Alkaline Papermaking using Precipitated Calcium Carbonate

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ABSTRACT

The paper industry has been making paper since before the 1950's using acid sizing where alum and rosin is used at a pH of 4 to 6.5. It has been shown that alkaline papermaking has many advantages over acid papermaking. The experience in designing project implementation and running of PCC plant in USA, Europe and India are discussed.

INTRODUCTION

Majority of the PCC used in the US and other developed countries is as filler in manufacturing of alkaline papers (Fig. 1). There is some use as paper coating pigment, where it is used to impart brightness, ink receptivity. Hence the following discussions will be based on use of PCC as filler. Only specialty papers like cigarette and bible papers were made by the alkaline sizing which uses alkaline size at pH of 7 to 9. The differences between acid and alkaline sizing is shown in Fig. 1.

In Europe (Fig. 2) where low cost chalk was available, the alkaline paper making was used in the manufacturing of fine papers for 70% of production by year 1985. But in the US only 15% of fine paper was made by alkaline process in 1985. But today almost 90% of the fine paper is being produced by alkaline process in the US. Again the main reason of this explosion (47.6% compounded annual growth since 1986 to 1995) is due to the availability of good sizing agents and most importantly the availability of low cost fillers like PCC with onsite production (Fig. 3 and 4).

Advantages of using PCC

The economic advantages of using PCC are:

1. Expensive fillers like titanium dioxide, calcined clays can be replaced
2. Higher percentage of filler is used to replace more expensive fiber.

Extensive evaluation of fillers available for alkaline paper making has been done in the laboratories and on paper machines. The fillers evaluated were clay, calcined clays, ground calcium carbonate, titanium dioxide, specialty silicas (as titanium dioxide extenders) and precipitated calcium carbonate (Table 1). It has been concluded that precipitated calcium carbonate is the filler of choice because of its higher optical properties per unit

	Acid	Alkaline
Sizing Chemical	Rosin	Alkl Ketene Dimer
	Alum	Alkenlyl Succinic Ahdhydride
Fillers	Clay	PCC
	Soapstone	GCC
	TiO2	TiO2
	Talc	Clay
Retention Aid	Cationic	Anionic/Cationic
Operating pH	4.0-5.0	7.0-9.0
electrochemistry	15-25	10 to Neutral
(Zeta-Potential	Mev	MeV

Why Convert to Alkaline Papermaking?

- Better Product Quality
- Lower Cost
- Higher Marketability

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- Beetter Product Quality
- Better Optical Properties
- Better Bulk
- Better End Use Performance
- No Aging and Yellowing of Paper (Performance)

Why Convert to Alkaline Papermaking?

- Lower Cost
- Use of Lower Cost Fillers
- Replacement of Fibers
- Higher Productivity Potential
- Lower Capital Cost
- Lower Corrosion
- Environmental Advantages

Why Convert to Alkaline Papermaking?

- Higher Maretability
- Spring board for Value Added Products
- Competitive Edge
- Market Pressure

Fig. 1 Differences between Acid and Alkaline Papermaking

Key Events	Year
Alkaline Printing Papers, Ecusata	1958
Om-site PCC Plant, Ecusta	1962
Alkaline Printing Papers, Glatfelter	1971
Sizging Development in Laboratory	1975
Ground Calcium Carbonate Prodcution	1978
Problems: Abrasion, Picking, etc.	1979
Customer Resistance : IBM, XEROX	1982
First Commercial on-Site PCC Plant	1984
Sizing Development- Paper Porduction	1985
Initial Major Mill Conversion	1986
First West Coast Mill Conversion	1986
Alkaline Papermaking Optimization	1988
Paper Mill Conversions	1991 - 95

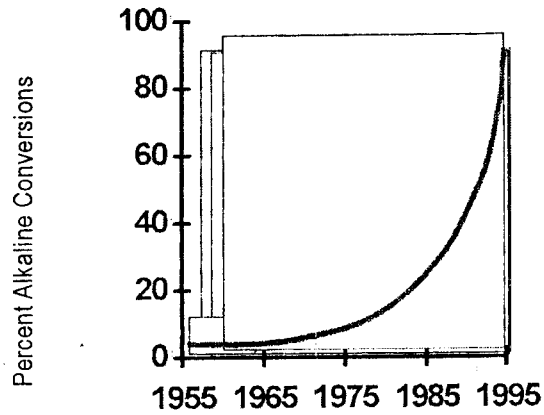

Fig. 2 Alkaline Papermaking Technology in United States

cost. On the basis of this, it is quite evident that PCC has major advantage over ground limestone marble or chalk (mostly known as ground calcium carbonate - GCC), because the particle size distirbution is unimodal and very narrow as shown in (Fig. 5). One major advantage is that control of particle size and shape is posible unlike that for GCC. It is also possible to make ultra fine PCC (less than 0.1 micron) economically as compared to GCC. The other major advantage is that PCC can be made with almost any limestone that is available. However the manufacture of desired quality of GCC requires high quality limestone or marble or chalk.

Another major advantage of using on-site PCC is its electrochemistry. PCC made on-site is cationic and since the fibers are anionic there can be attraction. The commercially available slurries of other fillers are anionic because of the addition of dispersents and hence do not have attraction to anionic fibers.

The quality aspects of alkaline paper made with PCC are as follows :

Permanence : The presence of PCC in alkaline papers, minimizes the degredation and subsequent discoloration of fibers. The presence of alkaline PCC neutralizes the acidic radicals in the atmosphere and hence keeps the radicals from attacking the fibers and prevents the reduction in strength and discoloration. This permanence

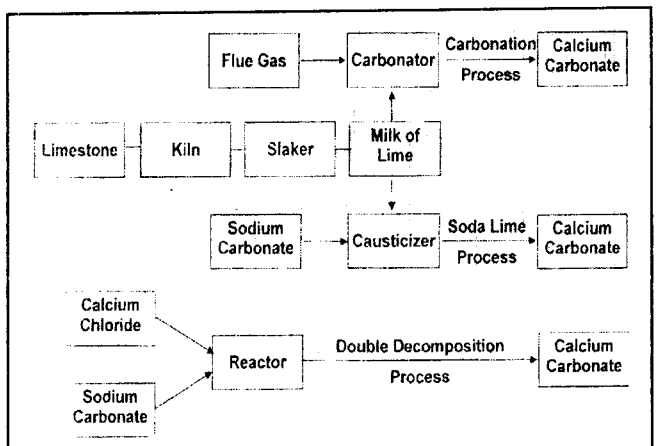

Fig. 3 Manufacture of Calcium Carbonate

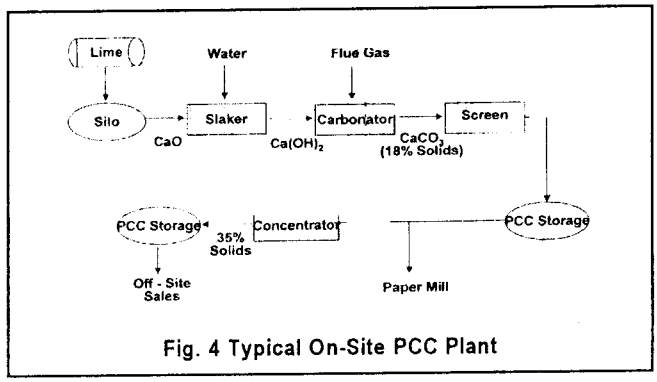

Fig. 4 Typical On-Site PCC Plant

Table 1 Differences between Commonly Used Fillers

	Clay	PCC	GCC	TiO_2
Brightness (ISO)	79-93	94-98	90-96	99
Scattering Coefficient	800-1200	1800-2500	1200-1800	4500-6000
pH	7.0	9.4	9.4	7.5
Price U.S. $/short tonne	120	120	120	2000

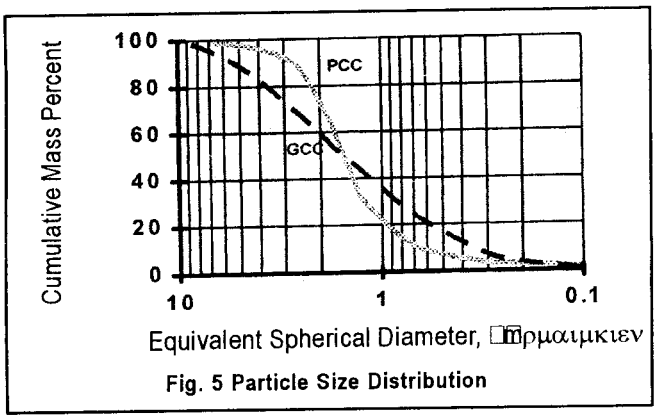

Fig. 5 Particle Size Distribution

is quite essential for printing papers used for books. The alkaline papers with PCC has been used for bible papers for a long time and hence these papers do not discolor with time.

Brightness: Normally the acid-sized printing and writing papers use clays with brightness of 76-90%, which gives low brightness papers. To increase the brightness sometimes titanium dixodie is used, which is very expensive. But in alkaline papers the use of PCC with 95-98% brightness increases the brightness of the paper by 2-5%, which is quite significant. This is shown in Fig. 6 where it is evident that alkaline papers with the same percent filer give higher brightness for alkaline sized papers as compared to acid sized papers.

Opacity: The use of PCC in alkaline papers increases the opacity of the paper by 2-5 points over similar acid sized papers. which is very significant This significantly reduces the ink show-through when the paper is printed. This is shown in Fig. 7 where opacity of papers made by acid and alkaline sizing is plotted versus percent filler.

Bulk: The use of PCC in alkaline papers increases the bulk of the papers by 2-5%. This is significant since the paper is sold by area. More area will be available for unit weight having the same thicknes as heavier papers. This is shown in Fig. 8. Since all the above data is shown on handsheets using Indian pulp and PCC made in India, we needed to do this on an Indian paper machine.

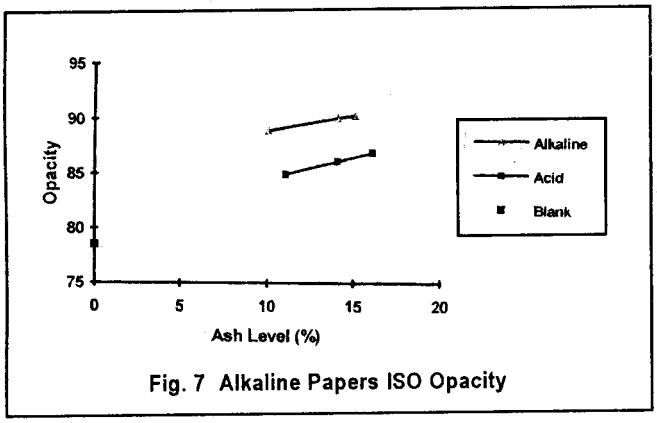

Fig. 7 Alkaline Papers ISO Opacity

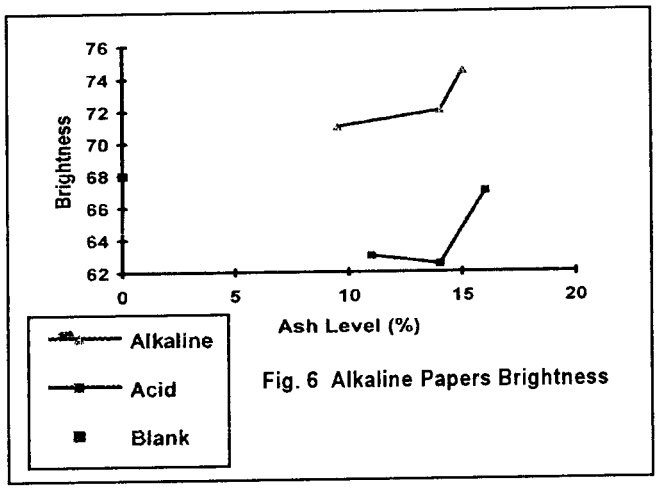

Fig. 6 Alkaline Papers Brightness

The PCC quality will be further improved to give better opacity at lower weights and all other advantages with use of PCC in paper. Laboratory studies done over a two month period had shown that the PCC being considered to use will have certain particle size, shape and size distribution. Based on the handsheet study which showed that use of PCC A could give about one to two point gain in sheet opacity. This will allow to lower the basis weight of the paper of 25.5 gsm instead of the present use of 27.5 gsm, which is very significant cost savings to the paper company. The shape and size of the PCC's used in this evaluations are shown as SEM photographs in Fig. 9. These pictures clearly show that this and Solvay PCC have very clearlydefined scalenohedral shaped crystals. The PCC-C and PCC-D are very badly defined and agglomerated. PCC-A and PCC-B show little better definition but is not good.

It can be seen from the above table that the main objective of this mill to make paper on their paper machine at lower basis weight and higher opacity as also shown in Fig. 10 was accomplished with the right type of PCC crystal and its shape and particle size distribution as shown in SEM

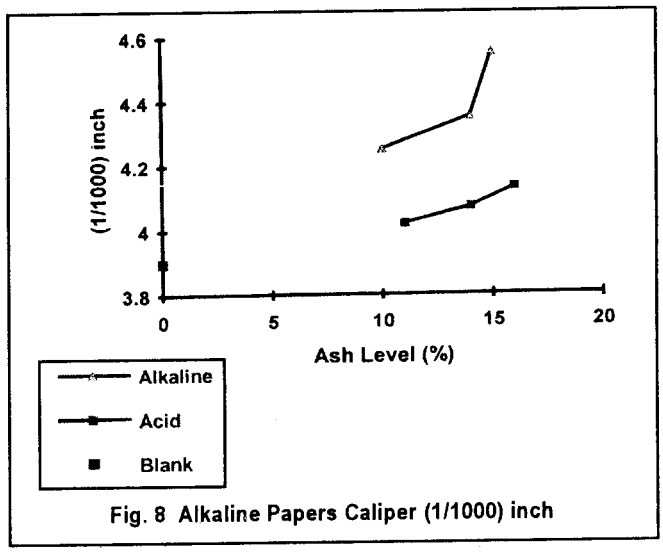

Fig. 8 Alkaline Papers Caliper (1/1000) inch

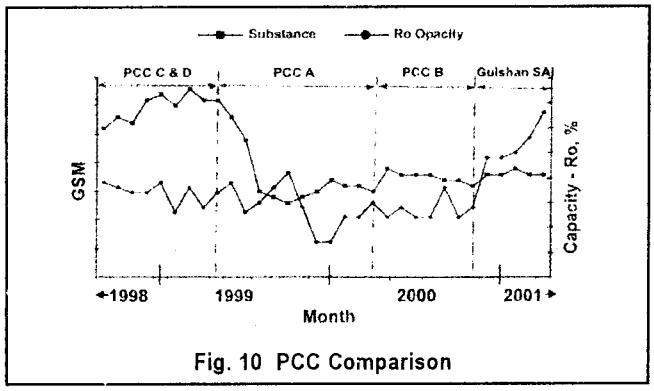

Fig. 10 PCC Comparison

Table 2 Paper Supply in the World by Categories

Paper Category	y Early Supply x 1000 tonnes
LWC	28,020
Uncoated Woodfree	48,600
Coated Mechanical	18,225
Uncoated Mechanical	15,865
Coated Papers	46,245
Printing & Writing	110,710

in Fig. 9. This work shows conclusively that beter defined crystals give better opacity at same basis weight. This has the highest sheet opacity at lowest basis weight. It is clearly evident that PCC-B at 27.25 gm has opacity of 70.4. but when the basis weight is reduced to 25.4 grams then the opacity drops to 69.2. While this gives at 25.4 grams the sheet opacity of 73 during this long term evaluation. Table 2 shows the paper supply allover the World. It can be seen from this Table that printing and writing papers in the World is 110 million tons/year in 2002. The uncoated wood free paper is estimated to be 48 million and coated paper is estimated to be 46 million tons/year.

The PCC production around the World is estimated to be 2-3 million tons/year and even if we assume that all printing and writing papers is converted to alkaline sizing with say, 10% filler level then PCC production to meet this demand should be 11 million tons/year it clearly indicates that a lot more PCC can be produced to satisfy this demand, which is presently satisfied only 25%. PCC as coating pigment is used only in small amounts, mostly to impart good ink receptivity and possibly smoother paper. It will also give little better brightness. Until recently, most of the PCC used as coating pigment was rhombohedral to reduce the porosity of the coating. The recent trend is to use unagglomerated Aragonitic PCC. The next phase of development is the use of PCC in groundwood containing papers. Several patents have been issued showing how PCC can be made so that it can be used at acid pH (5.0 or so). Significant developments and paper machine trials have been completed in the use of

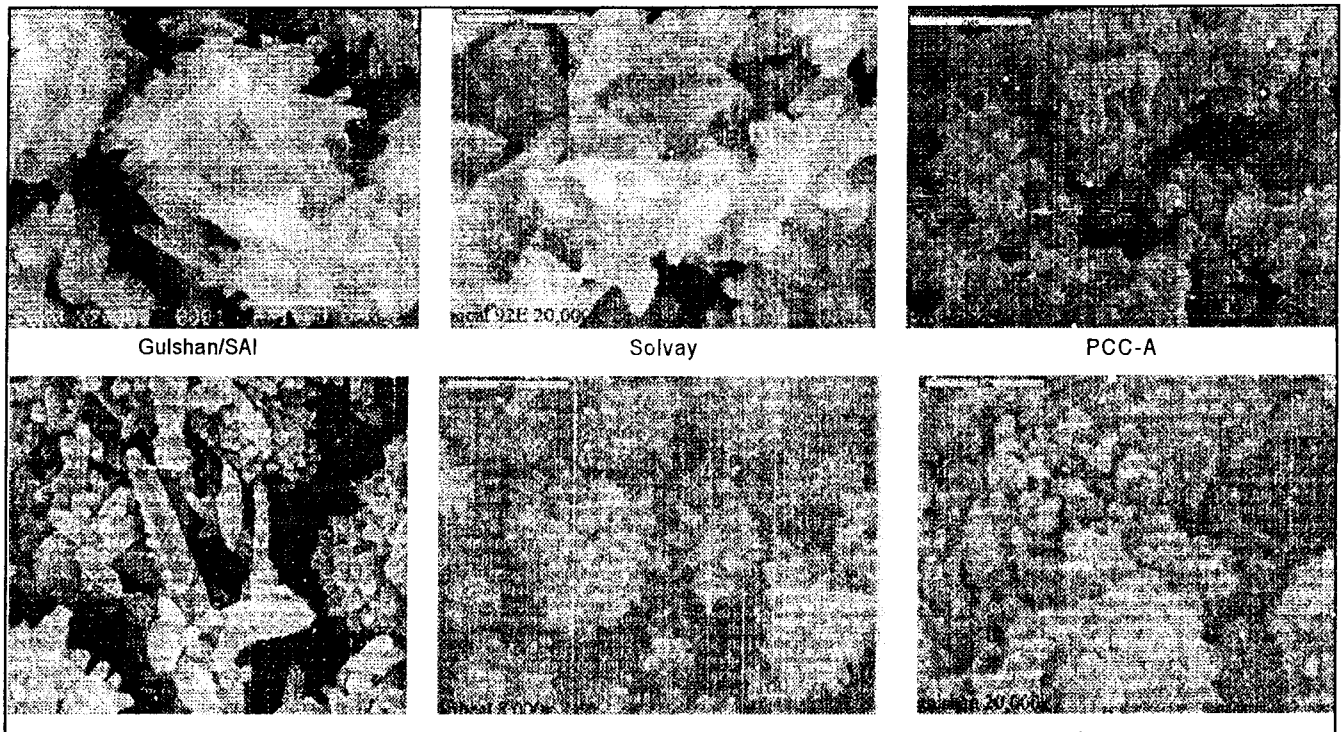

Fig. 9 PCC Comparison

acid -tolerant PCC in groundwood containing papers. In fact there are a few commercial PCC plants making acid tolerant PCC for use in groundwood containing Papers. The problem in using regular PCC is that it will evolve carbon dioxide when it comes in contact with acid conditions. It also reduces the brightness of the paper. The success of this phase will spill over for the use of PCC in newspapers. Several trials have been conducted and it is going to be commercial, if not it already may be. This development was initiated by USA Today whichdemands higher brightness because of its multicolor printing. Most of the local newpapers also have gone up on their brightness demand.

In USA it has been possible for the following reasons:

Replace fiber with cheaper PCC with on-site concept, because alkaline papers are stronger and can use more PCC than clay, ground calcium carbonate and titanium dioxide.

Replace most of Ti02, which is about $2000.00 per tonne with PCC about $ 100 or les per tonne.

In India it is difficult to justify any savings by going alkaline. In fact there is Rs. 1000-2000 ($20-$40) penalty per ton of paper. This is because:

The fibers are not strong so we can not replace fiber at Rs. 27000 ($ 540.00 per tonne with PC of Rs. 7000 ($140.00) - -Rs. 10000 ($200.00) per tonne.

CONCLUSION

The most important advantages of alkaline sizing being better optical properties, higher strength, higher bulk, no yellowing of paper and lower production cost. Today almost 90% of the fine paper is being produced by the alkaline process in the US. The main reason for this explosion is the availability of good sizing agents and most importantly the availability of low-cost fillers like PCC (with On-Site production). Most of the other countries, developed and developing (Malaysia, Thailand, Indonesia, China, Brazil etc), have gone alkaline. Two of the main reasons that would make alkaline paper economically feasible is to have PCC which will have less sizing demand and reduced use of alkaline sizing chemicals.