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INVESTIGATION OF WASTE PRODUCTS FROM ESPARTO PAPER MILLS: WITH A VIEW TO THEIR ECONOMIC UTILISATION.

by

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GENERAL INTRODUCTION.

Papermaking is an art which has descended to us from the ancient civilisations, assuming greater importance with the passing years, until to-day, although materials and methods are entirely different, it ranks as one of our most important industries. Cellulosic fibre or "pulp" forms the basic material in the manufacture of paper and huge quantities are required annually. This fibrous pulp can be obtained from a great variety of raw materials, derived from the vegetable kingdom, but, from economic and other reasons, the commercial selection is restricted to certain species of wood, straw, esparto grass and linen and cotton rags. Except in the purely mechanical process of grinding down wood to prepare an inferior pulp for common newsprint papers, etc., the fibrous constituents of the various raw materials are separated from the organic encrustants by boiling out the latter, under regulated conditions of heat and pressure, with some suitable chemical. In America and on the continent, where wood is the chief raw material employed for the manufacture of pulp, various processes are in vogue, the choice of process being subservient to the class of wood being treated by the mill. and, of course, the grades of paper for which the pulp is intended.

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In this country, however, where there is no wood pulp industry, and little, if any, preparation of fibre from straw, the soda boiling process is the only one in operation, the raw materials being esparto grass, rags, textile and rope wastes.

In all of the processes for the preparation of pulp, and in many for its subsequent manufacture into paper, tremendous quantities of waste materials are produced, and the desire to find some commercial use for them, or obtain valuable substances from them, has engaged the attention of numerous investigators for years. A vast amount of work has been accomplished and although the greater part has never passed beyond the experimental stage, manufacturers have been able to avail themselves of some of the uses proposed, and several of the large continental concerns are profitably doing so.

Unfortunately, the bulk of this research work has been carried out abroad and relates principally to the problems in the processes employing the sulphite, soda, and soda-sulphate methods of preparing fibre from wood and straw.

Certainly, several papers have been published and numerous patents taken out in this country, dealing with problems found in the esparto paper mills, but they have had little or no success, or even attention, partly because they have failed to pass a commercial test,/

test, partly because many of them have only dealt with some particular waste material in view of local conditions, but principally because it is the general belief that such subsidiary processes would be of little value, the units being so small when compared with the continental concerns.

While there is a certain amount of truth in this, it is also true that the problem has not had the attention that might have been given to it, and certainly, no paper dealing with all of the waste products in detail has yet appeared. The present work, therefore, was commenced with the object of making a detailed investigation of the various wastes produced and to discover, if possible, some application, or applications, which would have more hope of success than these previously suggested.

It should be borne in mind, that in work of this nature, while purely chemical research often leads to improvements, and even, from time to time, creates new side lines, advances may also be effected by the application of knowledge which has already been placed on record. Many previously waste products have been utilised, and a number of originally crude processes have been developed, by the application of chemical knowledge which has been gained before. The solution of a problem, therefore, may not depend upon/

upon the prosecution of entirely new investigations.

It should be added, that in keeping with the general character of the present work and the variety of wastes to be examined, ~~any~~ no particular line of investigation has ~~not~~ been prolonged to the detriment of others, but discontinued at a point from where it could be observed, whether or not, future work might be profitable.

The work has been divided into sections, each section being occupied with the examination and utilisation of a waste material, and placed in the order in which the wastes appear in the process of manufacturing the paper. While it is not proposed to utilise much space in describing the actual manufacture of the paper, sufficient details are given to enable one to understand the nature and occurrence of the various wastes.

The samples of material analysed and process data, except when otherwise stated, were obtained for the present work from mills situated in the near vicinity of Edinburgh. For private reasons these mills have been given letters instead of their original names.

ESPARTO GRASS MILLS.

The manufacture of paper from esparto grass had its origin in Britain and to-day remains almost exclusively a British industry, associated particularly with Edinburgh and central Scotland. The pulp obtained from esparto enters into the composition of a great variety of papers, generally with a certain amount of wood pulp, the proportion of the latter depending on the class of paper being made. All the mills prepare their own pulp from the grass but import the wood pulp from abroad.

The esparto grass, which is obtained from Spain, Morocco, Algeria, Tunis and Tripoli, arrives in this country in tightly packed bales, weighing about four cwts each. When the grass arrives at the mill, the bales are broken up and the grass put through a dusting or "willowing" machine, which opens out the grass and removes the dust. The esparto dust thus obtained is a valuable material, containing, as it does, anything from 25-50 per cent of a hard and high-melting vegetable wax. Some years ago this dust was generally sent to the boiler house to be burnt, but nowadays most paper mills have installed special dust collectors where an air current is made to deposit the dust in a special receptacle, whence it is ultimately discharged into bags and sold to manufacturers/

manufacturers for the extraction of the wax which it contains. The wax finds a use as a constituent of mixings for the manufacture of gramophone records.

The grass, having been put through the dusting machine, then passes to the digester house, where it is submitted to the disintegrating action of a solution of caustic soda in specially constructed autoclaves. When this operation is completed, the spent lye is run off and the grass, after being partially washed to remove the residual soda, is conveyed in some convenient manner to the breaking machine.

This machine consists of a shallow trough fitted with a central partition, around which the grass is made to circulate by means of rolls fitted with knives. The grass is broken up in the process and, at the same time, is more completely washed by a continuous stream of fresh water, the dirty water being removed by a specially constructed hollow drum, let down into the mixture, and the fresh water run in at one end of the machine. When sufficiently washed the grass is bleached by means of a solution of chloride of lime. This may be carried out in the breaking machine or in some other suitable apparatus. When the bleaching operation has been completed, the grass is washed until free from traces of bleach and then conveyed to the beaters.

These/

These beaters complete the reduction of the bleached grass to a pulp of single fibres and, at the same time, thoroughly incorporate the necessary loading material, colouring matter and size, successively added at this stage. When ready, the mixture passes by gravity to the stuff chest which acts as a reservoir and whence the pulp passes, via machine chests and troughs, to the wet end of the paper making machine.

During its journey from the stuff chest to the paper-machine, the pulp, after being diluted to the proper concentration constituency with water, is passed over a series of sand traps, which intercept grit, metallic fragments and such matter that is heavier than the pulp, and then through strainers which retain foreign matter, unbeaten particles and knots of fibre. The flow of pulp is governed by a system of valves, which can be quickly manipulated to alter the "substance" of the resulting paper.

The wet end of the paper-machine consists of an endless band of woven wire, some 40 to 80 meshes to the inch, from 48 to 205 inches wide, and a total length of 40 feet or more. During its passage over this wire band, the pulp mixture is subjected to side-shake, which interweaves or "felts" the fibres together, to produce a continuous web of wet pulp. The excess of water, aided by suction boxes placed underneath, passes through the wire and is caught by the/

the save-all. When the web of paper reaches the end of the travelling wire band it passes through a series of rolls where it is pressed and consolidated. It then goes forward to a long series of heated drying cylinders and finishing rolls to emerge finally as a continuous sheet of paper at the farther end of the machine, ready for reeling on to the roll placed there for the purpose.

WASTE MATERIALS.

The wastes produced by a paper mill may be classified into two sections:-

(1) Materials and chemicals lost in the process of manufacturing the paper; these include soda, bleaching powder and what is known as "backwater sludge".

The soda is lost in the grass and at various points of the recovery process, and the bleaching liquor in the residual sludge and other ways. In the more progressive mills these losses have been brought to an economic minimum, viz., to a point beyond which it would be impracticable and unprofitable to go. Unfortunately, in many mills, ~~these~~ avoidable losses are still very high, but being due mainly to crude methods of working and want of proper control, they will not be dealt with in this paper, except to point out/

out where they occur.

The sludge obtained from the paper-making machine is unavoidable and consists of varying proportions of fine fibre, clay and size, suspended in the excess of water which falls through the shaking wire table of the machine.

(2) Waste materials which are produced by the subsidiary processes of the mill; these consist of (a) organic material in the spent lye (black liquor), (b) carbon from the lixiviation of the recovered soda ash, (c) waste ~~lime~~ chalk from the causticising plant, (d) bleaching powder residue from the digestion of the bleach with water, and (e) waste cellulosic material removed from the strainers, placed in the troughs carrying the pulp mixture towards the machine.

The composition of all these waste materials, with the possible exception of the organic matter in the spent lye, may vary considerably, according to the methods and processes in vogue at the different mills.

PREPARATION OF THE PULP.

Composition of the grass. The cellulosic portion of esparto grass consists of bundles of fibre bound together with an organic cementing material, which consists of wax, carbohydrates, pectones and lignones, and commonly designated as "resinous"/

"resinous" matter. This resinous matter amounts to over fifty per cent., by weight, of the grass and has to be removed. The following table contains the two analyses generally given to illustrate the proximate composition of esparto grass.

TABLE I.

Composition of Esparto Grass (Hugo Müller)

	Spanish.	African.
Cellulose	48.25%	45.80%
Fat and Wax	2.07	2.62
Aqueous extract	10.19	9.81
Pectous substances	26.39	29.30
Water	9.38	8.80
Ash	3.72	3.67

Table 2 gives the composition of an ash obtained from a sample of Spanish grass.

TABLE 2.

Ash.

Silica	66.45 per cent
Ferric and Aluminium oxides	6.20 " "
Calcium oxide	14.05 " "
Magnesia and alkalis	13.30 " "

The nitrogen content of the grass was found to be generally about one per cent.

Digestion./

Digestion. The non-cellulosic portion of the grass can be removed in stages by successively boiling with water, a weak solution of caustic soda and then a strong solution of caustic soda. In mill practice, however, they are all removed at the one operation, by boiling with caustic soda under steam pressures of 25-50 lb. per sq. in. The solution strength of the caustic is sometimes varied to suit different grasses but the general practice is a solution strength of 5-6 per cent NaOH and a steam pressure of 45 lb. per sq. in., which is regarded as the economic optimum.

This digestion is carried out in specially constructed cylindrical boilers, with a "vomit", designed by Sinclair, and having a capacity of 600-1000 cubic feet. Although a certain proportion of the matter to be removed is extracted, i.e. dissolved out by the caustic liquor, the remainder, including the greater proportion of the silica, combines with the soda.

The requisite amount of soda solution is run into the digester and steam admitted into the bottom while the grass is being thrown in. In this way the grass becomes wet and soft, the bulk is greatly reduced and a much greater weight of grass can be treated at one operation. When the digester is loaded, the inlet is closed, the steam turned on to full working pressure and the charge boiled for the required/

required period. There is always a certain amount of ammonia given off with the steam which issues from the blow off cock but the amount is never very great. Table 3 gives the results of two tests carried out at S. Mill.

TABLE 3.

Blow off Steam from Grass Boilers.

S. Mill.

Oran grass.

	1st run.	2nd run.
Weight of condensing water (before run.)	156.0 lb.	156.0 lb.
Weight of condensing water (after run)	177.5 lb.	177.0 lb.
Difference	21.5 lb.	21.0 lb.
Duration of run	75 min.	65 min.
Temp. of water (before)	50 deg. F.	50 deg. F.
Temp of water (after)	150 deg. F.	160 deg. F.
Estimation of Ammonia.		
Ammonia in total water, grms/litre	0.6218	0.64
Ammonia in total water, lb./gal.	0.006218	0.0064
Ammonia in Cond. steam lb./gal.	0.05134	0.05395
Ammonium sulphate in condensed steam lb./gal.	0.1993	0.2223
Ammonium sulphate per 4 hours run	1.451	1.494
Average condensate per run of 4 hours	7.28 gal.	
Average condensate per hour	1.82 gal.	

When the operation is completed, the black liquor, or spent lye, is run off from the digester into large storage tanks, and the esparto, which remains in the boiler, is washed until free from soda, and then passes to the next operation.

This washing is carried out with the minimum amount of water in order to recover the maximum amount of soda at the least cost.

BLACK LIQUOR.

In former years the black liquor from the boiling operation, together with the washing water, was run into the nearest water course, but about fifty years ago, owing to the pressure exerted by the Rivers Pollution Act of 1876, and because it was found to be remunerative, all the liquors were preserved and the soda recovered. The recovery of the soda is effected by evaporating the liquor and wash waters, known as the "thin" black liquor, to a syrupy con~~stituency~~ consistency and burning this in a rotating kiln, the organic matter being readily ignited by the already burning contents of the kiln. During the combustion, which proceeds without the aid of external heating, the sodium compounds are converted into crude soda ash.

The evaporation is carried out in various types

of/

of vacuum, multiple effect evaporators, the limiting concentration of the feed liquor for profitable evaporation being about 1 per cent.

In order to insure a steady burning off of the organic matter the thin black liquor must be concentrated to a point at which it contains 13-14 per cent of available sodium oxide, corresponding to about 70-80 per cent. of dry organic matter and a volume reduction of about 12-1. This is known as the "thick" black liquor.

Table 4 gives the analysis of four samples of this thick black liquor drawn from S and K mills. Section A gives the results on a "received" basis and section B on a dry basis.

TABLE 4 (A)/

Table 4 (A).

Thick Black Liquor.

As received basis.

Proximate analysis.	S1.	S2.	S3.	K1.
Sodium oxide (available)	13.71	13.03	13.44	12.27
Calcium oxide	trace	nil	trace	trace
Silica	1.06	0.85	0.95	0.71
Ferric and Aluminium oxides	0.07	0.10	0.11	0.09
Sulphur trioxide	1.48	0.64	1.06	1.26
Carbon dioxide	3.46	1.36	2.42	1.50
Chlorine	1.66	trace	0.22	0.54
Organic matter	42.08	48.91	45.20	43.17
(Nitrogen included)	0.68	0.69	0.71	0.66
Moisture	34.51	34.04	35.47	37.56

Hypothetical Combination.	S1.	S2.	S3.	K1.
Sodium carbonate	8.53	3.28	5.83	3.62
Sodium hydrate	2.20	4.60	0.85	4.13
Sodium chloride	2.74	trace	0.34	0.89
Sodium silicate	2.15	1.73	1.93	1.44
Sodium sulphate	2.39	1.13	1.88	2.26
Ferric and Aluminium oxides	0.07	0.10	0.11	0.09
Calcium salts	trace	nil	trace	trace
Organo-sodium salts and organic matter	47.61	56.13	53.57	50.01
Moisture	34.51	34.04	35.47	37.56

Table 4 (B)

Dry basis.

Proximate analysis.	S1.	S2.	S3.	K1.
Sodium oxide (available)	20.93	19.75	20.76	19.64
Calcium oxide	trace	nil	trace	trace
Silica	1.62	1.29	1.47	1.14
Ferric and Aluminium oxides	0.11	0.15	0.17	0.14
Sulphur trioxide	2.26	0.97	1.64	2.06
Carbon dioxide	5.28	2.06	3.74	2.40
Chlorine	2.53	trace	0.34	0.86
Organic matter	62.24	74.15	69.88	69.13
(Nitrogen)	1.04	1.06	1.10	1.06
Hypothetical combination.				
Sodium carbonate	12.69	4.97	9.04	5.79
Sodium hydrate	3.36	6.97	1.32	6.62
Sodium chloride	4.18	trace	0.53	1.43
Sodium silicate	3.28	2.62	2.99	2.31
Sodium sulphate	3.65	1.71	2.91	3.62
Ferric and Aluminium oxides	0.11	0.15	0.17	0.14
Calcium salts	trace	nil	trace	trace
Organo-sodium salts and organic matter	72.69	85.09	83.05	80.11

The thickened liquor, though viscous, is still sufficiently fluid to pass to the "roaster" or rotating kiln, where it takes fire by the burning of the already ignited contents of the kiln. The glowing mass slowly revolves, the supply of air being regulated so that combustion is complete and the black ash falls from the forward orifice, ready for lixiviation. Since the introduction of the recovery process some fifty years ago, no change, except for mechanical improvements, has been made.

This is not due to the want of schemes for the better utilisation of the organic matter in the liquor than is afforded by its mere fuel value. Indeed, the problem is a very attractive one, and many attempts have been made to obtain useful by-products and many patents have been issued covering all kinds of industries.

As a complete list of the various schemes would occupy too much space, only a brief outline of the more important uses, or proposed uses, can be described. While some little progress has been made in the utilisation of the organic matter in the black liquors abroad, there is still a tremendous amount of work to be done before the utilisation of the waste can be considered satisfactory. The quantity of the material to be handled would seem to indicate that investigation should be directed towards the production/

production of some product in large amounts at small profit, rather than the preparation of small amounts of substances, relatively high in value. While the problem of the better utilisation of the black liquor from the soda-boiling of esparto grass may appear to be of a similar nature to that of the black liquor obtained from the soda-boiling of wood, the former is the more difficult. This is due to the greater amount of inorganic constituents present in the raw material which pass into the soda solution. yes.

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<u>Precipitation of the organic matter.</u> The humic or "resinous" matter of the black liquor can be precipitated in a variety of ways, many of which have been made the subjects of patents.

When the liquor is just neutralised with an acid, a precipitate is formed, which does not settle, but remains in suspension, filling the bulk of the liquid and making it thick and viscous. When the concentration of the acid is materially increased, however, the precipitate settles out fairly rapidly, especially if, before the acid is added, an electrolyte be added or the black liquor heated. The precipitate appears as a dark, brown, resinous mass which, according to Cross & Bevan, when purified, is found to consist of a definite body, having the formula $C_{21}H_{24}O_8$.

When/

When this resinous matter is treated with chlorine a yellow coloured compound is obtained. When treated with concentrated nitric acid another yellow dye is obtained, which forms definite bodies with bases, and which has the property of dying animal fibres a bright orange colour. In addition to this dye, a yellowish-white wax separates. It sometimes happens that this wax is but imperfectly dissolved in the caustic lye and separates out if the black liquor is allowed to stand. Cross and Russell (E.P. 8268, 1908) describe a recovery process for this wax but often the quantity present is not worth the trouble.

The precipitated matter can be used as a sizing agent but its use as such is restricted to coloured papers, owing to its imparting a pink colour. Other patents propose to use it for the preparation of brown sulphur dyes, wood stains, cattle fodder and moulding powder. Not one of these uses, however, would ulitise more than a fraction of the quantity of waste produced annually, and in all of them, the soda recovery is lost in the process. That alone would militate against the use of these and similar proposals unless very valuable products could be obtained. Neverthless, despite this fact, patents, having an acid precipitation as an integral part of their processes of utilisation, are still registered.

Precipitation of the humic matter can also be effected/

effected by calcium and other salts of the alkaline earths, the calcium salts giving almost complete precipitation, the others to a less extent. This has induced many attempts to regenerate the lye and precipitate the organic matter in one operation by boiling the liquor with lime. This can be accomplished, but the recovered lye is yellow in colour and the precipitate obtained is so slimy and voluminous that its subsequent removal presents difficulties which have been found to be insurmountable.

Electrolysis of the black liquor almost suggests itself as a better way of regenerating the lye and precipitating the organic matter in one operation and several trial experiments were carried out with a spent lye obtained from S. mill. Platinum electrodes were employed and the various electrolyses were carried out at different temperatures. The results obtained were unsatisfactory, filtration difficulties again asserting themselves. The precipitate, even when obtained in a hot solution, remained in suspension for weeks and could not be removed by filtration under suction, except in very small quantities, the slimy material almost immediately choking and clogging any porous medium. The precipitate is a brown resinous substance, similar to that obtained by the addition of acid to the lye, and like it, can be converted into bright yellow bodies by the action of chlorine/

chlorine and concentrated nitric acid.

Sidler and others (G.P. 388, 791, 1922) patent a process for regenerating spent lyes by electrolysis, using anodes of copper or other highly electropositive metal.

This was tried with the black liquor under examination, and although a cleaner separation of the precipitate was obtained, the recovered matter contained, on an average, 40.5 per cent of copper and the risidual liquor was coloured a light green by copper salts.

While these results are not very encouraging it might be a profitable line for future investigation.

Carbon dioxide, when passed into the black liquor, produces a precipitate, which in dilute solutions remains in suspension and is so fine that it is almost indistinguishable from the liquid itself and passes through all ordinary filtering mediums. When the precipitation is carried out in more concentrated solutions, and especially in the presence of an electrolyte, such as sodium chloride, the precipitate is more coherent.

Rinman, in his work on the better utilisation of the black liquor from the soda-boiling of wood, describes the use of this method in his several contributions to patent literature. He claimed to precipitate the major portion of the organic matter by/

by concentrating the liquors until they contain 100 grms. of Na_2O per litre, adding sodium chloride, 50 grms. per litre, and saturating the liquid with carbon dioxide at a temperature of 75°C. The precipitate thus obtained he employs for the preparation of acetone and other valuable products while the alkali in the residual liquor is recovered by the ammonia-soda process.

Other investigators challenge Rinman's statements on the amount of matter precipitated by this method but amend their own by admitting, that with different woods, the amount of organic matter precipitated may vary considerably. Rinman, himself, found technical difficulties in the use of carbon dioxide and in a later patent (G.P. 231, 254, 1910) he modifies his original process by substituting sodium bicarbonate as the precipitating agent. It is interesting to note that the use of sodium bicarbonate as a precipitating agent was made the subject of an English patent as far back as 1889 (E.P. 5779) but its purpose in this case was the removal of the accumulated silica and alumina.

Langlet (Papierfabr. 1914, 12, 212-215) describes in a paper, the failure of Rinman's process when tried on a semi-commercial scale.

Carbon dioxide when passed into the black liquor under examination (S. Mill), under the conditions described/

described by Rinman, only threw down some twenty-seven per cent of the total organic matter. The precipitate obtained was a sticky, gummy substance which remained in suspension for several days and was only removed with great difficulty by filteration under suction. The difficulties encountered in the filtration of the precipitates obtained in the above processes are due, principally, to the slimy nature imparted to them by the high silica content of the lye.

Many other agents have been suggested as precipitants and flocculants for the organic matter in the black liquor and include bauxite, alkaline and iron oxides, sodium aluminate and zincate; two of the more recent being that of Colas and others (B.P. 218, 288 and B.P. 200, 482, 1923) giving calcium acetate as a flocculating agent and the one of Bradley & McKeefe (Can. P. 245, 851 1925) which protects the use of a basic aluminium compound used in conjunction with carbon dioxide.

Rather a unique method of precipitating the organic matter is patented by Bergius and Hägglund (G. P. 311, 933 1917); the black lye is heated under pressure to 250-300°C when the bulk of the organic constituents is precipitated as a carbonaceous deposit after a period of two hours.

Oxidation of the organic matter. Another series of proposals for the better utilisation of organic matter contained in the black liquor, deals with its oxidation into chemicals of commercial value, such as acetic, formic and oxalic acids. Processes of this type include:- the preparation of oxalic acid by treating the dry residue with concentrated nitric acid at a suitable temperature (Reed, U.S.P. 1, 217, 218, 1917); treating the lye with an oxidising agent such as hydrogen peroxide or ozone in the presence of a metallic catalyst (Küttner and Profeld, G.P. 355, 836, 1921); oxidising the matter with chlorine and air in conjunction with ferric oxide (Badische Anilin and Sodafabr. G.P. 339, 310, 1918); treating the lye with a peroxide of an alkali or alkaline earth (Küttner and Profeld, G.P. 381, 798, 1922); treating lye under pressure with chlorates, hypochlorites or salts of nitrogen oxyacids along with selected metallic catalysts (D'Ans, E.P. 217, 685, 1923) and, treating the lye in closed vessels with oxygen and steam in the presence of suitable catalysts (Deriveau and others, F.P. 563, 747, 1922).

Calcination of the spent lye. Other workers recommend processes in which calcination of the dried lye at low temperatures, to promote the formation of sodium acetate, forms the principle.

One/

One of the earliest attempts in this direction was patented by Higgins (E.P. 13, 409, 1891) who evaporated the lye to dryness and then charred the residue at 400°C, getting in this way, fifteen per cent. of anhydrous sodium acetate. These results were verified on a large scale but the process was never adopted.

Another calcination process is patented by Drewson (U.S.P. 1, 298, 478, and U.S.P. 1, 298, 481, 1917) who evaporates the lye to 1.3 s. g., incorporates caustic soda or lime and heats to 250°C, the residue being extracted with water to obtain a strong acetate solution.

Distillation of the spent lye. The destructive distillation of the concentrated black liquor appears to be the most rational plan for tackling the problem, permitting, as it does, the recovery of the soda. Patents and papers, too numerous to mention, have dealt with this method of attack, most of them operating with the black liquor obtained from the soda-boiling of wood. While several of them deal with variations of a simple low temperature carbonisation of the liquor, such as design of retort, method of the feeding the liquor etc., others describe a more complicated process. White (U.S.P. 1, 197, 983, 1916) runs the liquor into a retort previously heated to between 230°C and 370°C; Schaht (G.P. /

(G.P. 303, 053 1915 and G.P. 301, 684 1916) distils the lye in a stream of inert gas; Goodell (U.S.P. 1, 499, 363 1924) sprays the lye into a highly heated retort; Griffin (U.S.P. 1, 487, 456 1924) sprays the lye on to a horizontal cylinder, heated to 350°C; Hägglund (G.P. 400, 661, 1922) preheats the lye and distils it under pressure at 350°C; Rinman (E.P. 120, 724 1918) incorporates caustic soda or lime before distillation.

The preheating and addition of lime and caustic soda before distillation are said to promote higher yields of acetone and methyl alcohol.

Lawrence, in a communication (Met. and Chem. Eng. 1917, 16, 416-417) describes Rinman's process when applied to the spent liquor from esparto grass, working at a temperature of 255-300°C.

An interesting variation of the distillation method for the utilisation of the spent lye from esparto grass is given by Budde (J.S.C.I, 1916, 401) who incorporates an excess of nitre cake with the lye before distillation and obtains acetic acid, furpural and ammonia as the chief products. He claims that all the nitrogen present in the grass is obtained as ammonia by this method.

Moore (Paper, 1920, 25, 1157-1161) treats the liquor with salt-cake, passes it through heated coils and then sprays it into a combustion chamber to obtain/

obtain the soda as sulphide, the heat produced in the process being employed to generate steam.

While many of these variations of the distillation process have certain advantages of their own, the simple destructive distillation at low temperatures would be the best way of drawing attention to a recovery process in this country, if for no other reason than that it produces the black ash as the paper makers understand it, for the subsequent recovery of the soda. Again, distillation at low temperatures gives a better yield of products; these consist chiefly of non-condensable gases, methyl-alcohol, acetone, amines and phenolic oils. The retort residue consists of carbon and crude sodium carbonate.

Table 5 gives in detail the results of two distillations carried out on the black liquor obtained from S. Mill.

TABLE 5./

Table 6 gives the results of a similar distillation conducted under a stream of superheated steam.

It will be observed that no great difference occurs in any of the products.

Table 5.

Carbonisation of Thick Black Liquor at Low Temperatures.

Original material.

Amount taken 100 grms.

Proximate analysis	As received.	Dry.
Sodium salts	13.03	19.75
Total organic matter	48.91	74.15
Nitrogen	0.69	1.05
Water	34.04	--

Carbonisation No.1. Temperature, gradual rise from room temperature to 550 deg. C.; time. two hours for rise and half an hour at 550 deg. C.

Carbonisation No.2. Temperature, gradual rise from room temperature to 700 deg. C.; time, for rise, three hours.

Primary products	No.1.	No.2.
Uncondensible gases	7.71%	7.89%
Aqueous distillate	48.15	49.51
Tarry or resinous material	7.90	7.60
Residue	36.24	35.00

Aqueous distillate A, percentage based on original material
B, " " " aqueous distillate

	No.1.		No.2.	
	A.	B.	A.	B.
Methyl alcohol	0.76	1.58	0.72	1.45
Acetone	0.25	0.52	0.22	0.44
Acetic acid	0.12	0.25	0.102	0.20
Ammonia	0.113	0.24	0.121	0.24
Methylamine	0.067	0.14	0.094	0.19
Dimethylamine	0.234	0.48	0.175	0.35
Trimethylamine	trace	--	trace	--
Phenols (pptd. by CO_2)	0.21	0.44	0.22	0.45

Tarry or Resinous Material.

A = percentage on original material
B = " " tarry material

	No.1.		No.2.	
	A	B	A	B
Bases (acid extraction)	0.73	9.34	0.70	9.21
Tar acids (alkali extraction)	1.41	17.84	1.37	18.03
Neutral substances soluble in ether	4.36	55.28	4.05	53.30
insoluble in ether	1.40	17.72	1.48	19.47

Residue

A = as above
B = percentage on residue

	A	B	A	B
Soluble salts	28.87	79.63	28.31	80.89
(including sodium acetate)	2.74	7.56	2.56	7.13
Carbon	7.17	19.73	6.42	18.34
Ash	0.26	0.72	0.27	0.77

Distribution of the Nitrogen

A = as above
B = percentage of nitrogen

	A	B	A	B
Ammonia	0.093	13.47	0.099	14.35
Volatile amines	0.103	14.92	0.097	14.06
Non-volatile bodies + nitrogen	0.134	19.42	0.144	20.37
Residue	0.360	52.18	0.350	50.74

The aqueous distillate commences to condense in the receiver when the temperature of the furnace (measured externally) reaches 220 deg. C. when most of the water present in the lye comes over with a rush.

A yellow wax or resin commences to condense at about 310 deg. C., at 390 a black resin drops from the inlet tube and at 490 deg. C. the vapours are streaming over.

The first drops of water to condense are alkaline to litmus paper and smell strongly of the alkylamines.

Table 6.

Under Superheated Steam.

Products		
	Gas	9.5 litres
	Aq. distillate	--
	Resins	7.8 grms
	Residue	33.0 "

Aq. Distillate	
Acetone	0.21
Methyl alcohol	---
Ammonia	0.112
Methylamine	0.145
Dimethylamine	0.167
Trimethylamine	trace
Phenols pptd. by CO_2	0.2

Residue	
Nitrogen	0.25
As per cent. of O.M.	
" " of residue	0.75
" " of nitrogen in O.M.	36.22

Distribution of Nitrogen	As per cent of O.M.	As per cent of N.
As ammonia	0.092	13.34%
" Vol. amines	0.118	17.10
" Non-vol. subs.+ Nitrogen.	0.230	33.34
In residue	0.250	36.22

Time - one hour for rise from room temperature to 550 deg. C. and one hour at 550 deg. C.

Steam pressure - approx. 1/4 lb. per sq. in.; just sufficient to prevent blowing back of the vapours into generator. Gasometer kept under slight suction.

O.M. = original material.

Unfortunately, the small amounts of the numerous products obtained in the aqueous distillate, the tedious process of their separation, and the complex character of the waxy or "resinous" portion of the distillate, do not help to commend the ordinary distillation to the paper maker as a solution to the problem. If the relatively large yield of resinous substances could be broken down to give simple compounds, which would have a commercial value, this solution might assume a different aspect.

The simplest method by which this could be accomplished would be a modified "cracking" and reduction of the hot vapours as they issue from the retort, a process similar to these recommended for the reduction of the higher phenols and hydrocarbons obtained from the low temperature distillation of coals and shales.

With this object in view a series of trial experiments were carried out, successive quantities of the lye being distilled in a stream of superheated steam and the mixed vapours led through an iron reaction chamber filled with a reacting substance.

The use of the superheated steam is two-fold; it acted as a carrier for the vapours and prevented premature "cracking" in the retort and connecting tubes, and supplied hydrogen in the chamber by interaction with the substances contained therein.

These/

These substances consisted of coke, iron turnings and carbon, activated carbon, alumina and activated carbon, and a mixture of calcium silicate, clay and carbon. At fairly high temperatures 550-700 C. the organic matter split into gas and carbon, the latter collecting in the reaction chamber. At low temperatures 400-450°C. no change in the resinous substances, except a diminished yield, could be obtained.

While the results obtained in these trial experiments are disappointing, this is a field of investigation which may yield profitable results with further work.

The latest process for the treatment of the black liquor obtained from the soda-boiling of wood, due to C.L. Wagner, is being exploited by the Ross Engineering Corporation of New York and is now being tested at a Mill at Muskegon, Michigan. The process, described in an article by F.E. Coombs (Chem. and Met. Eng., July 1927) consists of atomising the liquid and burning it in a preheated retort or furnace, one portion of the heat produced being employed to concentrate the liquor in another apparatus.

The tests showed that the heat liberated by the combustion of the atomised liquid was considerably in excess of that required to concentrate the liquor from 1.067 s.g. up to 1.332 s.g. in multiple effect evaporators./

evaporators. The tests also proved that it was possible by this to raise a large amount of steam which could be applied to other purposes, and, at the same time, to supply 500 gallons of the concentrated liquor, per hour, for the combustion furnace.

WASTE HEAT FROM ROASTER.

The "roaster" is the apparatus wherein the thick black liquor is incinerated to convert the sodium compounds into crude soda ash. It consists of a rotating kiln, similar in type to these employed by cement manufacturers, running on iron rollers and having a slight inclination from the inlet to the outlet. The thick black liquor enters at the rear of the roaster and the black ash, ready for lixiviation, falls out of the forward opening.

The hot gases from the kiln are generally led away, through brick flues, and discharged into the boiler house chimney. These hot gases constitute a great waste of heat and while this is not a waste product in the strict sense of the term, it is a waste that mill-owners would do well to utilise and economise on their coal bill.

Table 7 gives the data obtained on two recovery plants and illustrates the amount of heat available

Table 7.

Temperature, Draught, Volume of Gases and Amount of Heat available at two Soda Recovery Plants.

Gas Temperatures	L. Mill 1 Kiln Plant	T. Mill 2 Kiln Plant
Average	1,100 - 1,450°F.	1,100 - 1,380°F.
Mean	1,275°F.	1.214°F.
Draught		
Average	0.05 - 0.15 in.	2.2 - 3.2 in
Mean	0.1 in.	2.7 in.
Average Gas Analysis, percentage by volume.		
Carbon dioxide	15.24	9.09
Carbon monoxide	0.48	--
Oxygen	--	6.61
Nitrogen	79.00	79.00
Water vapour	5.28	3.30
Mean Specific Heat.		
Moist Gas	0.2460	0.2437
Volume of Gases		
Cubic feet per Hour	110,000	1,126,000
Total Heat Available		
B.T.U. per Hour	2,970,000	7,826,000
Pounds of Steam available per hour at 30 lb. pressure per sq. in. assuming a feed-water temperature of 150 deg. F. and boiler efficiency of 75 per cent.	2113	5564

The gas temperatures were very steady the variation recorded being due to alteration in the gravity of the feeding syrup; in number two this varied from about 44 deg. to 52 deg. Tw. The percentage of carbon dioxide in the gases also varies a great deal, in number two the variation was from 5.2 to 14 per cent.

These figures relate to the gases leaving the roaster flue and will apply to the gases entering a proposed waste-heat boiler etc., so long as the connecting flue is maintained in good condition.

WASTE CARBON.

This material, waste carbon or black ash waste, remains in the leaching tanks at the end of the washing operations, when all the sodium carbonate has been removed from the black ash. It consists of a light porous carbon, generally contaminated with varying small amounts of impurities; occasionally, these impurities reach a high figure (See Table 10). The amount of the waste material produced depends on the practice in vogue at the mill; if the black ash is lixiviated immediately it leaves the roaster, the waste carbon may amount to several tons per week, if, however, the bulk of the carbon is allowed to burn away by placing the product of the roaster on specially constructed floors, the amount produced is comparatively small.

Table 8 gives some indication of the differences found in the two ashes prior to lixiviation.

TABLE 8. /

TABLE 8.

Recovered Soda Ash.

As received.

	Before burning off.		After burning off	
Hypothetical Combination.	K.1.	M.1.	S.1.	L.1.
Sodium carbonate	62.95	64.04	75.20	73.48
Sodium chloride	8.95	7.88	10.28	9.51
Sodium sulphate	2.21	1.98	2.38	3.82
Sodium silicate	3.47	4.21	5.11	5.25
Sodium phosphate	trace	do.	do.	do.
Sodium sulphide	trace	0.22	-	-
Aluminium and Ferric oxides	0.52	0.45	0.65	0.66
Carbon	21.48	20.91	3.75	4.52
Other constituents	0.42	0.30	0.33	0.70
Moisture	-	-	2.30	2.06

Tables 9 and 10 give the results of analyses of several samples of black ash waste. The three samples given in Table 9 were drawn from K. Mill, at intervals of a month; the results show that the total amount of impurities does not vary to a great extent.

The two samples analysed in Table 10 were taken from S. Mill and serve to demonstrate the amount of impurities gathered, and the amount of soda left in waste carbons obtained from a badly conducted mill.

TABLE 9.

TABLE 10.

TABLE 9.

Waste Carbon, K. Mill.

Results expressed as percentage of dry material.

Analysis.	No.1	No.2	No.3
Sodium oxide	2.88	2.00	2.81
Calcium oxide	0.32	0.14	trace
Ferric oxide	0.23	1.76	0.12
Aluminium oxide	0.04	0.98	0.46
Magnesium oxide	0.04	0.07	-
Carbon dioxide	1.16	0.53	0.54
Silicon dioxide	0.32	0.67	0.58
Sulphur trioxide	1.32	1.73	1.45
Chlorine	0.25	0.16	0.43
Carbon	93.42	91.99	93.50

Hypothetical Combination.			
Sodium carbonate	2.19	1.01	1.31
Sodium chlorate	0.41	0.27	0.70
Sodium sulphate	2.33	3.07	2.64
Sodium silicate	0.65	-	1.17
Calcium carbonate	0.57	0.25	trace
Ferric oxide	0.23	1.76	0.12
Aluminium oxide	0.04	0.98	0.46
Silica (free)	-	0.67	-
Carbon	93.42	91.99	93.50
Other constituents	0.16	0.07	0.11
Moisture in original material	77.73	58.53	75.28

K. Mill: Eighty to ninety tons per week of wet carbon is the average production from this mill.

TABLE 10.

Waste Carbon, S. Mill.

Results expressed on dry material.

	As Received.		Washed.	
Analysis.	No.1	No.2	No.1	No.2
Sodium oxide	27.55	19.12	3.25	2.84
Calcium oxide	0.13	0.51	0.31	0.90
Ferric oxide	3.50	2.06	5.59	2.35
Aluminium oxide	0.93	3.60	1.06	6.56
Magnesium oxide	trace	0.18	0.20	0.23
Carbon dioxide	14.52	10.89	0.61	0.86
Silicon dioxide	1.26	11.09	0.85	14.37
Sulphur trioxide	3.52	2.85	2.04	2.08
Chlorine	3.65	1.91	0.12	0.22
Carbon	45.46	46.15	85.67	69.86
Hypothetical Combination.				
Sodium carbonate	34.75	25.30	1.13	0.37
Sodium chloride	6.02	5.06	0.25	0.36
Sodium sulphate	6.25	5.06	3.62	3.69
Sodium silicate	2.56	0.82	1.73	0.68
Calcium carbonate	0.23	0.91	0.55	1.61
Ferric oxide	3.50	2.06	5.59	2.35
Aluminium oxide	0.93	3.60	1.06	6.56
Silica (free)	-	10.69	-	14.04
Carbon	45.46	46.15	85.67	69.86
Other constituents	0.30	0.35	0.40	0.48
Moisture in original material	71.03	64.91		

No.1 is the carbon left in the cage at the top of the tank where the crude soda ash is placed for lixiviation.
No.2 is the carbon which falls to the bottom of the tanks during the boiling operation.
The "as received" basis represents the carbons when obtained from the mill, and "washed" what the analysis should be if the two samples had been properly washed before being dumped.

Because of its physical condition, it is very difficult to remove the water it contains by purely mechanical means. When removed from the leaching tank in which it has been allowed to drain, the carbon still contains about 75 per cent. of water, and, even when centrifugal force has been applied, the percentage of water seldom falls below 50 per cent., beyond this point the application of heat is necessary.

Grinding the wet material or pressing it in a high powered press materially aids subsequent drying.

Although a few patents have dealt with this material, no practical use has been found for this waste up to the present. It has been suggested that a promising field appears to be as a fuel, as its calorific value, when fairly free from impurities, is in/

in the region of 14,500 B.T.Us. Several mills have tried it as such but discontinued the practice when they found the material blew into the flues and choked the tubes of marine boilers when these composed the steam raising plant. A more successful method of making use of it as a fuel would be to grind the wet material and treat it alone, or better still, in admixture with the waste cellulosic sludge from the paper machine, in a flotation apparatus, employing tar as the flocculating and binding agent, and moulding the resulting mixture into briquettes.

The most satisfactory method of using this waste material, however, and especially in this country, where the amount produced by any one mill is relatively small, would be as an active and decolorising carbon. The nature of the original material and the mode of formation of the carbon, suggested that it could be employed as such and the following tables of experimental data demonstrate the realisation of this expectation, and illustrate its efficacy when compared with other carbons.

As it is difficult to determine the relative values of different carbons by means of solutions of dyes and caramel, the method chosen, with slight modification, was that of Firth (Trans. Farady Soc. 1921, 16, 474) who employed a chloroformic solution of/

of iodine to determine the combined adsorption and absorption of a carbon, which he termed the "sorption" value.

Experimental details:- half a gram of the carbon to be tested, ground to pass a 60 mesh sieve, was placed in a stoppered, glass bottle and 25 c.c. of a decinormal solution of iodine in chloroform run in. (The chloroform was previously dried over calcium chloride for several days). The bottle was then shaken for ten minutes at 25°C., allowed to stand for one minute and the supernatant liquid rapidly decanted through a plug of glass wool into a measuring tube. An aliquot portion was then run into a flask, about 50 c.c. of water added, and the residual iodine titrated with decinormal sodium thiosulphate solution. From this result the amount of iodine "sorbed" by the carbon was calculated.

The heating of the various carbons was carried out in a Lessing furnace, the carbon to be tested being placed in a silica tube which was then inserted into one of the two holes in the upper plate of the furnace, temperature control being gained by a pyrometer inserted into the remaining hole.

The following tables of experimental data are almost self-explanatory; the first series of three columns/

columns gives the results obtained on the original carbons which have been carefully washed with water until free from residual alkali. The second series gives the results obtained when the carbons had been boiled in strong hydrochloric acid. The first column in each series is occupied with results given by the dry material, the other two with the results given after the carbons had been heated to the temperatures stated. These temperatures are the ones usually employed for the preparation of activated carbons.

The second part of the table gives the results obtained when (a) the time of heating is increased and (b) when the heating is conducted in different atmospheres.

TABLE 11./

TABLE 11.

Iodine or "Sorption" Value.

Results expressed as grms. of iodine "sorbed" per grm. of carbon.

arbon	Boiled in distilled water and washed with hot water.			Boiled in strong HCl and washed with hot water.		
	Dry Mater-ial.	Heated to 600° C. 15m.	Heated to 900° C. 15m.	Dry Mater-ial.	Heated to 600° C. 15m.	Heated to 900° C. 15m.
.1.	.1851	.3178	.3723	.1530	.3478	.3868
.2.	.1343	.3105	.3746	.1222	.3485	.4061
.3.	.1316	.3103	.3768	.2152	.3797	.4145
.1.	.2671*	.3744*	.4745*	.2114	.2937	.4461
.2.	.1985*	.3077*	.3854*	.1821	.2220	.3498

.3. with increase of time - temp. 600°C. (acid treated)

Time:-	15 mins.	30 mins.	1 hour	2 hours
	.3797	.4088	.4178	.4117

.3. Time 1 hour, temperature 600°C. in:-

Superheated Steam	Carbon Dioxide	Carbon Dioxide (reduced pressure.)
.4052	.4030	.4182

These figures should be accepted with a certain amount of reserve, the high values probably being due, in part, to chemical action of the ash.

Table 12 gives the results obtained from a few commercial carbons and on ordinary bone ash.

TABLE 12.

Iodine values of various carbons for comparison.

1. Animal charcoal (University supply)
2. Klarite (University supply) prepared from sugar residues. Moisture 4.98 - Ash, as recd. 0.19. dry 0.20.
3. Special gas absorption and decolorising carbon, obtained from British Drug Houses. Moisture 19.99 Ash, as recd. 16.99, dry 2.00
4. Suchar (superfiltchar) Prepared by Suchar Engineering Ltd., Vegetable carbon used in neutral solution for refining sugar. Moisture, 15.14 Ash, as recd. 2.51. Dry, 2.96.

Results expressed as grms. of iodine "sorbed" per grm. of carbon from N/10 solution of iodine in dried chloroform.

Animal Charcoal	as recd.	.0378	Heated to 900°C.	.0475
Klarite	-	.050	Dried	.050
B.D.H. Carbon	-	.2578	-	.3134
Suchar	-	.3107	-	.3132

The figure obtained for the B.D.H. carbon on the "as recd." basis agrees with the one obtained by calculation from the dry material, but they do not agree in the case of Suchar; the above figures are the averages of several tests.

The catalytic values of the various carbons were next determined, the method again being due to Firth (J.S.C.I. 1923, 22, 242).

Experimental details:- one gram of the powdered carbon was carefully weighed into a small round-bottomed flask; 25 c.c. of hydrogen peroxide solution was measured out into a flat bottomed tube and the tube placed inside the flask. The flask was then connected with a gas burette and quickly tilted, thereby causing the hydrogen peroxide to come into contact with the carbon. Accumulation of gas in the liquid was prevented by rapid agitation. The experiments were carried out at room temperature, 61°F. A blank experiment with hydrogen peroxide alone yielded .30 c.c. of oxygen in three hours for No.1 solution and .36 c.c. of oxygen for No.2 solution. The two solutions were employed to determine if the same ratio of difference in the values given by the various carbons would be preserved with different strengths; it will be observed that, with the exception of the B.P.H. carbon, no material difference occurred.

TABLE 13. /

TABLE 13.

Catalytic activity.

(Volumes of oxygen liberated from a solution of H_2O_2)

K.3. water washed.

	No.1 sol. of hydrogen peroxide			No.2 sol. of hydrogen peroxide		
	dry material	heated to 600 deg.C.	heated to 900 deg.C.	dry material	heated to 900 deg.C.	htd. to 900 d.C.
1 min.	10.3 c.c.	38.6 c.c.	74.1 c.c.	18.9 c.c.	61.6 c.c.	92.2
2 -	17.5	55.6	111.6	27.6	87.7	143.5
3 -	22.8	66.3	140.9	34.4	109.2	184.4
4 -	25.9	74.9	168.4	40.2	124.3	212.7
5 -	29.1	85.4	195.7	44.6	137.9	233.5

K.3. acid treated.

	dry material	heated 600 deg.C.	heated to 900 deg.C.	dry material	heated to 600 deg.C.	heated 900 d.C.
1 min.	12.5	36.4	93.3	23.0	58.0	117.4
2 -	20.6	54.6	142.3	32.5	86.1	182.9
3 -	26.4	66.7	177.1	39.9	110.0	231.7
4 -	29.5	77.0	216.0	45.8	127.9	272.8
5 -	33.5	88.9	240.4	50.9	143.6	287.0

For comparison.

	Suchar dried	heated 600 deg.C.	B.D.H. dried	Suchar dried	heated to 600 deg.C.	B.D.H. dried
1.min.	9.5	18.7	14.8	9.7	24.3	12.7
2 -	11.6	24.0	18.7	11.6	33.2	20.3
3 -	12.2	29.1	24.0	13.3	41.2	27.0
4 -	12.7	32.9	28.4	14.6	47.1	33.6
5 -	13.4	36.6	32.6	16.1	52.1	41.2

No.1 solution of hydrogen peroxide contained 218 volumes of oxygen per 25 c.c. at N.T.P.

No.2 solution of hydrogen peroxide contained 410 volumes of oxygen per 25 c.c. at N.T.O.

The samples of Suchar and B.D.H. carbons were dried at 100 deg. C. before being tested.

Firth, in his paper on the activity of sugar carbons, points out that the "sorption" or iodine value may also be taken as a measure of the catalytic activity and his results support this view. (Table 14 is taken from Firth's paper.) With the waste carbons, however, it will be observed that the catalytic activity is very much greater than that which would be assumed from the "sorption" value.

TABLE 14./

TABLE 14.

The sorption activity of carbon.

(Firth Trans. J.S.C.I. 1923,22, 242).

Sorption activity
Iodine sorbed per gram of carbon.

Time	1.	2.	3.
5 min.	0.3549	0.3789	0.4359
30 -	0.3604	0.3875	0.4437
2 hrs.	0.3701	0.3967	0.4513
24 -	0.3785	0.4689	0.4689

Catalytic Activity.
Volumes of oxygen in c.c. corrected to N.T.P.

Time	1.	2.	3.
3 min.	0.28	2.2	9.1
9 -	0.85	4.6	17.2
18 -	1.15	7.5	25.3
54 -	1.40	12.15	42.5
108 -	1.59	17.4	56.8
172 -	1.70	20.7	61.8
216 -	1.70	22.3	66.2
24 hr.	1.80	25.1	85.8

No.1 - Cane sugar carbonised in a crucible at as low a temperature as possible. The resulting carbon was finely powdered, digested with conc. hydrochloric acid, washed with water and finally boiled with water until free from chloride. The carbon was then dried at 120 deg.C., allowed to cool and 0.5 gm. treated with the iodine solution.

No.2 - Carbon as in (1) heated in a quartz flask in a vacuum for two hours at 600 deg.C. and when cool treated with iodine solution as before.

No.3 - Carbon as in (1) heated in a quartz flask in a vacuum for two hours at 900 deg.C. and then treated as in previous experiments.

In order to ascertain if the decolorising value of the carbon could be raised by increasing certain of the impurities present in the lye, or by carbonising the lye in a closed retort, the following experiments were carried out, the results being given in Table 15, (A & B).

Section A. Some of the original lye was carbonised in a crucible placed in an electric furnace, the vapours being allowed to disengage freely and ignite, a process analagous to that occurring in the roaster.

Selected impurities were then incorporated into different weighed portions of the lye and the mixtures carbonised in a similar manner. All the carbonaceous residues were then ground to pass a 60 mesh sieve, boiled with water until free from soluble matter and the residue filtered off. Each residue was then boiled with successive quantities of strong hydrochloric acid until all the soluble matter had been removed, washed with water until free from chloride and dried. Two portions of the dry material were then treated in a Lessing furnace at 600° and 900°C respectively, cooled, and all three carbons tested in the usual manner.

Section B. The lye was placed in a sheet iron sleeve which fitted into a small, horizontal, iron retort. The retort was then placed in a suitable furnace and

the/

the contents carbonised at the temperatures stated in the table.

The residues from the carbonisations were treated in a similar manner to these obtained in the open carbonisations.

The impurities selected for incorporation with the lye in the first series of experiments are said to promote activity in the carbons and many of them have been quoted in patents.

<u>TABLE</u> 15A.

<u>TABLE</u> 15B.

Table 15.

Carbonisation of Spent Lye.

"Sorption" Value

Table A.

	Dry Material	Heated to 600°C. for 15 mins.	Heated to 900°C. for 15 mins.
Original material	.0950	.3462	.3602
Substance added.			
Calcium oxide (as Milk of Lime)	.2168	.2954	.3283
Calcium carbonate	.1861	.3472	.3694
Silica	.0824	.2465	.2808
Ferric oxide	.0639	.3457	.3682
Calcium phosphate	.1693	.3325	.3477

Table B.

Original material.

Time 3.5 hours Temp. Room to 550°C.	.1118	.2506	.0496
Time 2 hours Temp. Room to 550°C.	.0769	.1604	.0410
Time 3 hours Temp. Room to 700°C.	.0623	.2657	.0799
Repeat No.2 In stream of superheated steam.	.2089	.3757	.1619

The impurities were added in the proportion of six grms. to 100 grms. of the lye.

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It will be noted that the only carbons which give "sorption" values approaching these of the mill waste carbons are 1, 3 and 5 while the values obtained for the carbons from the retort carbonisations are exceedingly small. No one, however, is superior in value to the waste carbons and this would seem to indicate that the ordinary mill process produces the best carbon.

A point in favour of the heat treated waste carbons is that they settle very rapidly from liquids, organic or inorganic, when agitation is stopped. It is also interesting to note that while there appears to be no great physical difference in the two carbons obtained from the different processes, i.e. plants lixiviating the black ash immediately it leaves the roaster, and plants leaving it to burn out before lixiviation, the carbon from the latter method appears to crumble less easily than that obtained from the former. It retains its lumpy form through acid and heat treatment, a point in favour of its use as a gas absorbent.

When boiled with strong hydrochloric acid and washed with water the carbon waste can be obtained in a very pure state. Table 16 gives carbon No.3 from K. mill after acid treatment.

TABLE 16./

Table 16.

Silica	0.34%
Ferric oxide	0.27%
Sodium chloride	0.85%
Carbon	98.54%

Some of the industrial uses of alkali activated carbons are as follows:-

Decolorising in acid solutions.

Decolorising in neutral solutions after acid treatment (boiled in acid of suitable strength, washed with water until free of acid, and then dried and heated to some temperature in the vicinity of 600 or 900 deg. C.)

Gas absorption - recovery of gases and vapours of low concentration, as in the recovery of gasoline from natural gas or solvent vapours from the air.

Purification of gases, as helium, carbon dioxide, hydrogen, ammonia etc.

The catalysis of gas reactions - the oxidation of hydrogen sulphide or nitric oxide; or the chlorination of hydrocarbons, or the catalysis of the reactions between a gas and a liquid generally.

The storage of compressed gases, the capacity of a cylinder of compressed fixed gas being increased by putting highly active carbon in it.

The evacuation of vessels

The reduction of metallic salts - gold and silver.

It/

It may be of interest to add that several patents have been taken out and several papers published in Amercia, within the last two or three years, dealing with the waste carbons obtained from the black lye of the soda-pulp mills, and its use as a decolorising carbon and as a pulverised fuel. Several of the patents register the ordinary mill practice for the production of an activated carbon. McKee and Horton (Chem. & Met. Eng. 1925, 12, 56-59) describe the use of the carbon for decolorising purposes. Jacobs (U.S.P. 1, 623, 598, 1927) protects the ordinary process of incineration of the black liquor to produce an active carbon. U.S.P. 1, 500, 265, 1924 deals with the use of the waste carbon as a pulverised fuel, the specific of the patent being the reduction of the cohesion between the carbon and water by grinding the wet material and so facilitate subsequent drying.

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chalk

WASTE LIME FROM CAUSTICISING PLANT.

(Mud or Sludge).

This material, the product of the interaction of the recovered soda ash solution with caustic lime, in the process of regenerating the lye, is another waste product from the subsidiary plant. It will be observed from the following tables of analyses that the material consists chiefly of calcium carbonate and water, along with varying small amounts of free lime, sodium hydroxide and carbonate, carbon and other impurities, gathered and transferred by the soda and, or, originally present in the caustic lime.

These variations are due largely to the different methods employed for the recovery of the lye; in some mills the process is carried out in an extremely crude manner, while in others, the work is accomplished with greater care and better appliances. Again, in crude samples the moisture may be well over fifty per cent., but in samples which have been well drained, or treated in a vacuum filtering pond, the moisture is considerably less than this figure.

Concurrently with the variation in certain of the constituents and of the water content, the appearance of the sludge varies greatly. In some mills/

mills the waste is dumped as a grey, sometimes almost black, occasionally evil smelling, (due to the high per cent of carbon and incomplete combustion of the organic matter in the spent lye), slimy mud. In well conducted mills, however, the waste product is perfectly white appearance and has very small percentages of residual soda and carbon. Table 17 gives the results of analysis of samples drawn from a badly conducted mill. The waste from this mill is dirty slate grey colour and very slimy and caustic to handle.

TABLE 17./

TABLE 17.

Sludge (Waste Calcium Carbonate) from Causticiser.

S. Mill.

Over period of six months.

Analysis on Material dried at 100°C.

	No.1	No.2	No.3	No.4	No.5	No.6
Calcium oxide	51.09	51.17	49.49	48.75	48.05	48.81
Sodium oxide	1.74	2.70	1.57	3.32	3.65	3.01
Potassium oxide	0.16	0.23	0.12	0.32	0.34	0.25
Magnesium oxide	0.45	0.47	0.66	0.24	0.56	0.49
Aluminium oxide	0.95	0.66	0.67	0.48	0.71	0.80
Ferric oxide	0.19	0.07	0.12	0.13	0.16	0.15
Manganese oxide	trace	do.	do.	do.	do.	do.
Carbon dioxide	36.64	36.64	37.64	37.23	37.41	37.45
Silicon dioxide	2.67	2.11	2.98	2.72	3.01	2.25
Phosphorus pentoxide	0.15	0.17	0.15	0.14	0.14	0.09
Sulphur trioxide	trace	do.	do.	do.	0.06	0.04
Chlorine	0.15	0.23	0.18	trace	0.25	0.21
Carbon	3.37	2.43	4.47	3.06	3.27	2.59
Hypothetical Combination.						
Calcium carbonate	82.54	82.19	84.91	83.29	83.55	83.91
Calcium hydroxide	5.57	5.65	2.02	1.71	2.39	2.44
Sodium carbonate	0.74	1.15	0.67	1.42	1.56	1.28
Sodium hydroxide	1.69	2.62	1.52	3.21	3.51	2.90
Other constituents	9.30	8.39	10.88	10.37	8.99	9.47
Moisture in Original Material	50.86	48.46	47.65	43.80	52.56	49.54

Table 17 gives the results of analysis of samples drawn from a mill producing a white sludge.

TABLE 18.

K. Mill.

Analysis on Material dried at 100 deg. C.

	Causticisers.				Bing.	
	No.1	No.2	No.3	No.4	No.5	No.6
Calcium oxide	51.42	51.95	50.76	53.23	52.47	51.91
Sodium oxide	1.27	1.21	*3.04	0.61	0.57	0.57
Potassium oxide	0.09	0.13	0.26	0.05	0.03	0.04
Magnesium oxide	0.45	0.65	0.64	0.51	0.70	0.59
Aluminium oxide	0.65	0.72	0.56	0.79	0.67	0.67
Ferric oxide	0.12	0.09	0.05	0.13	0.14	0.14
Manganese oxide	trace	do.	do.	do.	do.	do.
Carbon dioxide	38.51	38.92	38.25	38.73	38.73	39.06
Silicon dioxide	2.72	2.58	2.55	2.41	3.45	3.16
Phosphorus pentoxide	0.09	0.12	0.07	0.16	0.13	0.12
Sulphur trioxide	trace	trace	nil	nil	nil	trace
Chlorine	0.25	0.18	0.10	trace	trace	trace
Carbon	1.25	1.13	1.65	1.12	1.20	1.32
Hypothetical Combination.						
Calcium Carbonate	87.80	88.02	85.70	87.78	87.80	88.56
Calcium hydroxide	2.28	3.01	2.89	4.98	3.95	2.83
Sodium carbonate	1.18	0.53	1.30	0.16	0.24	0.24
Sodium hydroxide	0.89	1.14	2.94	0.59	0.55	0.53
Other constituents	7.55	7.30	9.15	6.49	7.46	7.84
Moisture in Original Material	35.86	36.35	43.80	42.71	37.65	36.28

*Taken during coal strike, when the mill was working under difficulties and could not carry out their washing procedure as usual.

Generally this material is a waste product, although occasionally small amounts are disposed of locally to fill hollows, to farmers for agricultural purposes, and more rarely, to glass bottle manufacturers. The usual practice, except where the mill is in the fortunate position of being able to tip their sludge into an adjacent water course, is to dump the waste on to some convenient piece of waste ground. When it is considered that for every ton of caustic lime used a mill produces nearly two tons of waste material (calculated dry) it will be realised that the effective disposal of the accumulating bings in the vicinity of the majority of paper mills, is rapidly becoming an acute problem. Indeed, in some cases, the problem has become so acute, that certain mills have been compelled to close down their causticising plant and to purchase commercial caustic soda, while selling their recovered soda to more favourably situated concerns.

Attempts at reburning the waste lime have been tried and a few mills are said to have plants operating with a fair amount of success. In order to keep the impurities down to a reasonable figure, however, it is found advisable to renew from ten to fifteen per cent of the spent material with fresh lime every circuit.

The recovered lime is usually obtained in

rounded/

rounded nodules, ranging in size from very small pieces to lumps the size of a hen's egg. It is coloured a light green and slakes more slowly than fresh lime.

Excepting the recovery process, the most feasible use for this waste lime in bulk appears to be the increase of its use as a dressing for lime-lean soils. Prof. Hendrich of Aberdeen University has carried out a great amount of experimental work in this connection and has published several papers dealing with the success which has attended his efforts. (Hendrich, Trans. J.S.C.l. 1914,122, Trans. High and Ag. Soc. 1914, 1916, 1918, 1923).

His experiments were carried out on various soils, some having a very unenviable reputation for raising badly diseased turnips. He gives tables of experimental data obtained on tests carried out with gas, shell and waste lime, and points out the remarkable success of the latter material, which was obtained from paper mills in the vicinity. In every case the liming greatly increased the amount of crop and in the case of shell lime and paper works lime greatly diminished the amount of disease, the plot dressed with paper works lime being almost entirely free from badly diseased roots. One sample of waste lime gave a better result, both as to weight of crop and as to diminution of disease, and it is interesting to/

to note that this lime had as much as 4.37 per cent (as NaOH) of soda present. This indicates that the presence of soda was not injurious, although there had been some hesitation in using a lime with so high a percentage of soda present.

To this he adds (private communication) that any amount of sodium carbonate found in the by-product lime from paper mills was found to have no injurious effect upon vegetation, even when the lime was applied at the rate of eight tons per acre dried, or sixteen tons per acre in the moist condition, taken directly from the dump heaps. No evil effect upon the texture of the soil was noted even when large quantities of waste lime were used. Further, although the experiments quoted were carried out on non-clay soils, no bad effects are to be expected when the lime is placed on clay soils, because, although soda will produce a deflocculating action, lime, on the other hand, flocculates the soil and the waste lime never contains more than a comparatively small percentage of soda mixed with a large percentage of lime.

In the course of his first paper, Prof. Hendrich also draws attention to the following points of interest. Several paper mills have offered for years this waste product, free of charge, to farmers, but in no case has any substantial quantity been taken. The objection seems to be that it is sticky and/

and difficult to spread when wet. Moreover, farmers are unfamiliar with it and doubt if it is of any real value at all. He adds that it is quite possible to use it in an undried state and much could be utilised in the vicinity of the mills, but, when the ground to be dressed is some distance away, it would be better to dry it, as it is easily dried by artificial means.

While one can hardly dispute any of the remarks above, it seems unfortunate that the mill owners themselves do not help to better the utilisation of the waste lime in this, and in other directions, by the production of a cleaner sludge, especially when many of them purchase a very pure caustic lime, (see Table 19).

Yes Jgk

Certainly, no farmer, or any other potential user of the waste, could be expected to look with favour upon the dirty, slimy caustic material produced by many of the mills.

TABLE 19.

Caustic Lime.

S. Mill.

Calcium oxide	99.010%
Magnesia	0.607%
Alumina	0.060%
Ferric oxide	0.100%
Sulphuric anhydride	0.172%
Phosphoric anhydride	0.008%
Silica	0.220%
	100.177%

An excellent use for the spent lime, although in this case, restricted to waste material which is white or nearly white, and containing only small amounts of alkaline salts, would be as a stone-dusting material for dry mines. At the request of Prof. Briggs, Heriot-Watt College, an examination of the white sludge from K. Mill was carried out with this object in view. The results secured were very satisfactory. In fact, the material provides an excellent and cheap substitute for precipitated calcium carbonate, which is regarded as the nearest approach to the ideal dusting material, satisfying, as it does, all the factors which determine the choice of such a material. Ground limestone, even when reduced to a seeming, impalpable powder, retains its crystalline character. The sludge, in contrast, being a precipitated product, possesses an amorphous and porous structure and, therefore, a greater heat absorbing surface.

cost of transport is the main objection: the quantity available is small

It is white, easily dried by artificial means, absorbs very little moisture on exposure to ordinary atmospheric conditions (Table 20) and flies up easily to form clouds when disturbed.

TABLE 20./

TABLE 20.

Absorption of Carbon Dioxide and Moisture on Exposure.

Material dried at 100 deg. C. and spread to give maximum surface. Results expressed as percentage of original material.

Day.	Gain or Loss in Wt.	Total Gain.	Moisture Content.
1.	Gain	-	-
2.	- 1.48	1.48	0.68
3.	- 0.23	1.71	0.79
4.	- 0.06	1.76	0.81
5.	- 0.09	1.85	0.86
6.	- 0.11	1.96	0.91
7.	Loss 0.06	1.90	0.88
8.	- 0.02	1.88	0.87

The only deleterious element present is the caustic soda, the percentage of which, in the samples obtained from the bing, could not be detected by taste.

It will be observed from the mesh analysis table that the fineness of this waste easily conforms to the specification laid down for stone dusting materials (50% by weight of the dusting material when dry should pass a sieve with 200 meshes to the linear inch - 40,000 to the sq. in.)

TABLE 21./

TABLE 21.

Mesh Analysis.

1. Material dried at 100 deg. C.

Mesh Number.	Grms. Retained.	Grms. Through.
50	2.63	97.37
100	2.18	95.19
150	1.93	93.26
200	1.55	91.71

2. Material dried at 250 deg. C.

Mesh Number.	Grms. Retained.	Grms. Through.
50	1.24	96.76
100	2.86	95.90
150	2.95	92.95
200	3.15	89.90

Although it was thought that the small percentages of caustic soda and lime found in wastes suitable for the dusting of mines, would have no evil physiological effect, provided they were carbonated, a sample of the material was forwarded to Dr Haldane, the physiologist, by Prof. Briggs, with a request for his opinion on this point. His reply endorsed the view taken above, - that the material would be safe and suitable if all the caustic present is converted to carbonate. yes

The material is very easily dried by the application of heat and this could be easily and cheaply/

cheaply accomplished by spreading it out on top of wide flues or other suitable places. Where, however, this is not practicable, or, when its subsequent use makes it necessary to carbonate any caustic present, and the drying has to be done by a kiln, the cost of drying may provide thought for consideration.

Table 22 gives some idea of these drying costs but these figures can only be taken relatively, as the first three items depend on local conditions.

TABLE 22.

Drying Costs.

(From the plant of the Fusion Corporation.)

	£	s.	d.
Cost of process labour per ton of finished material	-	4	1
Cost of power per ton of finished material	-	-	6.3
Cost of fuel per ton of finished material	-	2	8.75
Oil, Stores, Repairs & Depreciation	-	-	11.75
Works cost per dry ton (naked)	£-	8	3.80

In the event of boiler flue or other sufficiently hot gases being available, item 3 "Cost of Fuel" would be eliminated. Further, in the event of the plant being, say, double the above capacity, the labour would only be increased by about 30 per cent.

These figures are based upon a plant having an output of 60 tons per week of "finished" material, the raw material containing 40% water. The plant of of the rotating type, the hot gases from the fire grate passing through the centre of the tube; the carbon dioxide in the latter converting any hydroxide into carbonate, It is simple in operation and capable of being worked by unskilled labour.

Another excellent outlet for this waste lime would be for the neutralisation of acid effluents, such as pickling acid and acid mine waters. Although, in a number of cases, caustic lime is preferred, the fine diversion of the waste material makes it an excellent substitute, especially when a paper mill is in the near vicinity, and it could be had at very little cost.

Another use as a neutralising agent would be for the acid sludge from petroleum refining plants; the product is similar to asphalt and, although inferior to good natural asphalt, can be employed for the preparation of roofing materials.

If certain of the impurities could be kept sufficiently low, there is no reason why the amount taken by glass manufacturers could not be materially increased; its fine state of diversion is certainly a favourable factor for its use in this connection. The carbon must be low, only about 1 per cent being permissable. It is a curious fact that while carbon is an ingredient of the mixtures for several glasses, when added as a constituent of waste lime, it imparts a dirty colour to the glass. This may be due to the combination of impurities found in the waste lime.

The silica content is of no great importance, it may or may not be allowed for; magnesia tends to make the glass hard and viscous, and the amount must be/

be very low. Sometimes, of course, it is deliberately added, for instance, in America, as dolomite; the iron content should not be above 0.3 per cent. (as Fe_2O_3), for good white glass it should be less than 0.1 per cent; alumina enters into the composition of most glasses, being derived from the walls of the melting pots, it is added specially for optical, opal and other special glasses; manganese salts, in the amounts found, are of no consequence.

The waste lime could be employed as a flux for various metallurgical operations if the magnesia was low enough to prevent the formation of slags with high melting points. It was thought that the waste might find a use as a substitute for whiting in the preparations of inferior rubber, but the soda, even in very small amounts, prohibits any use in this direction.

WASTE BLEACH SLUDGE.

This is the waste sludge left from the lixiviation of the bleaching powder with water; after the first digestion, the residue is given one to three washes with water and dumped.

In certain mills, however, more pains are taken with the final exhaustion, and the slimy looking sludge is either pumped or run into ponds, where it is allowed to drain for a further withdrawal of the supernatant liquid or, it is subjected to suction filtration in vacuum filtering devices. Table 23 illustrates the differences of residual available chlorine found in sludges.

TABLE 23./

TABLE 23.

Analyses based on dry material.

Analysis.	No.1	No.2	No.3	No.4	No.5	No.6
Calcium oxide	66.42	63.65	64.43	55.95	66.43	65.78
Magnesium oxide	0.79	1.74	0.84	1.12	1.47	1.23
Sodium oxide	0.32	0.27	0.29	0.26	0.33	0.31
Manganese	trace	trace	trace	trace	trace	trace
Fe and Al oxides	1.86	1.35	1.19	1.01	1.11	1.22
Silica	2.75	1.33	4.54	4.93	2.04	3.05
Carbon dioxide	10.61	10.42	10.58	12.96	10.58	10.65
Cl (available)	2.94	6.01	4.44	1.83	1.11	1.21
Cl (as chloride)	trace	trace	nil	[illegible] 2.50	trace	trace
Cl (as chlorate)	nil	nil	nil	[illegible]	trace	nil
Sulphur trioxide	0.60	0.75	0.68	0.75	0.08	0.09
Phosphorus pentoxide	trace	trace	trace	trace	trace	trace

Hypothetical Combination

	No.1	No.2	No.3	No.4	No.5	No.6
Calcium hydrate	64.20	60.30	62.70	51.76	68.83	68.13
Calcium carbonate	24.12	23.68	24.05	31.84	24.05	24.21
Calcium chloride	trace	trace	nil	2.70	trace	trace
Calcium chlorate	nil	nil	nil	2.02	trace	nil
Bleaching Powder	5.26	10.76	7.95	3.51	1.98	2.17
Other constituents	6.42	5.25	5.30	8.17	5.14	5.49
Moisture in original	77.00	87.98	82.79	75.22	66.73	65.84

Nos. 1,2 and 3, S. Mill as dumped; No.4, weathered sludge.

Nos. 5 and 6, K. Mill, as dumped from suction filter.

The last traces of hypochlorite are only removed with great difficulty and even in the more economically conducted concerns it is considered impracticable to do so; in sludges from the latter the traces range from 0.5 to 1.5 or 2 per cent, calculated on the dry material.

Unfortunately, all the mills are not so particular and it is often found that waste sludges having as much as 7-11 per cent of available chlorine, calculated on the dry material, are regularly dumped. (See samples 1, 2 and 3 Table 23).

A mill produces, on an average, about five tons of waste, calculated as dry material, for every fifteen tons of bleaching powder used.

The water content varies according to the practice of the mill; when dumped without a final draining or filtration, it may be as high as 90-95 per cent, but when dumped from a draining or suction pond it is usually in the region of 60-70 per cent.

Small amounts of the waste sludge are occasionally employed locally for lime washing walls of out-houses. The only attempt to make use of this material was made the subject of an English patent in 1890, which proposed using it as a causticising agent in the recovery of the soda lye (E.P. 13,504, 1890).

It may be possible to use this material for some/

some special purpose, peculiar to local conditions, but otherwise it will continue to remain a waste product, the only satisfactory solution of the problem being the adoption of some other bleaching process, such as the electralytic process of the "Manchester" type, largely employed on the continent, and which prepares a solution of sodium hypochlorite from brine solution.

BACKWATER SLUDGE.

The term "backwater" is applied to the excess of water which falls through the meshes of the shaking wire table of the paper-machine, carrying with it, a certain proportion of fine fibre,loading material and size.

Table 24 demonstrates the differences to be found in backwater materials running from different makes of paper:-

TABLE 24.

Composition of Backwater Sludge.

(Menzies & Aitken, J.S.C.I., 1899, T.p. 1097.)

Make of Paper.	Clay.	Fibre.	Size.
Demy 53 lb.	24.93%	72.48%	2.59%
" 28 lb.	36.90	60.60	2.50
" 26 lb.	41.30	55.50	3.20
" 24 lb.	38.50	58.52	2.98
" 20 lb. (a)	24.00	69.34	6.66
" 20 lb. (b)	14.60	77.90	7.50
" 20 lb. (c)	13.50	78.72	7.78
" 17 lb.	13.50	83.84	2.66

This backwater is caught in a shallow box, known as the save-all and from where it may be sent back to dilute the pulp to the proper constituency before/

before it reaches the table of the machine. Some mills do not trouble to re-use it as a diluent, but run it straight from the save-all to some suitable arrangement for separating out the suspended matter.

This may consist of a cone-shaped or other classifier or a series of long, rectangular, brick ponds, where the fibre and clay slowly settle out and whence the water, free from suspended matter, finally passes off. The residual sludge is then dumped.

The composition of this sludge may vary considerably; this variation may be due only to differences occurring in the backwater materials but, when, as several mills do, other effluents are run into the settling ponds, the composition of the sludge becomes more complex. Table 25 gives some idea of the variations to be found in a sludge from a mill running waste bleachsludge into the settling ponds.

TABLE 25./

TABLE 25.

Backwater sludge from pond.

(S. Mill).

Results expressed as percentage of material dried at 100 deg. C.

	No.1	No.2	No.3	No.4
Silica	15.58%	15.33%	36.01%	30.54%
Alumina	11.95	12.99	29.98	25.64
Calcium oxide	25.33	9.86	8.58	4.92
Sulphur trioxide	3.60	1.25	0.82	1.38
Nitrogen	-	-	0.17	0.14
Carbon	10.20	16.90	7.07	12.36
Hydrogen, Oxygen, Carbon dioxide combined water and other constituents.	33.34	43.67	17.37	25.02
Hypothetical Combination				
Aluminium silicate ($Al_2O_3,2SiO_2$)	26.05	32.91	65.30	55.81
(With two molecules of water giving China clay, $Al_2O_3,2SiO_2,2H_2O$, =	30.27	32.91	75.97	64.94
Silica free	1.48	-	0.69	0.37
Calcium sulphate	6.12	0.19	1.39	2.35
Cellulose (calculated from the carbon and confirmed by the calorific value	23.89	39.15	15.92	27.81
Calcium carbonate, Calcium oxide and Water of combination	42.46	27.75	16.70	13.66
Casein (if nitrogen is due to this)	-	-	0.89	0.76
Loss on drying to 100 deg. C.				
As per cent. of the original material	75.84	68.58	24.36	70.96

Nos.1, 2 and 4 represent the waste when freshly settled and No.3 when left to weather for some time.

As hygroscopic water and some water of combination are expelled on drying at 100 deg. C. it is consequently difficult to find a rational basis on which to base the percentage of china clay but the above results may be taken as proximate.

The semi-solid sludge, when removed from the ponds is generally a light, putty coloured mixture, the constituents of which defied all methods of separation without the destruction of the fibrous portion. Separation by water-lift and various methods of froth-flotation made very little impression, the ash from the original material and from the floated portions only differing by 1- 1.5 per cent.

It is perhaps interesting to add that a froth - flotation plant has been recently designed in Canada for the special purpose of recovering the solids from the backwaters.

The cellulosic portion of the sludge can be converted into oxalic acid by alkaline oxidation and good yields were obtained under suitable conditions.

An ingenious use for the sludge from a mill running backwater and bleach sludge to the same ponds was patented by the Indurite Products Co. (Fairgrieve E.P. 218, 793, 1923) who employ it as a filler for artificial resin, the lime from the bleach acting as the catalyst and the remainder of the constituents as the filler.

It was thought that this cellulose waste might be employed for the preparation of decolorising carbons and several samples were prepared from different sludges. When tested, however, by the iodine/

iodine method, previously described, the values were found to be very low, ranging from .0702 to .1518 when the final heating was at 900°C.

An ideal use for this waste fibrous material would be as an inert filler, especially for magnesia cement, in place of the sawdust now employed, as this would consume large amounts. Several test mixings were tried and they gave satisfactory evidence that the sludge could be used in such a manner. The mixings made were similar to these employed in commercial practice, when sawdust is the filler incorporated; - three parts of filler to one part of magnesium oxide by weight, the mixture being made into a paste with 22° Bé solution of magnesium chloride.

These results, of course, apply to sludges containing backwater materials only, and not to mixed sludges, particularly these which are contaminated with waste bleach effluent, as the free lime has an injurious effect on the setting of the cement. It should be noted, that while these tests gave proof that the sludge made an excellent filler for magnesia cement mixings, further work would require to be sone before its commercial utility could be definitely accepted. Such work would include the determination of its resistance to time, and its stability under varying atmospheric conditions, but bearing in mind/

mind the more inert nature of the sludge compared to that of sawdust, there is no reason to doubt that the result of these prolonged tests would be satisfactory and would repay the trouble taken, especially in view of the fact that the near future will probably witness extensive developments in the use of magnesia cement for floors, and stucco and plaster work generally.

The tendency now, however, is to use a mixture of sawdust (treated with $CaCl_2$) and portland cement: this gives a very useful product with the advantages of wood and of cement – can be sawn, nailed etc (Novocrete – a very good material).

WASTE MATERIAL FROM STRAINERS.

This is the last of the waste materials to be considered and as the amount produced by any one mill is so very small, a few cwts. per week, only a few words will be said about it. This waste is caught in the strainers, placed for the purpose, in the troughs carrying the pulp mixture towards the machine, and consists of the roots and other hard parts of the grass which have resisted the disintegrating effect of the soda-boiling and subsequent treatment.

When removed from the strainer traps it appears as a stringy mass, having a water content of about 75-85 per cent, and an ash value of 3-3.5 per cent., taken on the dry material. It can be oxidised by alkaline oxidation to give oxalic acid and the yields are very good when the conditions are suitable, as much as 80-85 per cent of oxalic acid, calculated on the weight of the original material (dry), being obtained. Otherwise, the material is of little value and the amount produced, being so small, would scarcely repay any trouble taken to collect it for the preparation of oxalic acid or other similar substances.

ABBREVIATIONS.

B.P. = British patent.

E.P. = English patent.

F.P. = French patent.

G.P. = German patent.

U.S.P. = United States patent.

Can. P. = Canadian patent.

Chem. & Met. Eng.	Chemical and Metallurgical Engineering, U.S.A.
J.S.C.I.	Journal of the Society of Chemistry and Industry.
Paper.	Paper, U.S.A.
Papierfabr.	Papier Fabrikant, Germany.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. High & Ag. Soc.	Transactions of the Highland and Agricultural Society.
