Thermochimica Acta, 152 (1989) 97-104
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

REACTIVITY OF LIME IN PAPER MANUFACTURE

D.R. GLASSON [1] and T. MALINOWSKI [2]

[1] John Graymore Chemistry Laboratories, Department of Environmental Sciences, Plymouth Polytechnic, Plymouth PL4 8AA, Devon, England.

[2] Pulp and Paper Research Institute, 90-950 Lodz, Poland.

SUMMARY

In modern pulp and paper manufacturing processes, lime is used in the recovery and recycling of the chemical reagents. After treatment of wood chippings with aqueous sodium hydroxide and sodium sulphite solutions to separate the lignin and the cellulose, the spent liquor is evaporated leaving sodium carbonate which is causticised with hydrated lime, viz., $Ca(OH)_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaOH$. The sodium hydroxide solution is recycled and the lime is recovered by thermally decomposing the calcium carbonate at temperatures up to about 1000 °C. The calcined product (mainly quicklime) is rehydrated and recycled in the causticiser.

The present research deals with the reactivity of the lime in the causticiser, its recovery and rehydration. Surface areas and porosities are determined from gravimetric B.E.T. nitrogen gas sorption recorded on a vacuum microbalance (μg to mg sensitivity using 0.25 g samples or less); changes are correlated with experimental conditions. Phase composition and microstructural changes are monitored by thermal analysis, X-ray diffractometry and electron-microscopy. It is important to avoid "dead-burning" the lime when it is recovered from the calcium carbonate in the presence of sodium salts (ca. 2 %) which promote sintering, so that optimum calcination temperatures and times must be determined.

INTRODUCTION

In earlier pulp and paper manufacturing processes wood chippings were converted to lignin and cellulose by sulphite solutions, notably calcium sulphite although magnesium, sodium and ammonium sulphites were also used. Thus hydrated lime was dissolved in water and an excess of sulphur dioxide to form calcium sulphite.

In later manufacturing processes, the wood chippings are treated with aqueous sodium hydroxide and sodium sulphite solutions in digesters at 160-180 °C and about 7-8.5 atmospheres pressure. The lignin dissolves and the cellulose residue is purified by washing and bleaching. Lime is used in the recovery and recycling of the chemical reagents. The "black" spent liquor and washing solution are mixed and concentrated in evaporators to about 45 % solids. Sodium sulphite and sulphate are added before further concentration to 60-65 % solids, mainly lignin. After transfer to the soda recovery boiler, the liquid is evaporated completely and the solid burnt. The residue in the highest (oxidising) zone consists of sodium carbonate (5 %) and sodium sulphite and sulphate (95 %), whereas that in the lowest (reducing) zone contains sodium

0040-6031/89/$03.50

carbonate and sodium sulphide. The sodium carbonate-sulphite mixture is dissolved in water to give a green liquor which is causticised by hydrated lime, viz., $Ca(OH)_2 + Na_2CO_3 = CaCO_3 + 2NaOH$. The position of equilibrium is over 90 % to the right-hand side, so that the supernatant "white" liquid consists mainly of sodium hydroxide and sodium sulphide for recycling. The "lime mud" produced consists mainly of calcium carbonate with small amounts of adsorbed calcium hydroxide and sodium carbonate, sulphide, sulphite and sulphate (from oxidation) and colouring matter. The lime is recovered by decomposing the "lime mud" at temperatures of up to about 1000 °C. The calcined product (mainly quicklime) is rehydrated and recycled in the causticiser.

The present research deals with the reactivity of the lime in the causticiser, its recovery and rehydration. Changes in surface area and porosity from B.E.T. nitrogen gas sorption are correlated with experimental conditions. Phase composition and microstructural changes are monitored by thermal analysis, X-ray diffractometry and electron-microscopy. The information obtained illustrates the factors affecting the optimum conditions for the industrial processes.

EXPERIMENTAL

Materials

A typical sample of "lime mud" was thermally analysed using a Stanton-Redcroft mass-flow balance, MF-H5. The sample had the following composition:- $CaCO_3$ 94.2 % $Ca(OH)_2$ 3.25 % Na salts 1.75 % Colouring matter and moisture 0.8 %. The sodium salts consisted mainly of Na_2CO_3 with small amounts Na_2S, Na_2SO_3 Na_2SO_4 and NaCl. The total Ca and Na contents were confirmed by atomic absorption spectroscopy. The "lime mud" on calcination produced almost pure quicklime containing 96.9 % CaO and 3.1 % sodium salts.

Normally the batches of quicklime are immediately hydrated before being used again in the causticiser, but on long storage the quicklime hydrates and carbonates and such a sample contained 27 % $Ca(OH)_2$, 53 % $CaCO_3$ and only 20 % CaO + Na salts. For reference studies on the decomposition of hydrated lime, a batch of I.C.I. Limbux was used. TG indicated 24.5 % water content in good agreement with the theoretical 24.32 % for $Ca(OH)_2$.

Procedure

Separate portions of the "lime mud" were calcined for various times at each of a number of fixed temperatures in air in an electrical furnace. The specific surfaces, S, of the cooled samples were determined by a gravimetric B.E.T. method (ref. 1), using nitrogen gas sorption at -196 °C recorded on a CI Microforce Mark 2B vacuum microbalance (µg to mg sensitivity using 0.25 g samples or less). The adsorption isotherms also indicated any porosity present (from hysteresis) and pore size ranges. Average crystallite sizes were deduced from the specific surfaces of the less porous materials and compared with aggregate sizes observed by scanning electron-microscopy (JEOL T20).

RESULTS AND DISCUSSION

In Fig. 1(a) a nitrogen adsorption isotherm is shown for the "lime mud".

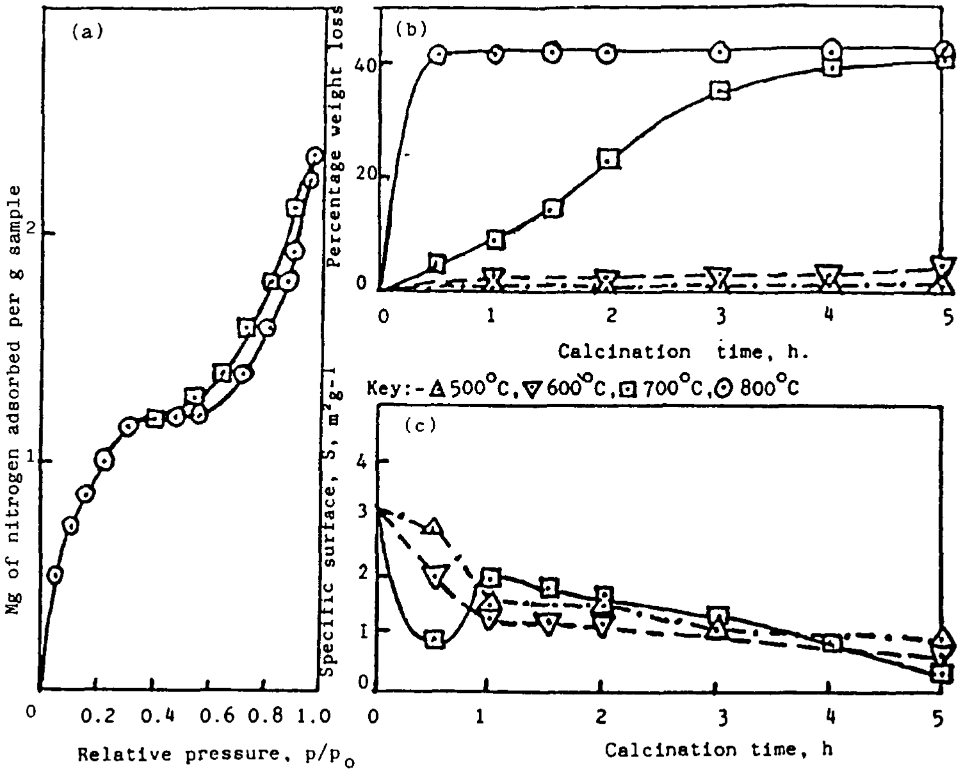

Fig.1 (a) Adsorption of nitrogen on "lime mud" at 77 K,
(b) and (c) Calcination of "lime mud" at different temperatures.

The surface area of the "lime mud" is 3.2 $m^2 g^{-1}$ and there is a small amount of adsorption hysteresis at relative pressures above 0.4 corresponding to the mesopore range (pore sizes between 2 and 50 nm diameter).

Changes in weight when the "lime mud" is calcined isothermally for different lengths of time are presented in Fig. 1(b) and are compared with the surface areas of the quicklimes formed in Fig. 1(c). At 500 °C none of the calcium carbonate present will decompose, since the dissociation pressure of $CaCO_3$ only exceeds the partial pressure of CO_2 in the atmosphere (generally about

0.23 mm Hg) above 535 °C; therefore only the calcium hydroxide can decompose. Earlier research (ref. 1) has shown that at 500 °C in air, $Ca(OH)_2$ mainly decomposes to CaO, but the remainder carbonates to $CaCO_3$. Thus the loss in weight at 500 °C of the "lime mud" is restricted to only 1.3 %, cf. Fig 1(b), compared with the theoretical 1.6 % for removal of moisture (0.8 %) and complete decomposition of the $Ca(OH)_2$. When calcium hydroxide decomposes at 500 °C in air, the quicklime produced has a considerably higher surface area (ref. 1) and this is shown in the present research when Limbux decomposes mainly in

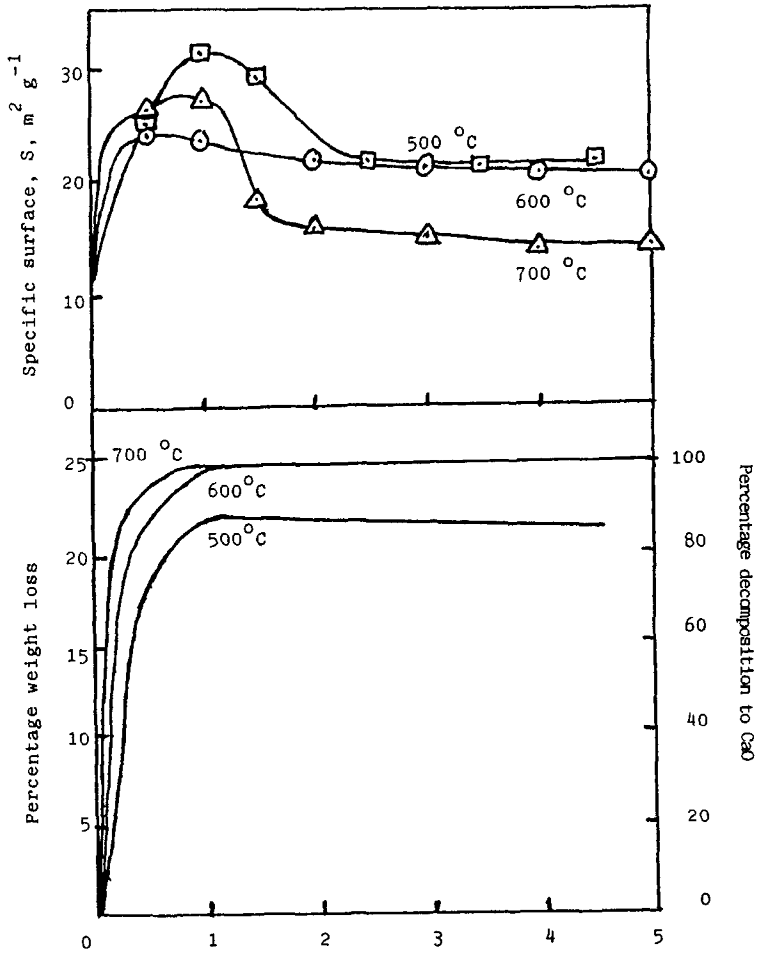

Fig. 2. Calcination of Limbux hydrated lime at different temperatures.

1 h and the surface area increases from 11 to 31 $m^2 g^{-1}$, cf. Fig. 2(a). There is some carbonation by atmospheric carbon dioxide, since the net loss in weight does not exceed 21.5 % instead of the theoretical 24.3 %, representing 4.7 % carbonation, cf. Fig 2(b). This is confirmed by X-ray diffraction showing the appearance of $CaCO_3$ in the X-ray patterns for the samples calcined for ½, 1, 2 and 4½ h. Above 535 °C atmospheric carbonation cannot occur, so that at 600 and 700 °C there is complete decomposition to quicklime within 1 hour.

It is known from earlier research (ref. 2) that calcium carbonate sinters appreciably at 500 °C. Hence in the calcination of the "lime mud" (Fig. 1(b) and (c)), the increase in surface area when the calcium hydroxide decomposes in the first hour is more than balanced by the decrease in surface area as the calcium carbonate sinters. There is further loss of surface after the first hour as the sintering of the calcium carbonate continues.

At 600 °C the calcium hydroxide in the "lime mud" rapidly decomposes and some of the calcium carbonate decomposes after 5 h to the extent of 7.2 % out of 94.2 % initially present. Again the increase in surface due to formation of quicklime is more than balanced by the sintering of the calcium carbonate, so that the surface area continuously decreases. At 700 °C there is more considerable loss of surface during the first half hour as most of the calcium carbonate sinters and only about 7 % decomposes. Subsequently there is an increase in surface as more of the calcium carbonate decomposes and the loss of surface due to the remaining calcium carbonate diminishes. Finally, there is some loss of surface due to sintering of the quicklime which becomes appreciable above 700 °C, cf. sintering of quicklime from Limbux at 700 °C (Fig. 2) during 1 to 5 hours calcination time.

At 800 °C the "lime mud" is completely decomposed in the first hour and the quicklime sinters more considerably, so that the surface area decreases (Fig. 3) from 3.2 to 0.6 $m^2 g^{-1}$, corresponding to an average crystallite size for the quicklime of 3 µm. Subsequently the surface area increases somewhat by 0.8 $m^2 g^{-1}$ and this is ascribed to some active lime being formed when the sodium salts react with the $CaCO_3$ during the first hour to give Na_2CO_3 + CaS or $CaSO_3$ and the latter calcium compounds subsequently oxidise or decompose to lime, i.e., causing desulphurisation. Finally, the active lime sinters and the surface area decreases. The behaviour at 900 °C and 1000 °C is similar, but at 1000 °C there is also decomposition of $CaSO_4$ which has been formed either by disproportionation of $CaSO_3$, viz., $4CaSO_3 \rightarrow CaSO_4 + 3CaS$, or by reaction between $CaCO_3$ and Na_2SO_4. Thus the increase in surface is somewhat greater before the active lime finally sinters and the surface area decreases faster than at 800 and 900 °C (between the fourth and fifth hours in Fig. 3).

There is also a general lowering of surface areas due to the sodium carbonate and sodium chloride promoting sintering of lime, cf. ref. 3. These salts have

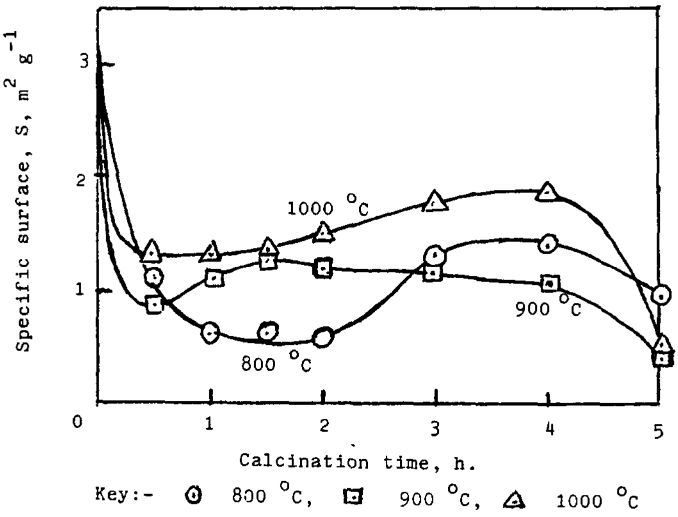

Fig. 3. Calcination of "lime mud" at higher temperatures.

melting points of 850 °C and 800 °C. Their low Tammann temperatures (½ m.p. in K) at 290 °C and 265 °C enable them to accelerate sintering of lime. Above 670 °C (or 940 K, one-third m.p. of lime) sintering by surface diffusion becomes appreciable, but sintering by crystal lattice diffusion only becomes appreciable above the Tammann temperature of lime, viz., 1140 °C or 1413 K, ½ m.p. of lime. Thus the sodium carbonate and sodium chloride can promote lime sintering by surface diffusion between 670 °C and 1000 °C by diffusing into the lime cracks and fissures formed when the lime was first produced from calcium carbonate of greater volume. The sodium salts can also assist the merging of the lime crystallites by lattice diffusion at higher temperatures. After desulphurisation, the quicklime sinters considerably at 900 °C and 1000°C (Fig. 3) with the surface areas decreasing to below 0.5 m^2 g^{-1} and the average crystallite sizes reaching about 4-5 µm. Longer calcination at these temperatures or calcination at higher temperatures must be avoided, so that the quicklime does not become "dead-burnt" and difficult to hydrate and recycle in the causticisation process. This is confirmed by comparison of the electron-micrographs of the "lime mud" (Fig. 4) calcined at 800 and 900 °C for 5 h, where the particles become more rounded at the higher temperature, as sintering proceeds.

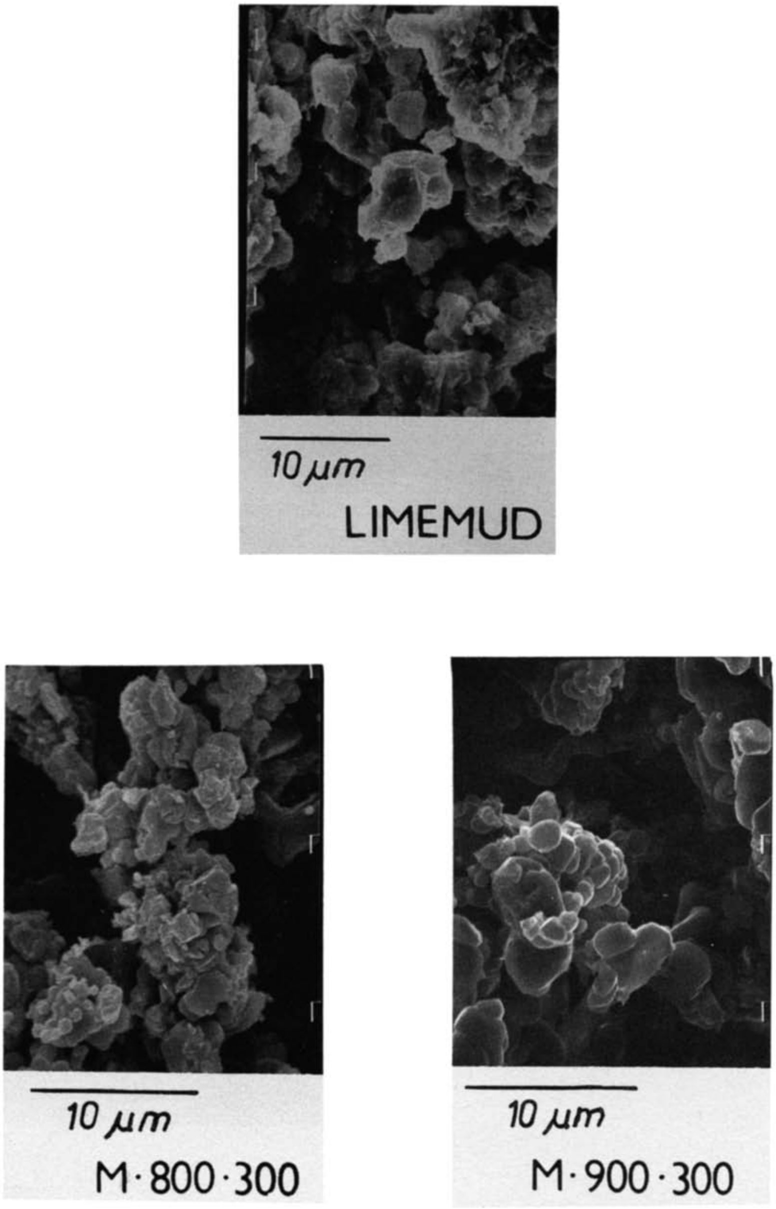

Fig. 4. Electron-micrographs of "lime mud" calcined at 800 and 900 °C for 5 h (300 min).

ACKNOWLEDGEMENTS

The authors thank Mr B. Lakey and Mr P. Davis for their assistance in the electron-microscopic and X-ray testing of materials, also the British Council, Imperial Chemical Industries and the Science and Engineering Research Council for sponsorship.

REFERENCES

1. D.R.Glasson, J.Chem. Soc., 1956 pp 1506-10.
2. D.R.Glasson, J.appl. Chem., Lond., 10 (1960) 793-798.
3. D.R.Glasson, J. appl. Chem., Lond., 17 (1967) 91-96.