodium silicate solution extracted from fly ash, lime milk and fiber and its usage in fine paper. The in-situ synthesis technique was used to prepare man-made calcium silicate loaded in paper. The paper is in line with the copy paper standards. The experiments determined the optimum conditions for papermaking as follows, the pre-processing time of fiber immersed in the silicon solution 6h, pulp freeness 42°SR, the SiO2 concentration of the silicon solution 65.5g/L, the effective calcium concentration milk of lime 175g/L, stirring speed 550r/min, the reaction temperature 95°C, the reaction time 90min. Under these conditions, the filler retention rate in fine paper can reach more than 80%. A scanning electron Microscope-Spectroscopy (SEM-EDX), X-ray diffraction (XRD), infrared spectroscopy (FT-IR) was used to analyze paper products and structure. The results showed that the calcium silicate generated within the cell lumen, cell wall, and other open spaces of the fibers, and good bonding was demonstrated between the filler and fibers.

KEYWORDS: Fly ash, fine paper, in-situ synthesis, calcium silicate, filler.

## INTRODUCTION

China is the first coal-fired power country of the world, with the rapid development of power industry. A sharp increase in emissions of fly ash produced by coal-fired power plants. By 2020, fly ash emissions will reach about 500 million tons, which caused tremendous pressure to China's national economy and environmental protection.

Paper is mainly composed of plant fibers and mineral fillers. The conventional mineral fillers mainly includes ground calcium carbonate (GCC), precipitated calcium carbonate (PCC) and talcum powder, etc, due to the reason that such fillers had large density, small surface area and other factors. But it is difficult to combine with fiber, so the ratio of filler filled in the pulp generally does not exceed 30%.

Relevant studies have shown that the amorphous $SiO_2$ can be chemically extracted from fly ash and converted into man-made calcium silicate filler which ultrafine light and porous which can increase the amount of the filler fill into the paper from 40% to 45% .

However, the traditional way which man-made calcium silicate filler added directly to pulp was simple physical mixing, and calcium silicate fillers have limited taking-up position capability and weak adhesion bonds with fiber surface and mesh space by fibrillation. That make a lot of calcium silicate separated from the fiber gap and the surface during the papermaking process. It's difficult to disperse, easily flocculate and the paper strength is low because of poor bonding force.

Since the special structure of man-made calcium silicate and this poor bonding with paper fibers, the consumption of additional bond enhancing chemicals during the papermaking process is necessarily relatively high. Moreover, difficulties in dewatering the resultant pulp cause high consumption of energy for drying, increasing the production costs of the paper.

In fact, the moisture content of synthetic calcium silicate product is up to about 70 %. The high moisture content of the material makes transportation cost high, thus reducing the radius of economic transportation.

The characteristics of fly ash containing amorphous silicon oxide, If make the fly ash desilication reaction with sodium hydroxide solution, It can get the sodium silicate solution which containing $SiO_2$ , Take the sodium silicate solution in place of water and dispersing fibers of pulp, it can provide siliceous for in-situ synthesis of calcium silicate. When the fibers were fully soaked in sodium silicate solution, beaten the pulp, during the beating process, It can drive siliceous into the walls, the surfaces and the network of fiber, the siliceous suspension became uniformly distributed among the fibrous network. This distribution created favorable conditions for the hydrothermal synthesis of calcium silicate in the composite and in the structure of fibers.

Through specific reaction conditions, a nother kind of experimental raw lime milk was added into pulp for reaction in-situ synthesis calcium silicate in the walls, the surfaces and the network of fiber. Then use the composite pulp to prepare fine paper. The optimum conditions were determined by experiments, and the in-situ of synthesis calcium silicate in fiber and the paper properties were characterized.

The reaction equation that uses sodium silicate solution extracted from fly ash and lime milk to in-situ synthesis of calcium silicate in fiber is as follows:

$$SiO_2 + Na_2O + Ca(OH)_2 === SiO_2 \cdot CaO\downarrow + 2NaOH$$

## MATERIAL AND METHODS

Bleached softwood pulp from Silver Star Company, Chile, was used in this study. The pulp (40g) was immersed in 316 mL sodium silicate solution containing 65.5 g/L silica for 6h, and then it was disintegrated at 30000 rpm for 20 minutes to ensure that all the fibers were well dispersed and the pulp concentration was adjusted to 10%. The filtrate of the concentrated process was marked and preserved. Pulp was beating by PFI mill for about 3300 rpm to 3500 rpm, then equilibrium water content and measuring the beating degree. The beating degree at about 42°SR was appropriate.

Adding an appropriate amount of concentrated filtrate from pulp, and immersing it in sodium silicate as mentioned above, the mass was disintegrated at 15000 rpm for 30 min to ensure that all of the fiber was well dispersed. We put the pulp into the reactor, and then we took the reactor in a constant temperature water bath pot. We adjusted the temperature and we let

gradually to raise to a predetermined temperature. We used mechanical blender for mixing during the heating process, and adjusted the rotational speed from 100rpm to 500 rpm. After reaching reaction conditions, 111ml lime milk containing 175.0 g/L calcium oxide was added slowly. When the reaction reaches a predetermined time, we stopped stirring and heating.

The pulp was washed and filtrated by Büchner funnel. Filtration process continuously rinsed with hot water until the filtrate is close to neutral pH condition. The pulp was disintegrated as above mentioned, then the water was added to adjust the concentration to 2% and handsheets with basis weight of 70 $g \cdot m^{-2}$ were made by Kaiser rapid sheet papermaking apparatus. The ash content of the produced paper was determined by ignition at 900°C. The results gathered were used to obtain the degree of in-situ of synthesis filler in the paper produced. The handsheets physical characteristics were also tested according to relevant Chinese National Standards.

## RESULTS AND DISCUSSION

### The orthogonal experimental results

According to influencing factors of the in-situ synthesis calcium silicate, the mathematical statistics method was designed by a three factors and four levels orthogonal experiments under the conditions that use the same amount of dry fiber, sodium silicate solution and lime milk (Tab. 1). As measured by paper ash content, the orthogonal experimental results are shown in Tab. 2.

*Tab. 1: Factors and levels table of orthogonal experiment.*

| Levels | Factors | | |
|---|---|---|---|
| | (A) reaction temperature (°C) | (B) reaction time (min) | (C) stirring(rpm) |
| 1 | 85 | 30 | 100 |
| 2 | 90 | 60 | 250 |
| 3 | 95 | 90 | 400 |
| 4 | 100 | 120 | 550 |

*Tab. 2: Results of orthogonal experiments.*

| No. | A | B | C | Ash content |
|---|---|---|---|---|
| 1 | 1 | 1 | 1 | 41.2 |
| 2 | 1 | 2 | 2 | 42.3 |
| 3 | 1 | 3 | 3 | 44.6 |
| 4 | 1 | 4 | 4 | 44.9 |
| 5 | 2 | 1 | 3 | 42.3 |
| 6 | 2 | 2 | 4 | 41.2 |
| 7 | 2 | 3 | 1 | 44.7 |
| 8 | 2 | 4 | 2 | 43.3 |
| 9 | 3 | 1 | 4 | 43.3 |
| 10 | 3 | 2 | 3 | 44.8 |
| 11 | 3 | 3 | 1 | 44.4 |
| 12 | 3 | 4 | 2 | 43.3 |
| 13 | 4 | 1 | 2 | 42.2 |
| 14 | 4 | 2 | 1 | 43.4 |
| 15 | 4 | 3 | 4 | 45.7 |

| 16 | 4 | 4 | 3 | 44.4 |
|---|---|---|---|---|
| $k_1$ | 43.385 | 42.307 | 42.820 | |
| $k_2$ | 42.843 | 42.938 | 43.407 | |
| $k_3$ | 43.935 | 44.880 | 43.657 | |
| $k_4$ | 43.852 | 43.890 | 44.130 | |
| $R_j$ | 1.092 | 2.573 | 1.310 | |

The results of orthogonal experiments showed that the best permutation and combination were A3, B3, C4. The corresponding conditions was reaction temperature 95°C, reaction time 90min, reaction speed 550 rpm.

## Physical performance test of paper

The test results of the paper got by best conditions as shown in Tabs. 3, 4 and 5. The paper was made by pilot paper machine.

*Tab. 3: Basis weight, tightness and optical properties of paper.*

| Basis weight ($g \cdot m^{-2}$) | Tightness ($g \cdot cm^{-3}$) | Whiteness (%) ISO | Opacity (%) | Scattering coefficients ($m^2 \cdot kg^{-1}$) |
|---|---|---|---|---|
| 70.43 | 0.48 | 86.12 | 91.24 | 57.83 |

*Tab. 4: The apparent performance of paper, water absorption value and ash content.*

| Paper formation/Y | | Roughness ($mL \cdot min^{-1}$) | | Cobb absorption ($g \cdot m^{-2}$) | | Ash content (%) |
|---|---|---|---|---|---|---|
| Top | Bottom | Top | Bottom | Top | Bottom | |
| 88.23 | 87.91 | 1348 | 1422 | 96.22 | 93.84 | 44.88 |

*Tab. 5: Paper strength properties.*

| Burst index ($kPa \cdot m^2 \cdot m^{-1}$) | | Tensile indexn ($N \cdot m \cdot g^{-1}$) | | Tearing index ($mN \cdot m^2 \cdot g^{-1}$) | | Fracture length (km) | | Folding number number of times | | Stiffness ($mN \cdot m$) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Top | Bottom | MD | CD | MD | CD | MD | CD | MD | CD | MD | CD |
| 0.74 | 0.66 | 21.14 | 9.62 | 6.85 | 6.47 | 2.24 | 10.6 | 8 | 2 | 0.23 | 0.07 |

The above results showed that the paper with in-situ synthetic calcium silicate was basically met the requirements of copy paper. However, the content of calcium silicate as filler in paper was more than 40%, the filler retention rate was more than 80%. However, the traditional filler in the paper does not exceed 30%, the rention rate was less than 60%, so in-situ synthetic of calcium silicate filler was far higher than conventional filler.

Fig.1 showed the surface SEM images of the In-situ synthesis calcium silicate paper. From Fig. 1(A) and (B), it can be seen that the space of fiber crossing, outside of fiber wall has the white granular calcium silicate was generated. From Fig. 1(C) and (D) it can be also seen calcium silicate deposition and production in the fiber cavity wall and lumen.

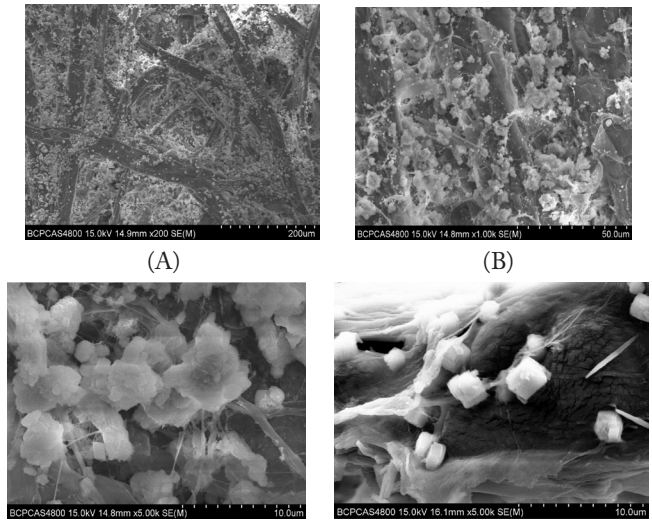


*Fig.1: Surface SEM images of the in-situ synthesis calcium silicate paper.*

Fig. 2 shows the SEM and EDX results of the in-fiber synthesized calcium silicate paper. The EDX analysis results from the box of Fig. 2 are shown in Fig. 3 and Tab. 6. Fig. 3 shows that energy spectrum diagram of the particulate matter created during the in situ synthesis exhibited silicon, oxygen, and calcium absorption peaks. The elemental analysis shown in Tab. 6 shows that particulate matter synthesized and deposited on the fiber was calcium silicate.

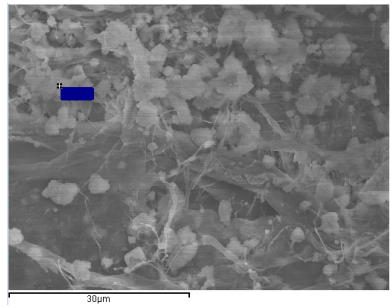


*Fig. 2: In-situ synthesis of calcium silicate.*

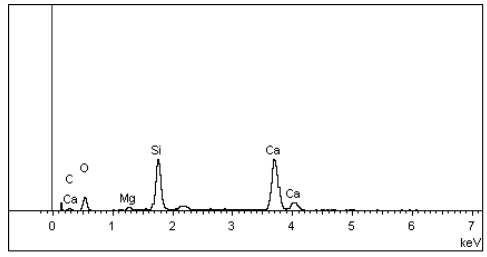


*Fig.3: EDX results of in-situ synthesis calcium silicate fiber spectral analysis.*

*Tab. 6: In-situ synthesis calcium silicate fiber element analysis.*

| Element | Weight fraction (%) | Atom fraction (%) |
|---|---|---|
| O K | 51.62 | 69.48 |
| Si K | 16.63 | 12.78 |
| Ca K | 28.01 | 15.09 |
| Al K | 0.40 | 0.32 |
| Mg K | 0.32 | 0.28 |
| Fe K | 0.29 | 0.20 |
| Total | 100.00 | |

## Fiber in-situ synthesis of calcium silicate analysis results

Fig. 4 is the X-ray diffraction analysis (XRD) of fiber in-situ synthesis of calcium silicate. The diffraction shot data coincide with calcium silicate purity. The filler with the $CaSiO_3 \cdot xH_2O$ is high, and it does not contain CaO, $Ca(OH)_2$, $SiO_2$ and other impurity phase.

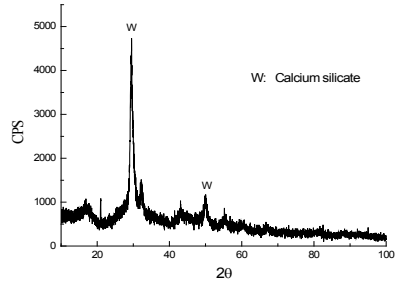


*Fig. 4: The X-ray diffraction pattern of in-situ synthesis calcium silicate.*

Fig. 5 is the scanning electron microscopy (SEM) image of in-situ synthesis calcium silicate. It showed that the microstructure of calcium silicate particles were mostly honeycomb, layered, and layered curls, with well-developed surface porosity of particles. These were generally loose and porous.

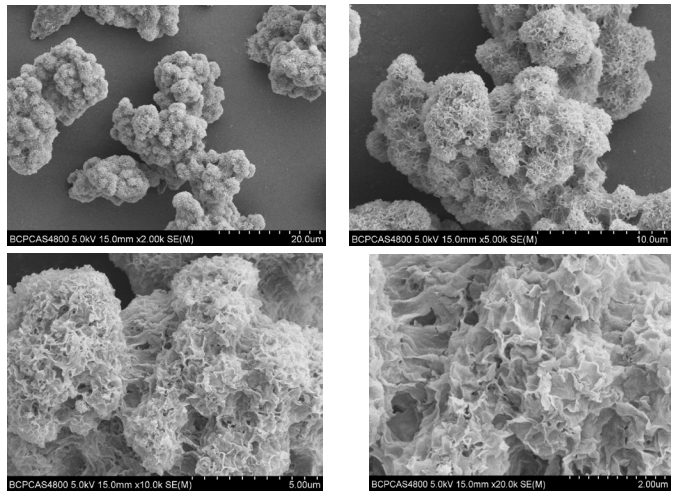


*Fig. 5: SEM of in-situ synthesis calcium silicate.*

The infrared spectra of in-situ synthesis calcium silicate is shown in Fig. 6. As can be seen, they had a very similar peak at 1630 $cm^{-1}$ for characteristic water adsorption and a peak nearby 999 $cm^{-1}$ corresponding to the internal tetrahedron Si-O-Si asymmetric bond stretching vibration.

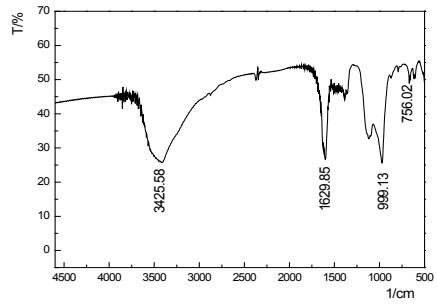


*Fig. 6: Infrared spectra pictures of in-situ synthesis calcium silicate.*

The peak nearby 700 $cm^{-1}$ is the absorption peak corresponding to Si-O-Si bond symmetrical flexible vibration. Because calcium silicate has hydrophilic group it can be combined with water by chemical bonds, so the calcium silicate can mix with fiber in the pulp. The same time, it has good chemical groups for binding.

## CONCLUSIONS

In-situ synthesis of calcium silicate in lumen, cell walls, and interior spaces of fibrillated fiber was achieved. Then it can be used in the pulp to prepare copy paper. The best conditions were reaction temperature 95°C, reaction time 90min, reaction speed 550r / min. Under these conditions, the copy paper filler retention rate was up to 80% and the paper strength met the requirements of copy paper.

The surface and cross-section of the paper made with man-made calcium silicate was analyzed by SEM and EDX, and the results showed that the particulates synthesis and precipitation in fiber lumen, cell walls, interior spaces of fibrillated fiber were calcium silicate.

The XRD, SEM, and IR analyses of the synthetic calcium silicate indicated that in situ synthesis produced calcium silicate of high purity, with strong chemical bonding with the fiber.

## REFERENCES

1. Ahmad, I., Baharum, A., Abdullah, I., 2006: Effect of extrusion rate and fiber loading on mechanical properties of Twaron fiber–thermoplastic natural rubber (TPNR) composites, J Reinforced Plast Compos 25: 957–65.
2. Bakare, I.O., Okieimen, F.E., Pavithran, C., Abdul Khalil, H.P.S., Brahmakumar, M., 2010: Mechanical and thermal properties of sisal fiber-reinforced rubber seed oilbased polyurethane composites, Mater Des 31(9): 4274–80.
3. Bermond, C., 1997: Establishing the scientific base for energy efficiency in emerging pressing and drying technologies, Appl. Therm. Eng. 17: 901-910.

4. Belgacem, M.N., Gandini, A., 2008: Monomers, polymers and composites from renewable resources, Oxford: Elsevier 543 pp.
5. Bura, R., Cheung, M., Liao, B., Finlayson, J., Lee, B.C., Droppo, I.G., Leppard, G.G., Liss, S.N., 1998. Composition of extracellular polymeric substances in the activated sludge floc matrix, Water Sci. Technol. 37: 325-333.
6. Bledzki, A.K., Gassan, J., 1999: Composites reinforced with cellulose based fibres, Prog Polym Sci 24(2): 221–74.
7. Coutinho, F.M.B., Costa, T.H.S., Carvalho, D.L., 1997: Polypropylene–wood fiber composites: effect of treatment and mixing conditions on mechanical properties, J Appl Polym Sci 65(6): 1227–35.
8. Culler, S.R., Ishida, H., Koenig, J.L., 1986: Silane interphase of composites: effect of process conditions on gamma-aminopropyltriethoxysilane, Polym Compos 7(4): 231–238.
9. Dignac, M.F., Urbain, V., Rybacki, D., Bruchet, A., Snidaro, D., Scribe, P., 1998: Chemical description of extracellular polymers: implication on activated sludge floc structure, Water Sci. Technol. 38: 45-53.
10. Frollini, E., Paiva, J.M.F., Trindade, W.G., Razera, I.A.T., Tita, S.P., 2004: Plastics and composites from lignin, In: Natural fibers, polymers and composites, New York: Academic Publishers Pp 193-225.
11. Finnveden, G., Ekvall, T., 1998: Life-cycle assessment as a decision-support tooldthe case of recycling versus incineration of paper, Resour. Conservation Recycling 24: 235-256.
12. Garnier, C., Görner, T., Lartiges, B.S., Abdelouhab, S., de Donato, P., 2005: Characterization of activated sludge exopolymers from various origins: a combined size-exclusion chromatography and infrared microscopy study. Water Res. 39: 3044-3054.
13. George, J., Sreekala, M.S., Thomas, S., 2001: A review on interface modification and characterization of natural fiber reinforced plastic composites, Polym Eng Sci 41(9): 1471–1485.
14. Geng, X., Deng, J., Zhang, S.Y., 2007a: Paper mill sludge as a component of wood adhesive formulation, Holzforschung 61: 688-692.
15. Geng, X., Zhang, S.Y., Deng, J., 2007b: Characteristics of paper mill sludge and its utilization for the manufacture of medium density fiberboard, Wood Fiber Sci. 39: 345-351.
16. Habets, L.H.A., Knelissen, H.J., 1997: In line biological water regeneration in a zero , discharge recycle paper mill,0000 Water Sci. Technol. 35: 41-48.
17. Huber, P., Nivelon, S., Nortier, P., 2012: Scaling risk assessment in a closed circuit recycled board mill by speciation methods, Tappi J. 11: 53-61.
18. Huber, P., 2011: Kinetics of $CO_2$ stripping and its effect on the saturation state of $CaCO_3$ upon aeration of a $CaCO_3$-$CO_2$-$H_2O$ system: application to scaling in the papermaking process, Ind. Eng. Chem. Res. 50: 13655-13661.
19. Kabir, M.M., Wang, H., Lau, K.T., Cardona, F., 2012: Chemical treatments on plant-based natural fibre reinforced polymer composites: an overview, Compos Part B: Eng 43(7): 2883–2892.
20. Kalia, S., Dufresne, A., Cherian, B.M., Kaith, B.S., Avérous, L., Njuguna, J., Nassiopoulos, E., 2011: Cellulosebased bio- and nanocomposites: a review, Int J Polym Sci http://dx.doi.org/10.1155/2011/837875.
21. Ku, H., Wang, H., Pattarachaiyakoop, N., Trada, M., 2011: A review on the tensile properties of natural fiber reinforced polymer composites. Compos Part B. Eng 242(4): 856–873.

22. Mohanty, A.K., Misra, M., Drzal, L.T., 2005: Natural fibers, biopolymers, and biocomposites, CRC Press, Taylor & Francis Group.
23. Rojo, E., Oliet, M., Alonso, M.V., Del Saz-Orozco, B., Rodriguez, F., 2013: Mechanical and interfacial properties of phenolic composites reinforced with treated cellulose fibers, Polym Eng Sci, http://dx.doi.org/10.1002/pen.23772.
24. Rojo, E., Alonso, M.V., Domínguez, J.C., Del Saz-Orozco. B., Oliet. M., Rodriguez. F., 2013: Alkali treatment of viscose cellulosic fibers from Eucalyptus wood: structural, morphological, and thermal analysis, J Appl Polym Sci 130(3): 2198–2204.
25. Tajvidi, M., Falk, R.H., Hermanson, J.C., 2006: Effect of natural fibers on thermal and mechanical properties of natural fiber polypropylene composites studied by dynamic mechanical analysis, J Appl Polym Sci 101(6): 4341 - 4349.
26. Wool, R.P., Sun, X.S., 2005: Bio-based polymers and composites. Burlington, California, London: Elsevier Inc.
27. Xie, Y., Hil,l C.A.S., Xiao, Z., Militz, H., Mai, C., 2010: Silane coupling agents used for natural fiber/polymer composites: a review. Compos Part A, Appl Sci Manuf 41(7): 806–19.

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