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Characterizations of Lime Sludge from Indian Paper Industry: A Step towards Sustainable Growth for Indian Cement Industry

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Abstract— ***The kraft process of wood into wood pulp in the paper and pulp industry in the chemical recovery section generates lime sludge (LS) through the burning of the lime kiln. This by-product lime sludge from the paper industry has the major chemical composition of calcium carbonate in the form of calcite, moisture and minors are silica, magnesium, iron and aluminium. Here, we characterized the collected industrial lime sludge by-product from different parts of the country and evaluated its potential application in engineering construction material. The chemical composition of all samples contains CaO in around (52-55) %, SiO2 (1-4) %, Al2O3 and Fe2O3 make up less than 1% by weight. Minor alkalis of Na2O, K2O and SO3 content are less than 1 wt%. XRD profile and TG/DTA results showed that all lime sludge samples have major calcite (CaCO3) phase. The particle size distribution showed that grains are in the range of 11µm to 23µm which is compatible for cement manufacture and construction. Investigation by optical microscopy of microstructure and morphology revealed that calcite grains are presents as rounded shape agglomerated form. The characterization of all obtained results are encouraging for replacement of limestone in the cement and construction industry by using lime sludge which is technically suitable and economically viable for waste management in favour of circular economy.***

Index Terms— ***Lime sludge, Calcite, Particle size, Cement, Circular economy***

I. INTRODUCTION

Modern industrialization has boosted the style of living from the traditional rural economies to highly sophisticated one. Though it is an indication of development, but it has also brought a grave ecological situation with hazardous industrial waste generated on a daily basis. Amongst them, lime sludge (LS) is one of the industrial wastes generated from paper and pulp industry approximately 4.5 million tons per annum in India [1]. The LS waste mainly produced from paper industry, other sources are fertilizer, sugar, carbide and soda ash industries. Lime sludge is generated by kraft process through chemical recovery section in paper mill. During chemical recovery process, the smelt are dissolved in water to form green liquor. Through causticization process, the smelt or green liquor which is mainly soda ash (Na_2CO_3) reacts with calcined lime CaO to produce caustic soda (NaOH) along with calcium carbonate (lime sludge) [2-3].

Now a days researchers are focusing on the utilization of industrial waste as a source of raw material for other industries. With ever-growing world population, the demand of building materials also increases. Here, LS comes in picture, which contains majorly $CaCO_3$, can be an alternative raw material of lime stone for cement industry. Many papers and research articles have been published based on utilization of LS in cement fabrication [4-6]. Vasistha et al. formulated an eco-Portland cement clinker by using lime sludge and fly ash, which has C_3S, C_2S, C_3A, C_4AF as clinker composition [4]. In addition, the mortar prepared matches the requirements of masonry cements. Wei et al. has undertaken a study in which the lime sludge addition improved the burning ability of clinker which in turn reduced the temperatures for calcium carbonate ($CaCO_3$) decomposition and liquid phase formation [5]. Kumar et al. has demonstrated in his study that up to the 25% of replacement of LS and FA in cement mortar gives higher 28 days strength [6]. Various studies have also been done to understand the effect of lime sludge in concrete. Several studies using M20 and M30 grade aggregate in concrete with lime sludge replacement (10-20) % proved increase in compressive strength [7-8]. Srinivasan et al. reported that compressive strength of concrete can be increased by replacement of lime sludge up to 30% in M30 grade concrete. Beyond this limit replacement of LS, the compressive strength decreased drastically [7]. In case of M40 grade concrete Pitroda et al. suggested up to 10% replacement of cement by lime sludge without reduction in strength [8]. Hence, LS can be suitable alternate material for cement and construction industry.

The aim of this study is to collect LS from pulp and paper

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industries from different locations of India as mentioned in Table I and its characterization to analyse the potential utility of LS in construction industries.

II. MATERIALS AND METHODS

The industrial LS samples were collected form three paper and pulp industries as given in Table-I from different parts of the paper and pulp industries of India. The same samples were characterized for further studies. The chemical composition such as CaO, SiO_2, Fe_2O_3, Al_2O_3 along with alkalis and SO_3 content were analysed by chemical method following standards IS 4032:1985 and IS: 1760:1991 and by XRF (Model: ZSX Primus II) made by Rigaku Corporation, Japan. XRD (Model: Smart lab SE) made by Rigaku Corporation, Japan was used to study the major and minor phases present inside LS at the wavelength CuK_{α}=1.54 nm with the scanning rate of 1^{o}/min from (10-70) degree. Thermal analysis was done by (Diamond TGA/DTA) (Model: Perkin Elmer) to determine thermal behaviour and weight loss of LS from temperature range of 30^{o}C to 1000^{o}C at 10^{o}C/min. Particle Size distribution (PSD) was measured by PSD analyser (Model: Microtrac S3500), Germany to observe particle sizes and morphological studies has been done by Optical Microscopy (Model: Nikon LV100pol), Japan.

Table 1. Collected samples from different regions of the country

Constituents	LS 1	LS 2	LS 3
Moisture	3.31	27.96	34.87
LOI	40.55	41.65	40.28
Silica	3.96	0.79	3.96
Iron Oxide	0.13	0.14	0.36
Alumina	0.36	0.22	0.58
Calcium Oxide	52.16	55.16	52.87
Magnesium Oxide	1.43	0.52	0.87
Sulphuric Anhydride	0.12	0.06	0.05
Sodium Oxide	0.76	0.93	0.72
Potassium Oxide	0.11	0.06	0.01
Eq. as Na_2O	0.83	0.97	0.73
Chloride	0.012	0.009	0.006

III. RESULTS AND DISCUSSION

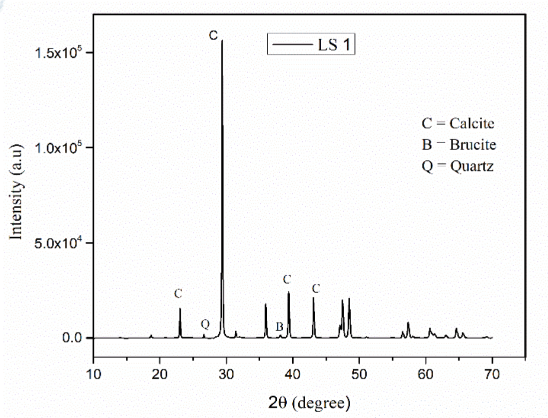
A. Chemical analysis of lime sludge

The chemical analysis data of lime sludge samples was tabulated in Table II. The three LS samples were oven dried for 24 hours for moisture remove and moisture was found to be 3% in LS 1 whereas moisture content was very high in LS 2 and LS 3 (27-34) %. This may be due collection of samples from different parts of the country having different source of raw material and chemical process parameters. The loss on ignition (LOI) of all samples were almost same approx. 40%. The CaO content of LS varied from (52-55) %. SiO_2 in LS 2 and LS 3 was higher than that of LS 1. MgO content in all the samples were less than 1% which don't have any adverse effect. The iron oxide and alumina content made up also less than 1% by weight. Minor volatiles like (Na_2O, K_2O, Cl^-, SO_3) were present less than 1% by weight in all the three samples. Since the chemical composition of lime sludge is having similar composition as high grade lime stone and its amount present is within the limit as defined by IS codes (IS 1760:1991 and IS 4032:1985), it can effectively replace the limestone for Portland cement manufacture in cement industry [9].

Table 2. Chemical analysis of three different collected LS

Sl. No.	Region	Composition	Sample Code
1	South India	100% wood based	LS 1
2	North India	40% wood and 60% agro based	LS 2
3	North India	30% wood and 70% agro based	LS 3

B. XRD Phase analysis of lime sludge



(a)

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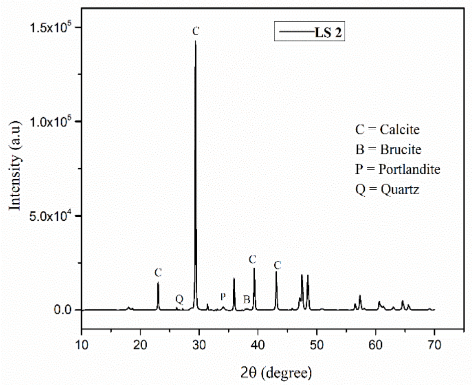
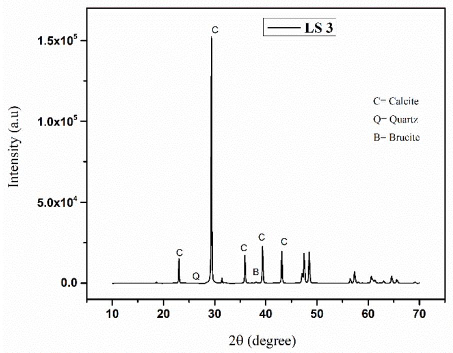


(b)



(c)

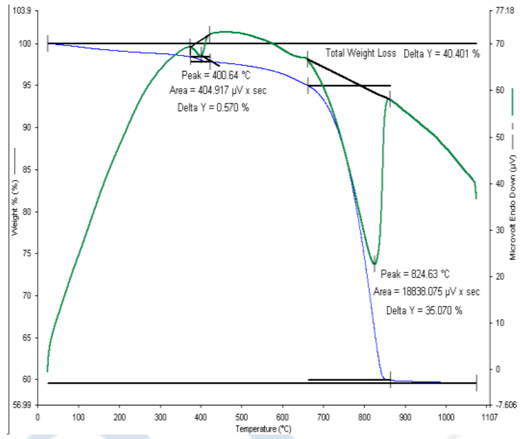
Fig. 1. XRD pattern: (a) LS 1 (b) LS 2 and (c) LS 3

Major and minor phases were analysed and presented in the Table III. According to the earlier study obtained by Buruberri et al. [10] and comparing with the results of present observation, calcite was predominantly presented in all the LS samples given in Fig.1. Minor phases like silica, Brucite, Portlandite, Sillimanite and Aragonite were also available in LS samples. These XRD results were in align with the obtained chemical analysis results.

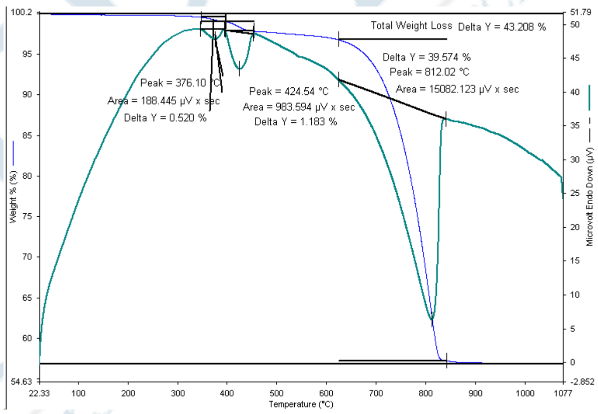
Table 3. XRD phases of three different collected LS

Phase	LS 1	LS 2	LS 3
Calcite	Major	Major	Major
Quartz	Minor	Minor	Minor
Brucite	Minor	Minor	Minor
Sillimanite	Minor	Minor	-
Portlandite	-	Minor	Minor
Aragonite	-	Minor	-

C. Thermal analysis by DTA/TGA of lime sludge



(a)



(b)

Fig. 2. Thermal TG/DTA traces: (a) LS 1 and (b) LS

Thermal analysis of LS samples have been conducted by TG/DTA and the results are shown by the Fig. 2. DTA has shown an endothermic peak in LS 1 and LS 2 at 824°C and 812°C, respectively which may be due to the decarbonation of calcium carbonate and the corresponding weight loss were found to be (36-39)%[11]. Endothermic peak was observed at 400°C for LS 1 and 376°C for LS 2, respectively with the weight loss of 0.5%. These peaks are attributed to the water associaated with magnesium hydroxide [12]. Other endothermic peak at 424°C was observed for LS 2 which may be due to the presence of Portalandite whose presence was also confirmed by XRD. The TG/DTA data of LS 3 was almost same with LS 2. The total weight loss of all the samples was observed to be approximately (40-43)%.

A. Particle size distribution (PSD)

Table 4. PSD of three different collected LS

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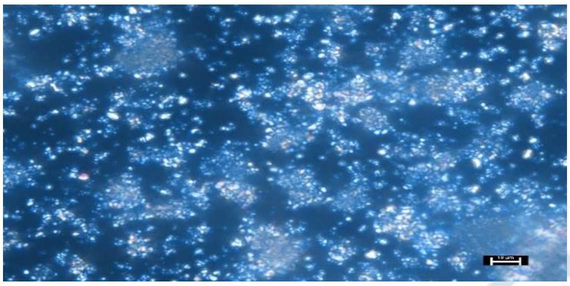
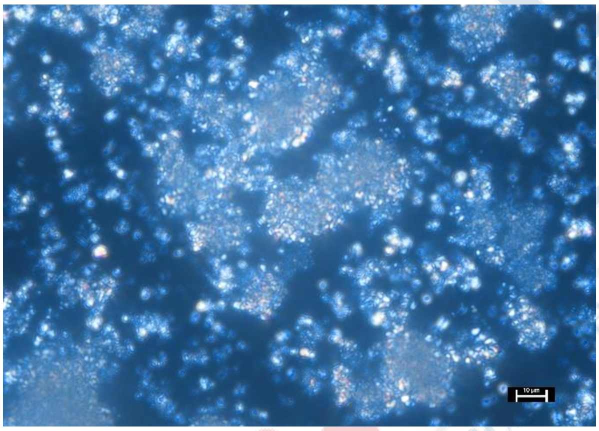
Table IV showed the various sizes of the PSD for LS 1, LS 2 and LS 3. It was observed that average size (D50) of LS 1 was 11.23 µm, whereas average size (D50) of LS 2 and LS 3 were almost same in the range of (23-26) µm. This results proved that lime sludge particles were compatible with other conventional cementitious raw materials. It can usuable to replace most precious raw materials limestone to achieve similar or better properties in the cement manufacture.

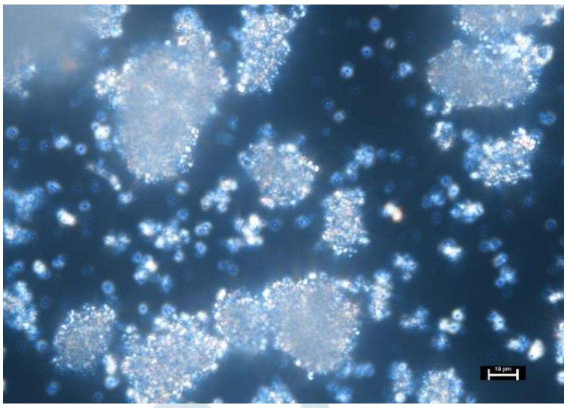
B. Morphology by optical microscopy



(a)



(b)



(c)

The optical microscopy image of three lime sludge samples were given as below Fig.3. The major minerals present were calcium carbonate in the form of calcite with other accesory minerals like quartz and iron oxide. Micro globular calcium carbonate minerals with rounded grain margins were uniformly distributed in the samples. The size of calcium carbonate in LS 1 was in the range of (1-6) µm which was also confomity with PSD results. Most of the carbonate mineral grains were present as agglomerate form. In LS-2 & LS 3 clusters of calcium carbonate grains were also uniformly distributed in the sample. Subhedral quartz grains were randomly distributed in the sample having the size range of (2-15) µm in all the samples whereas iron oxide of subhedral to micro globular grains were randomly disseminated in the LS (b) es.

IV. CONCLUSISONS

The byproduct lime sludge of paper and pulp industry is mainly composed of calcite with others constituents silica, iron oxide and alumina. Also, some minor organic volatiles

Samples	D10 (µm)	D50 (µm)	D90 (µm)
LS 1	0.59	11.23	34.84
LS 2	8.77	23.75	44.49
LS 3	5.02	16.60	37.39

were present in the accptable limit for raw materials in the cement manufacture. Particle size of calcites are compatible in granulometry with other raw materials and morphology reveals that calcites are in agglomerate with the presence of other minor constituents like quartz and iron oxide. These lime sludges are worthy raw materals for replacement of limestone for the potential application in favour of sustainble development in Indian cement and construction industry to resume circular economy.

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