

Preparation & Characterization of Activated Kaolinite

Thesis Submitted

By

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(111CR0566)

Under the guidance

Of

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*In the partial fulfilment of the degree of
Bachelor of Technology*

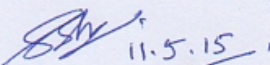


**DEPARTMENT OF CERAMIC ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA**



CERTIFICATE

This is certified that the work contained in the project entitled "Preparation & Characterization of Activated Kaolinite" by Siddharth Sekhar Das (Roll 111CR0566) in partial fulfilment of the requirements of the award of Bachelor of Technology Degree in Ceramic Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance. To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.


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ABSTRACT

Kaolinite has been used for many purposes since ages. Kaolinite is the major mineral segment of kaolin. The clay sample (china clay) was collected. Calcination of china clay was carried out at a temperature of 750°C to form metakaolin. The chemical analysis results of raw clay sample showed that the clay is composed of alumina and silica. Activated clay was synthesized by acid and alkali leaching process of metakaolin. Two strong acids HCl and H₂SO₄ were used for acid activation and KOH was used for carrying out alkali activation. The residue formed was characterized by X-Ray Diffraction study to confirm the phases. The particle morphology was studied by FE-SEM study, and the specific surface area was studied by BET analysis. TG-DSC analysis was also carried out to see the mass loss and formation of any new compounds. These analyses were carried out separately for all three samples of activated clay. The results showed an increase in surface area of the leached clay which hints that activated clay can be used as a catalytic agent in many chemical reactions and an adsorber to remove impurities.

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CHAPTER-I

INTRODUCTION & OBJECTIVE

1.1 Introduction

Since ages kaolin is considered as a major raw material because of its wide usage. One of the major mineral component of kaolin is kaolinite, which has major impurities like feldspars, smectites, and illites. The applications of kaolinite are widely used each year in the world for a various purposes such as ceramics, rubber filler, paper coating, cracking catalysts and cements. Hydrated aluminium silicate is the major component of kaolin which is of the composition $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. As per the structural composition, kaolinite consists of alumina octahedral sheets and silica tetrahedral sheets which are stacked alternately and has the theoretical formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. The theoretical elemental composition is 46.54% SiO_2 , 39.5% Al_2O_3 , and 13.96% H_2O . It has a layer lattice structure.

It is also one of the most widely used industrial materials. It is chemically inert over a varied pH range, has very good covering power and is also white in colour. It is soft and has a non-abrasive nature. It is very less conducting to heat and electricity. Some uses include, paper coating, fillers for paints and plastics. It requires many specifications such as particle size, colour and brightness and viscosity. But other uses require minimum specifications, for example chemical composition is very much important in case of cement. It can also be used as a filler and as a coating material on the surface of paper such that the quality of printing can be improved due to which it is used in paper industries as well.

For the chemical treatment of clays acid activation is a widely used technique. It is because it has been studied that the chemical treatment of clay sample helps in improving the surface and also the catalytic properties of the clays. Acid activation consists of the leaching of the clay with different organic acids, which results in disintegration of clay particles and the mineral impurities are removed which results in changing the chemical composition and the structure of the clay as well. The surface area of the particles, number of acid centres and also

porosity also increase due to this. The increment is directly related to the intensity of the acid treatment. [1]

Metakaolinite is the metastable phase that we get from the calcination of kaolinite. It is more reactive under chemical treatments. The Kaolin was transformed to metakaolin at a temperature range between 550-950°C by calcination process. This transformation takes place along with the loss of structural water from the clay material. The solids obtained after that are strongly influenced by the calcination of kaolin.

For the preparation of porous materials, selective leaching of clay is one of the possible methods. The term leaching means the use of acids or alkaline solutions which helps in dissolving the impurities present like Fe, Mg and Al or Si cations. But on the other hand it is really very difficult to improve the properties of kaolin by these chemical methods, because the material has got a very high passivity. Even under very strong conditions this is not significantly affected by any acid or alkaline treatments. Strong conditions imply concentrated solutions and high temperatures.

There are many benefits of using hydrochloric acid for leaching alumina over any other acids; as many literatures report. It is because the slurries can be filtered easily, the titanium dioxide present will not be soluble in HCl and the iron present can be removed easily, which is present as impurities in many clays. But, it is the severe corrosion of the material that takes place is the most serious problem with the use of hydrochloric acid. Therefore in order to avoid corrosion of materials corrosion resistant plastics and rubbers are used.

Many reports have also been found regarding the separation of silica residue from a chloride solution, where the filtration takes place very fast.

1.2 Objective

The prime objective of the work is to prepare activated kaolinite from metakaolins which can be obtained by the calcination of kaolin. And also to study the behaviour of the sample under certain acid and alkaline treatments.

CHAPTER-II

LITERATURE REVIEW

2.1 Belver et al. ^[1] did a study on the synthesis of the metakaolins which was carried out by the calcination of kaolin. The calcination was carried out at four different temperatures. The XRD patterns of the calcined items were studied which indicated various pattern examples. The pattern of kaolinite disappeared but the pattern of mica remained. Acid activation of the sample was carried out with HCl of concentration of 6M at room temperature. The temperature was maintained at 90°C and reflux conditions were provided using a reflux tube. The times of treatment varied from 6h to 24h. No change in the properties or in the structure or of the metakaolins were found. The treatment which was done under reflux conditions for 6h helped in the removal of a large portion of the Al³⁺ cations which were octahedral in shape, and a formless silica was also developed.

2.2 Faten Slaty et al. ^[2] The raw kaolinite is alkali activated with an aqueous solution of sodium hydroxide. The compressive strength of the sample which was obtained can be influenced by the properties of the reaction solution. The silica sand content was increased up to 1:1 ratio w.r.t kaolinite which improves the quality of the solution mixture and the compressive strength increases due to this factor. This is in fact the major reason for the increment of compressive strength. The compressive stress is due recorded as 48 mpa under dry conditions and 23 mpa under wet conditions and the ratio was optimised under curing conditions.

2.3 A.A. Al-Zahrani et al. ^[3] studied the effects of leaching temperatures required for leaching and took it from (25°C to boiling temperature), period of activation was in the range of (10-150 minutes), acid concentration of (1M – 6M). Kaolinite clay was calcined at different temperatures ranging between 400°C and 800°C at diverse calcination periods of (5 to 120 minutes). The calcined clay was then leached with hydrochloric acid (3M HCl) acid under some specific leaching conditions. The ideal calcination conditions were found to be around 600°C and 1 hour for calcination temperature and time period respectively.

2.4 C.Bazin et.al ^[4] studied about the recovery of alumina from Kaolin. It was observed that in case of sulphuric acid or hydrochloric acid leaching process the amount of alumina was

extracted by 10 percent and this process can be exactly used for calcined clay. The aluminium present in the calcined clay was leached by using sulphuric acid (at 100–120 °C temperature). Silica as a deposited and considered as residue which was insoluble in the process of leaching. The residue was separated from the aluminium chloride solution by using fluid separation technique. The highest amount of alumina was extracted by a hydrochloric acid leached process rather than the of sulphuric acid leached method. For calcined clay the percentage of extraction was observed to be more.

2.5 K. Okado et al. ^[5] studied that the acid treatment of clay reduces the Al_2O_3 content and increases the SiO_2 substance. Composition changes very rapidly in the early stages of leaching of the sample. However, after about a time span of 1.5 hours the rate decrease step by step.. Impurities present like Fe_2O_3 and K_2O are removed by leaching from 0.3 to 0.1 mass percentage yet the TiO_2 content increased from 2.0 to 3.8 mass percentage. The sum of the remaining SO_4 in the H_2SO_4 treated tests found was about 0.3 mass percent even after the last washing was done.

2.6 Temuujin et al. ^[6] researched XRD examples of the unground and ground kaolinite, and of ground samples which was leached for varying times. The little measure of impurity mica and quartz distinguished in the XRD originates from the first kaolinite. After grinding, all the kaolinite peaks vanished. Leached metakaolinite shows micro pores but no macrospores or mesopores in the structure.

2.7 Y. Abdullahi et al. ^[7] investigated about the process regarding leaching of silica. The silica residue was obtained from kaolinitic clay after the treatment through acid. The main objective was to prepare different concentration of silica from calcined clay or kaolinite. The calcined clay was also leached with a sodium hydroxide solution. The kaolinite was calcined and transformed to metakaolinite at 1000°C for 1 hour which can activate the silica content in the kaolinite. The amount of silica which was extracted from the Kaolinite was soluble in a medium using 5, 10, 20, 30, and 40% w/w NaOH..

CHAPTER-III

EXPERIMENTAL METHOD

3.1 Experimental

Initially raw china clay was taken and was characterised by XRD, BET and TG-DSC to study the phases present and measure the surface area of the raw clay. Then it was calcined at a temperature of 750°C. Calcination helped in the conversion of the material to metakaolin.

Two types of Chemical Activations were carried out i.e.

1. Acid Leaching
2. Alkali Leaching

The Kaolin or Clay was used as a starting material. The chemical composition of kaolin is given in Table 1.

The clay sample was ground in an agate mortar to decrease the particle sizes, particles below 0.5 mm in size. Powdered kaolin was calcined at a temperature of 750 °C for a time period of 2 h to form metakaolin in an electric furnace to loosen the alumina components. Then the metakaolin undergoes various leaching process listed below:

1. Leaching of Clay by 6M HCl
2. Leaching of Clay by 6M H₂SO₄
3. Leaching of Clay by 6M KOH

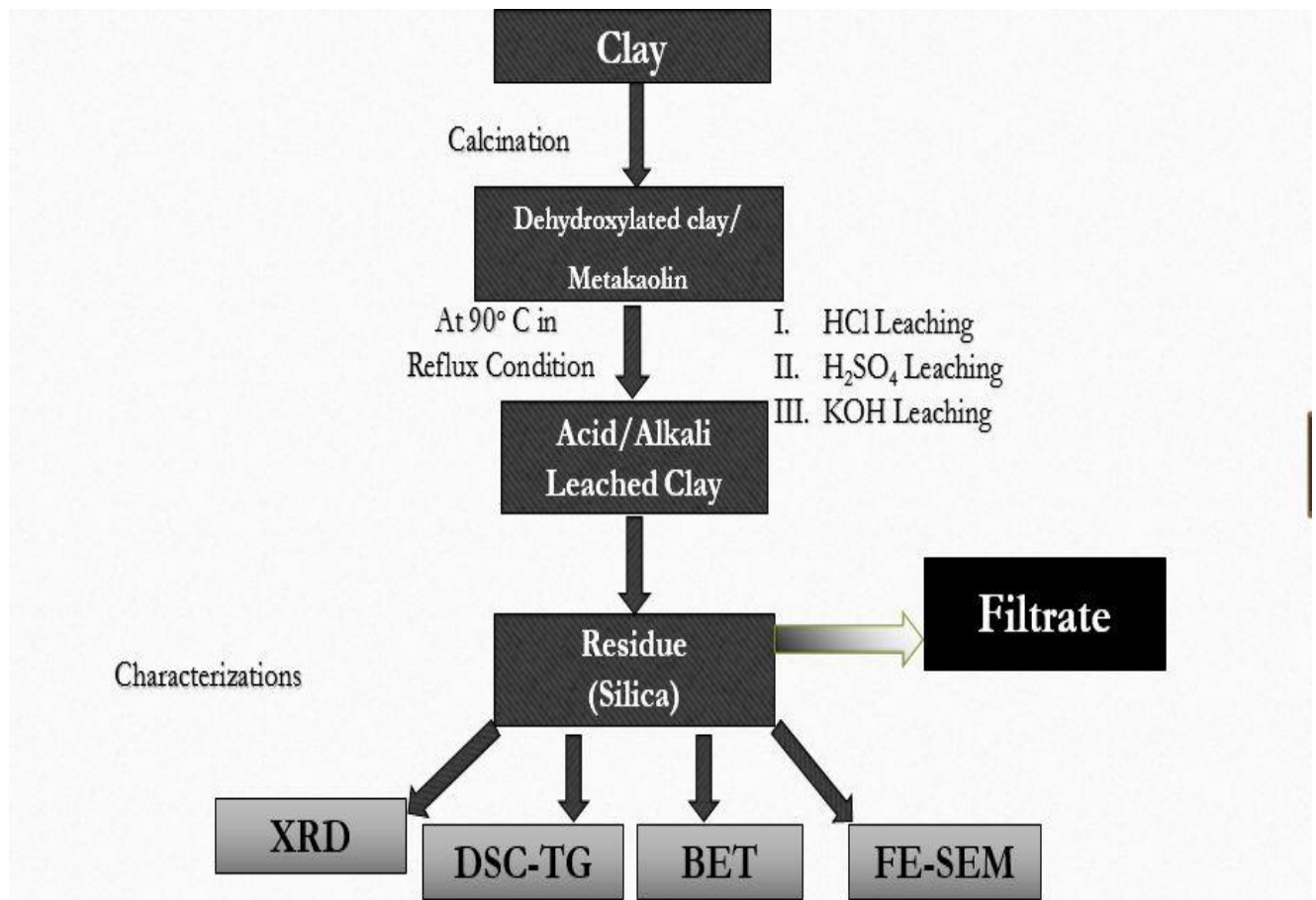
3.2 Leaching process

The powder sample of kaolin was dispersed in an acid/alkali solution to attaining a solid/liquid ratio of 1:20 by weight. The mixture of kaolin powder and acid/alkali was taken in a 500 mL round bottom flask. The reaction flask was fitted with a reflux condenser and the mixture was stirred with the magnetic stirrer for 6h. The temperature of the mixture was set at 70°C. After the mixture of kaolin and acid/alkali had been leached, it was cooled to room temperature and filtered to

remove leach residue, which mainly consisted of silica and filtrate was collected for synthesis of aluminium hydroxide.

The residue was dried in an oven and was characterised by different analytical methods.

3.3 FLOWCHART OF SAMPLE PREPARATION



3.4 TG-DSC Analysis

The Differential Scanning Calorimetry is generally used to study the reaction nature and change of mass which occur during the firing stages of the sample. The measurement or heat treatment was done up to 1200°C at a rate of 10°C/min. Argon atmosphere was maintained during the analysis.

3.5 Phase Identification (XRD Analysis)

X-Ray Diffraction study was used to find the different phases and crystallography of the elements present in the sample. For this, the samples were calcined and crushed into fine powder. The scanning range was maintained at 20°C with a step size of 0.05°. The data which was obtained was analysed with the Philips X-Pert High Score software and the peaks were identified.

3.6 Microstructure Analysis (FE-SEM)

The microstructure were analysed using Field Emission Scanning Electron Microscope (Nova Nano SEM/ FEI 450). The powder samples were used for taking the microstructures. Particle size, particle morphology were studied.

3.7 BET Analysis

BET plots were analysed which gives an exact specific surface area of materials by nitrogen adsorption measured as a component of relative weight. Which utilizes a completely computerized analyser. The technique measures surface area and pore size which are evaluated to determine the total specific surface area in m²/g which provides important information about the effects of surface porosity and particle size in many applications. This was done to know the specific surface area.

CHAPTER-IV

RESULTS & DISCUSSIONS

4.1 Raw material analysis

4.1.1 Chemical analysis of Raw China Clay

<u>COMPOUND</u>	<u>WEIGHT PERCENTAGE</u>
SiO₂	49.53
Al₂O₃	29.50
Fe₂O₃	2.15
CaO	2.25
MgO	0.753
Loss on Ignition	14.09

Table-1

Raw china clay was taken and chemically analysed for determining the amount of different constituents present in it. It was found that clay sample contains SiO₂ and Al₂O₃ as two major constituents and Fe₂O₃, CaO, and MgO as impurities. The detail results were tabulated as table-1.

4.1.2 TG-DSC analysis of raw china clay

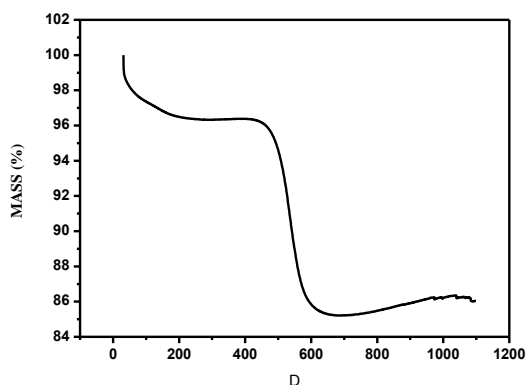


Fig-1 Thermogravimetric analysis of raw clay

Figure-1 shows the thermogravimetric study of clay sample. The graph indicates the loss of primary water at a temperature of about 200°C and the loss of hydroxyl groups or the removal of secondary water at a temperature of about 600 °C.

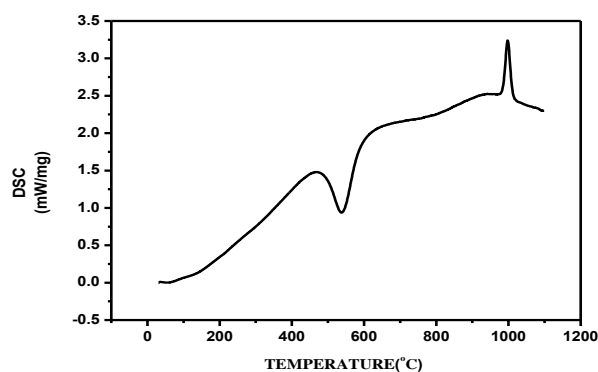


Fig-2 DSC of raw clay.

The DSC graph (Figure-2) of the raw china clay indicates the formation of two peaks one endothermic and another exothermic peak. The endothermic peak around 580 °C indicates dehydroxylation. The exothermic peak is because of the formation of a spinel phase or gamma-alumina phase.

4.1.3 Specific Surface Area of Raw clay

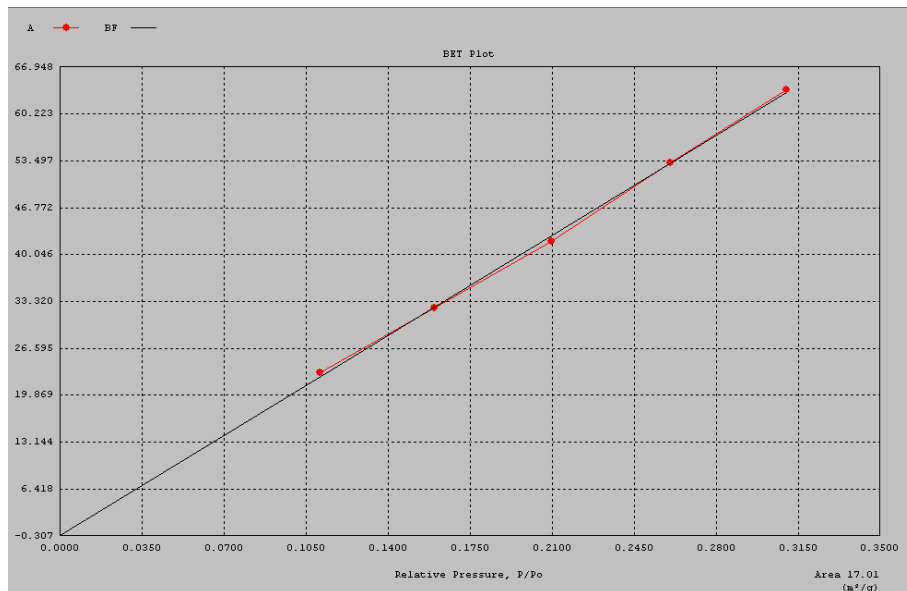


Fig-3 BET plot of raw clay.

The specific surface area of the raw china clay was found out using the BET method. And the surface area of the raw china clay was found **17 m²/gm.**

4.1.4 XRD analysis of raw china clay

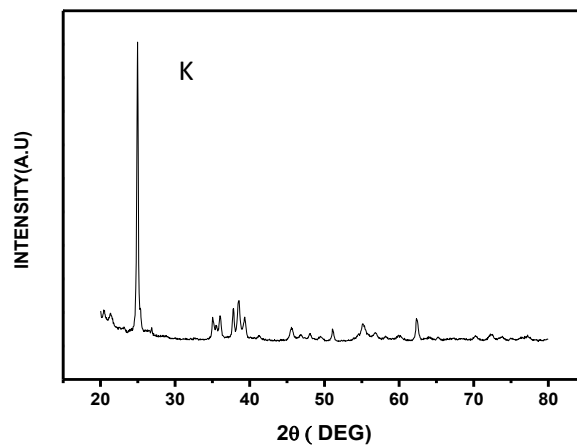


Fig-4 XRD patterns of raw china clay

The phase analysis of the raw china clay was done using the X-Ray Diffractometer. The only peak present in the figure is due to kaolinite as per Fig-4

4.2 CALCINED CLAY

4.2.1 TG-DSC analysis of calcined clay

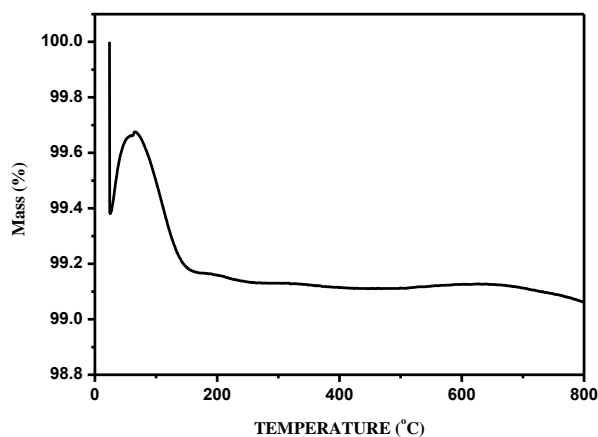


Fig-5 TG of Calcined Clay

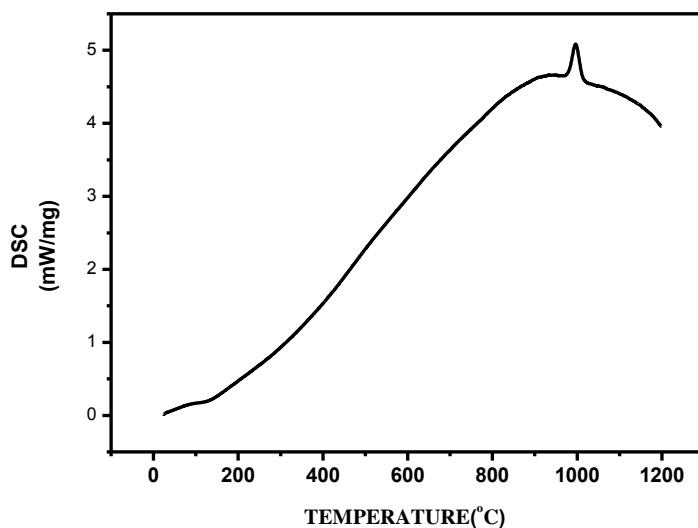


Fig-6 DSC of Calcined Clay

Figure-5 and 6 represent the TG-DSC curve of calcined clay. As the clay sample was calcined at 750°C so the weight loss due to dehydration and dehydroxylation is absent here. The only one exothermic peak at around 1000°C is due to γ -alumina or spinel phase formation.

4.3 ACID LEACHED CLAY

4.3.1 HCL LEACHING

4.3.1.1 CHEMICAL ANALYSIS

Amount of silica in HCl leached clay - 82.53 %

By the help of chemical analysis technique we find the percentage of silica present in the clay leached by HCl, and it was found to be **82.53 %** which proves that the major component of the leached clay is silica.

4.3.1.2 TG-DSC analysis of HCl leached clay

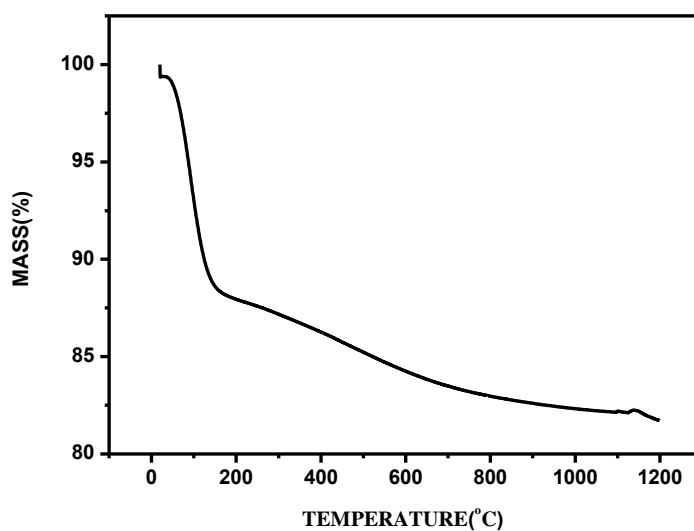


Fig-7 TG of HCL leached Clay

The thermogravimetric analysis of the clay sample leached with HCl shows two-stage weight losses (Fig-7). First one within 130°C is due to the removal of adsorbed water and the second one in the range of 150°C to 900°C is due to dehydroxylation of $\text{Si}(\text{OSi})_3\text{OH}$ compound formed during acid leaching process [1]. In the first stage here weight loss is higher, after acid leaching the amount of amorphous silica increases, so the amount of adsorbed water also increases.

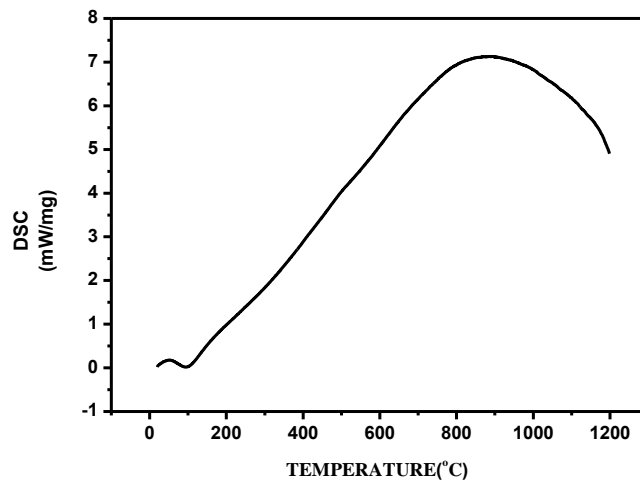


Fig-8 DSC of HCL leached Clay

Fig-8 shows the DSC analysis of the clay sample leached with HCl. The endothermic peak is seen at a temperature around 110°C.

4.3.1.3 Specific Surface Area of HCl Leached Clay

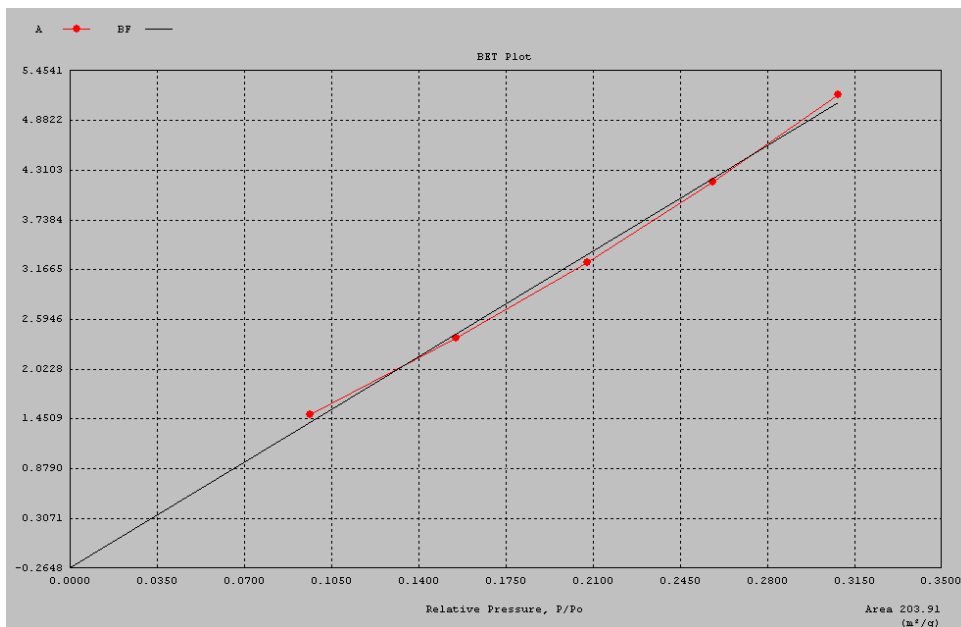


Fig-9 BET plot of HCL leached Clay

The specific surface area of the HCl leached clay was found out using the BET technique, and the surface area was measured $203.9 \text{ m}^2/\text{gm}$. The surface area of the sample has increased markedly compared to the raw clay sample.

4.3.1.4 XRD analysis of HCl Leached Clay

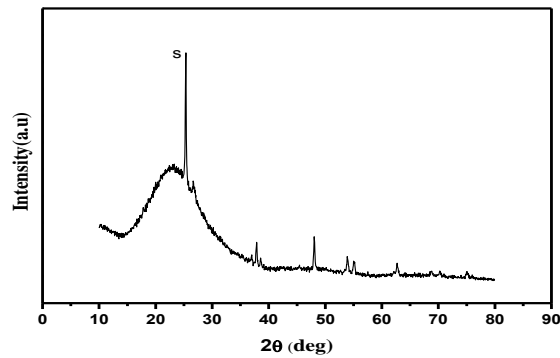


Fig-10 XRD of HCl leached Clay

Fig-10 shows the phase analysis of the clay sample leached by HCl. The phase analysis confirms the presence of silica phase in the sample. One characteristic feature of this graph is the presence of a hump or wide band in the range $2\theta = 15-35^\circ$. This may be due the presence of amorphous silica in the leached clay.

4.3.1.5 FE-SEM analysis of HCl Leached Clay

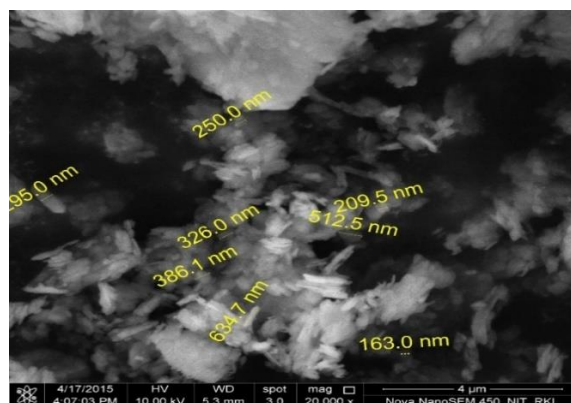


Fig-11 FE-SEM of HCL leached Clay

Fig-11 is the image taken by field emission electron microscope which shows the plate like structure of the clay sample and they are stacked in a disordered manner.

4.3.2 H₂SO₄ LEACHING

4.3.2.1 CHEMICAL ANALYSIS

Amount of silica in H₂SO₄ leached clay - 83.73%

By the help of chemical analysis technique we find the percentage of silica present in the clay leached by H₂SO₄, and it was found to be **83.73 %** which proves that the major component of the leached clay is silica.

4.3.2.2 TG-DSC of H₂SO₄ LEACHED CLAY

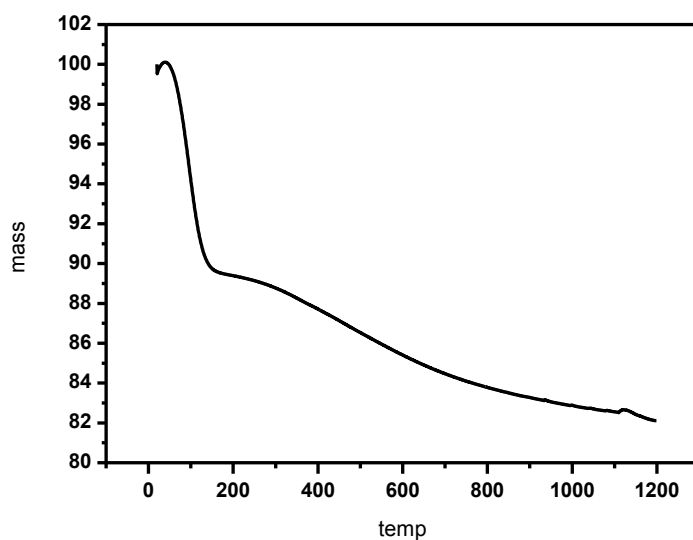


Fig-12 TG of H₂SO₄ leached clay

Fig-12 shows the thermogravimetric analysis of H₂SO₄ leached clay sample.

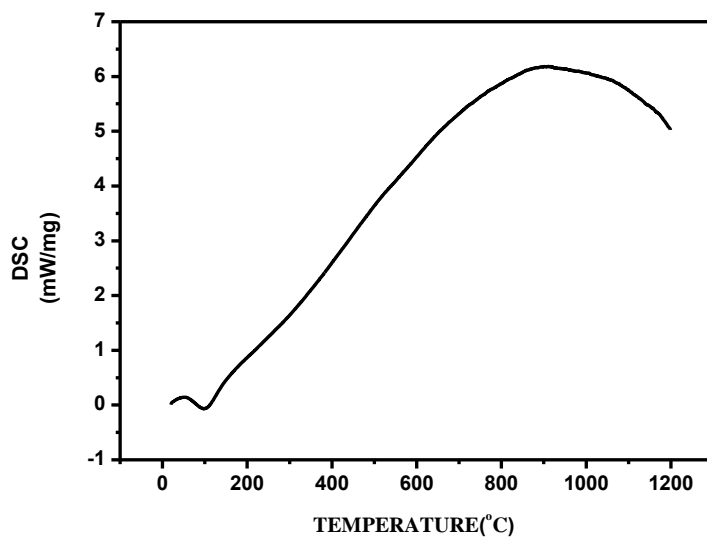


Fig-13 DSC of H₂SO₄ leached clay

Fig-13 shows the DSC curve of the clay sample leached with H₂SO₄. There are no basic differences in the TG-DSC pattern of HCL leached clay and H₂SO₄ leached clay.

4.3.2.3 Specific Surface Area of H₂SO₄ leached clay

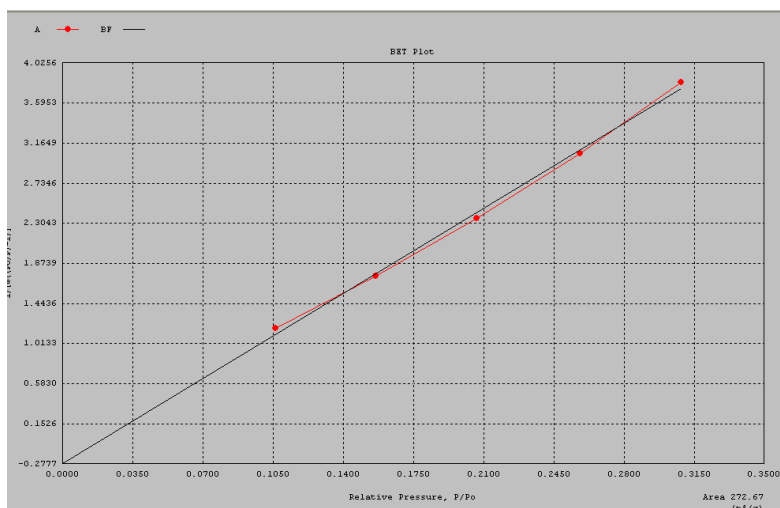


Fig-14 BET plot of H₂SO₄ leached clay

The specific surface area of the H₂SO₄ leached clay was found out using the BET. And the surface area of the raw china clay was measured **272.7m²/gm**. The surface area of the sample increases more when the clay sample leached with HCl.

4.3.2.4 XRD of H₂SO₄ LEACHED CLAY

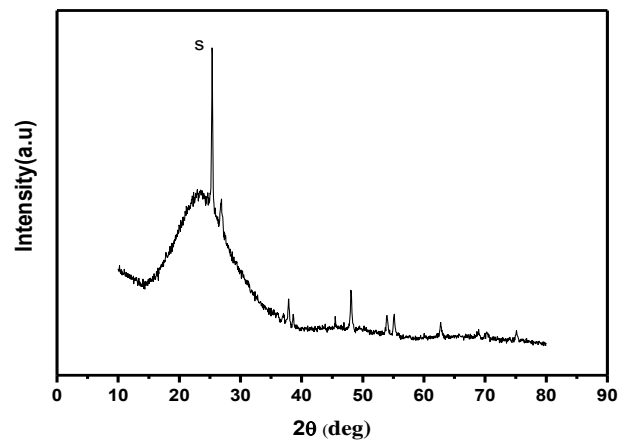


Fig-15 XRD of H₂SO₄ leached clay

Fig-15 shows the XRD analysis of clay sample leached with H₂SO₄ and by performing the phase analysis the presence of silica phase is confirmed. The presence of amorphous phase is also confirmed by the pattern.

4.3.2.5 FE-SEM of H₂SO₄ leached clay

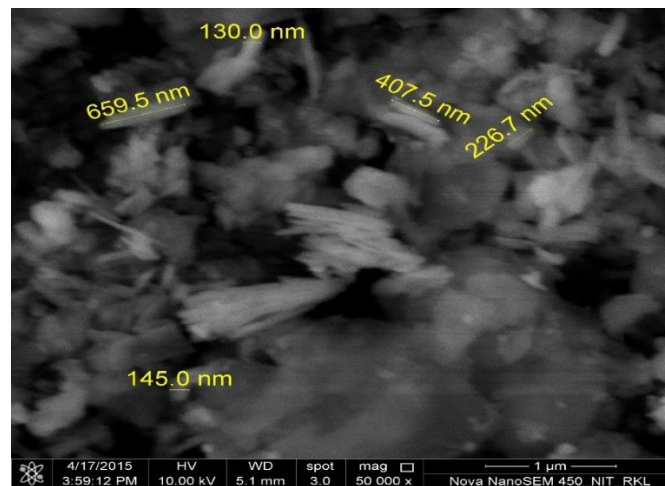


Fig-16 FE-SEM of H₂SO₄ leached Clay

Fig-16 micrograph was taken by field emission scanning electron microscope, which shows the particle size and particle morphology of the clay sample leached by sulphuric acid. One striking point is that here some particles are appeared like fibre or needle-shaped.

4.4 ALKALI LEACHING

4.4.1 KOH LEACHED CLAY

4.4.1.1 XRD of KOH LEACHED CLAY

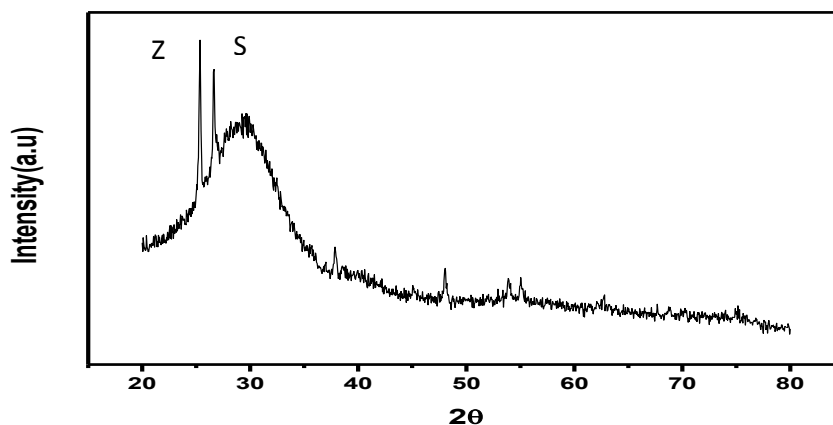


Fig -17 XRD of KOH leached

Fig -17 shows the phase analysis of the clay sample leached with an alkali i.e. KOH, and it shows the formation of a Zeolite phase. This phenomenon indicates only a part of the silica present in metakaolin layer leached out as free silica and the remaining part participate in the zeolite formation process.

4.4.1.2 FE-SEM of KOH LEACHED CLAY

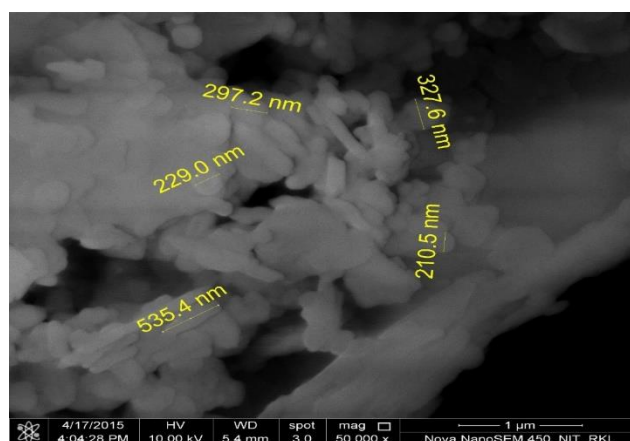


Fig-18 SEM of Alkali leached clay

Fig-18 is the field emission scanning electron micrograph of alkali leached clay, which shows that primary particles are scale shaped, and they are stacked to form the secondary particle.

CHAPTER-V

CONCLUSION & FUTURE WORK

5.1 Conclusion

Acid activated and Alkali activated clay were prepared. All the characteristic analyses were carried out and the results were compared. It is seen that the alumina phase disappears on acid activation of clay sample. Amorphous phase along with silica are present in acid leached clay whereas zeolite phase is formed after alkali activation of clay. It is also seen that the surface area of the clay increases on activation which proves the effectively of this activated clay for the catalytic application.

5.2 Future Work

There is also a plan for the modification of the preparation routes to get better activity and properties of the material.

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