

DEVELOPMENT OF IMPROVED TAP HOLE CLAY FOR BLAST FURNACE TAP HOLE

A

**THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENT FOR THE DEGREE OF
MASTER OF TECHNOLOGY**

In

Ceramic Engineering

By

SMRUTI REKHA DASH



**DEPARTMENT OF CERAMIC ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA
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Under the Guidance of

Prof. S. Bhattacharyya

&

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CERTIFICATE

This is to certify that the thesis entitled "**DEVELOPMENT OF IMPROVED TAPHOLE CLAY FOR BLAST FURNACE TAP HOLE**" submitted by Ms. Smruti Rekha Dash in partial fulfillment of the requirements for the award of **Master of Technology** in Ceramic Engineering with specialization in "Ceramic Engineering" at National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by her under our supervision and guidance.

To the best of our knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award any Degree or Diploma.

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Date:

Smruti Rekha Dash

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ABSTRACT

This work describes the development of Tap hole clay based on Standard Tap hole caly. This study included the analysis of existing Tap hole composition from the XRD analysis, preparation of resin, optimization of resin composition and the replacement of some component of the Standard Tap hole clay (like Kyanite and Si_3N_4) and to adjust the composition which will properties (AP, BD, PLC, CCS) close to the Standard. The test revealed that increase in Corundum or Quartz increases the hardness (which is suppressed to provide wear resistance), Graphite increases drillability but the clay do not similar well. Kyanite can be effectively replaced by Silimanite and Si_3N_4 by Ferrosilicon Nitride. Two composition have been finally identify which have promising values and can be further optimized to provide an alternate composition to Standard 1 Tap hole clay. Other supplied Standards- i.e. 2, 3, 4 did not have much promising value and hence they were not optimized.

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Chapter 1

INTRODUCTION

INTRODUCTION

Tap hole is an outlet for hot metal produced in a Blast Furnace. Tap hole clays are used for plugging of the Tap hole of Blast Furnace. The major objective of this material is not only to plug the Tap hole but also to be drilled for the subsequent cast. The mud gun pushes the Tap hole clay into Tap hole of Blast Furnace where it hardens and checks the hot metal and slag from coming out of Blast Furnace.

Today, the choice and the use of tap-hole clay are correlated to many factors:

- The blast furnace operative conditions, which depend mainly on the size and the exploitation, the clays participate to the process as key elements to ensure reliability and safety in order not to disturb the blast furnace productivity.
- The particular arrangement of the tap-hole area and its management: this requires that the clays not only drive and resist to the molten metal attack but that they also have positive influence on the hearth drainage and on the peripheral iron flow by the hole length.
- The environmental aspects are assumed both as politic in the improvement of the human working condition at the cast house level and as a general environmental protection extending the blast furnace domain to the surrounding town.
- And, of course, the economical aspects in order to propose an optimal unit cost per ton of hot metal produced, knowing that the tap-hole clay costs remain still one of the heavy voices of the general cast house management costs.[1]

The Blast Furnace top-hole is a uniquely difficult environment for the refractoriness and the mechanical equipment used. A blast Furnace campaign may be twenty years with no repair of the hearth walls and tap hole (replacement of the tap hole branch refractories excluded). The tap hole clay must consistently and safely perform the following:

- Flow when pushed by the clay gun, to plug the tap hole.
- Cure within the tap hole during the plug to tap time but without shrinkage to ensure a tight seal
- Be drilled in an acceptable time.
- Allow a stable, controlled melt stream at tap without spray
- Withstand erosion and corrosion by iron and slag.
- From a stable substrate for the next plug
- Provide a stable and controllable tap hole length.

These factors are best achieved by considering not just the clay but the tap hole environment as a whole. [3]

1.1 The integrated Tap hole Concept

Tap hole length is of vital importance for achieving a long blast furnace campaign. A longer tap hole draws liquids from nearer the centre of the hearth, whilst a short tap hole may promote peripheral flow leading to hearth wear in the characteristic 'elephant's foot' [1]. This is a function of the amount of clay injected and also of the erosion resistance of the clay. Similarly, operators require a tap hole which wears in a smooth and predictable way. A smooth hole promotes laminar flow and a smooth tapping stream, which in turn reduces wear in the trough and can make a significant contribution to controlling cast house refractory costs. Obviously this requires the clay to be erosion/corrosion resistant but produce a smooth bore during drilling and tapping.

In the past, tap hole clay had been used for a mere purpose of plugging of tap hole and discharge of iron and slag produced inside blast furnace. However, recently in Japan tap hole clay is exposed to severer condition as the size of the blast furnace gets bigger and operation gets more severe [2]. Requirements for tap hole clay are a) stable operation by hearth drainage, b) reduction of workload and achievement of small refractory consumption by longer tapping duration, and c) achievement of longer furnace life by protection of hearth side wall with long tap hole length.

Tap hole clays are plastic refractories. The main objective of this refractory is not only to plug the tap hole of the blast furnace but also to be drilled easily and smoothly when required for subsequent tapping. The progressive use of high capacity blast furnaces and an increased output of hot metal have greatly increased the demands expected of refractory materials, particularly tap hole materials. The requirement of tap hole materials are:

- (1) Improved plasticity- provides better workability
- (2) High corrosion and abrasion resistance – provides constant tap hole diameter and tap hole length
- (3) Good sinterability – provides good strength
- (4) Adhesive strength – required for proper adhering of new tap hole mix with old one
- (5) Good gas releasing capacity – reduces the formation of gas pressure inside
- (6) Easy tapping or drilling.

Modern blast furnaces work with a tap hole length 2-3.5 meter. The tap hole mixture has the task of closing the tap hole and to protect the walls on the inside as they are particularly stressed by the intense tapping flow. A mushroom shaped block must develop inside the blast furnace.

A good tap hole clay should have proper binding in a short time, fast closing of tap hole, constant tap hole length and easy drilling. When tar is used as a binder for tap hole clay, the disadvantages are that such compositions harden slowly as it has poor bonding strength at the tap hole temperature. In addition, tar containing compositions generate considerable smoke and foul gas which causes environment and health problem.

According to Delabre et. al. [3], the major functional role and properties of the tap hole are:

1. Pliability in a close range at the injection temperature, so that the material can be pushed through the mud gun at a reasonably low pressure.
2. After plugging the hole, the mud should have sufficient mechanical strength and chemical resistance for the protection of tap hole including corrosion and erosion resistance.
3. The tap hole should be easy to drill during tapping of hot metal.

1.2 Role of tap hole mass

- Allow Controlled Flow of Metal & Slag
- Ideally retain its shape & size throughout casting period
- Protect Hearth Lining in the Vicinity of Tap Hole
- Seal the metal flow when plugged in hole.
- Improve life of iron trough & hood by controlled flow of metals and slag

The following basic objectives have led to major improvements during recent years.

- The tap hole should be opened and closed carefully in order to avoid damage to the carbon bricks and thus incursion of iron.
- The created tap hole channel should have a smooth surface in order to ensure that the iron
- The desired tap hole diameter should be met as close as possible to allow the correct flow rate. Hard plugging mixes should be used to ensure that the hole keeps its diameter as long as possible.

1.3 Tapping Methods

There are basically two types of tapping methods, viz. drilling method and bar setting method.

Tap hole drill

- Water drilling technology ensures better cooling of the drill bit.
- Drilling by rotation only considerably reduces the danger of cracks in the tap hole area.

- Complete hydraulic drilling leads to full capability of adjusting all involved opening parameters and finally to automated openings of the tap hole
- Tap hole length monitoring is very important if one wants to really know the status of the tap hole.

Clay gun

- Increased plugging pressure enables the machine to handle harder plugging mixes.
- A soft touch system ensures a quick and smooth closing of the tap hole
- Capability of adjusting all the involved plugging parameters leads to automated plugging.

The tapping rate (amount per unit of time; t /min) of iron and slag is determined by the tap hole diameter, the tap hole length, the thickness of the molten iron and slag layer level), as well as gas pressure in the furnace and other factors. Of these, the influence of the tap hole diameter is significant, especially since the diameter varies as the mud material is worn out by the outgoing slag and molten iron.

1.4 Tap hole length and Design

In many of the modern blast furnaces, a tap hole length of 2 to 3,5 meter is used. The tap hole clay not only seals the tap hole, but also builds up itself on the inner wall of the hearth and hence prevents premature wear of the brickwork in this area.

The inner walls of the hearth in the area of the tap hole are reinforced at the relining of the blast furnace. The refractory lining consists of carbon bricks. In a number of cases monolithic lining material and casting compounds on a corundum-SiC base are also used. Injection compounds are sometimes used for intermediate repairs in the area of the tap hole.

1.5 Role of Binders

The majority of the tap hole clay mixtures which are used for blast furnace tap hole mud applications are kneaded with coal tar and or liquid resin as the binder source. These binders adjust the mix plasticity and achieve good binding properties. When tar is used as the binder (including pitch and asphalt) the mix have a good plasticity but since tar is thermoplastic in nature, it takes time for the tap hole clay to harden and the mix is not properly hardened (due to the absence of strong C-C bonds which form properly hardened mix by the furnace heat) from the polymerization of the tar binder causing poor bonding and low strength of tap hole clay. Further, high volatile matter in the binder also results in large porosity of tap hole clay and it corrodes faster. Moreover, coal tar contains benzopyren which is carcinogenic and thus causes environmental pollution. Thus direct use of coal tar as a binder is not advisable.

The other type of binder that is used is phenol resin. There are two types of phenol resin e.g. novolac type and resol type. While the former is thermoplastic in nature, the latter is thermosetting. When novolac type resin is used, about 10% hexamethylenetetramine is used as a hardener. Both the phenol resins give a high carbonization yield at higher temperature and exhibit high strength. However, phenol type resin has poor shelf life due to polymerization and increasing viscosity during storage and kneading of the mix becomes difficult and therefore large amount of resin is required to ensure proper plasticity. Novolac resin also has low thermal stability and its decomposition temperature is further lowered by the absorption of moisture. Therefore, phenol resins cannot be satisfactorily used in the conventional form for preparing tap hole clay mix. So, the refractory technologists are in pursuit of tap hole compositions which will satisfy their requirements.

On the other hand, the substitution of tar by phenolic resin cause the mix to solidify prematurely in the mud gun which makes further pushing of clay difficult. It is for these reasons, a suitable tap hole mix is still being pursued.

1.6 Development of tap hole mixture

A modified tap hole mixture which will have minimum of the disadvantages mentioned previously could be developed from either or both of the following proposed routes:

The rheological behaviour of the tap hole clay primarily depends on the binder characteristics. Apart from binder, the rheology also depends on the ratio of the binder to the refractory material particularly grain size distribution, grain morphology and size. The aging behaviour of tap hole mix with the binder is caused by the adsorption and absorption of the binder in the grains and transformation of the binder itself by the evaporation of the more volatile products as well as by oxidation and polymerization. The storage life of the tap hole clay is also dependent on the storage climate.

Now a days it is also a practice to realize the advantages of both tar (or its derivative) and resin, by mixing them together. However, tar (or its derivative) cannot be easily mixed as they form an emulsion. In order to form a uniform liquid mixture, a tar phenol resin blending bonding agent can also be tried by using some special mutual solvent. Besides use is also made of fine polystyrene fibres which improves the adhesive strength and gas releasing property.

1.7 Material design concept of tap hole clay

Tap hole clay plays a very important role in blast furnace cast house operation. As shown in Fig.1, there are 3 basic factors, i.e. ramming, tapping, and sidewall protection. Subsequent requirements and methods are complicatedly mutually related. First of all, it is necessary to

have appropriate extrusion pressure at the time of ramming so that tap hole clay can create compact texture inside tap hole. Therefore, it is important to understand the aging characteristic of clay and control extrusion pressure so that ram pressure becomes approx.80% of mud gun's power. Second, it is necessary to create smooth and good tap hole for longer cast duration without damaging it by too much hammering or oxy opening for prevention of cracks and longer cast duration. Therefore, adjustment of the tap hole clay strength by controlling sintering

characteristic is important in accordance with the type of drilling machine such as pneumatic or hydraulic drive. This longer cast duration contributes to not only reduction of clay consumption or other consumables but also reduction of workload at cast house such as gun up and drilling. Third, tap hole clay is also expected to protect hearth side wall by creating protection layer of tap hole clay called mushroom inside tap hole. In order to create good mushroom, it is important to have higher plasticity and excellent adhesion with old clay inside furnace under the condition of hot and confined space. By achieving all aforementioned requirements, it becomes possible not only to reduce refractory consumption but also to have stable operation.[4]

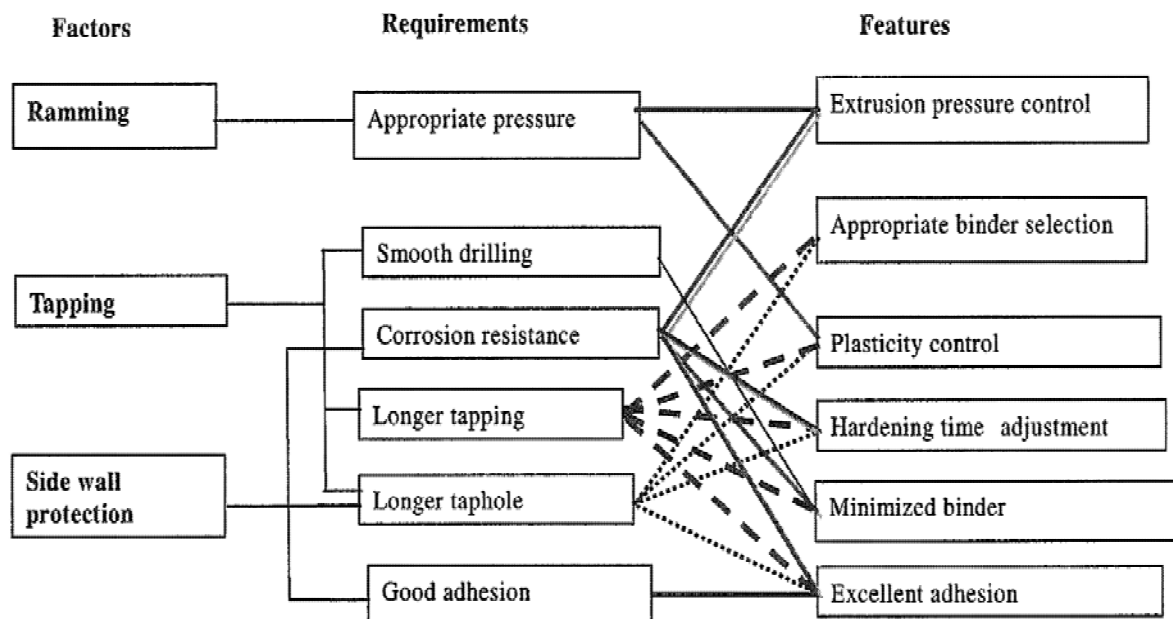


Fig.1 Material design concept

1.8 Main characteristics for good performance tap hole clay [5]

The following are the main characteristics of the tap hole clay for its improve performance:

- Long tap hole length-This depends on the adhesion strength between old & new clay mud.

- Long Casting Duration & Uniform Casting Rate –It depend on the texture development of the clay inside the blast furnace when the tap hole clay is exposed at high temp where corrosion, erosion and high temperature -all three play an important role in determining the properties of the tap hole clay.
- Drilling operation-The ease of the drilling operation depends on the expansion behavior of tap hole clay during sintering, phase composition and their properties.

The following Table describes the different main raw materials, additives and binders used in the tap hole clay along with their main functions.

Table 1.8 The main raw material constituents of the tap hole clay mixes and its main functions

| Raw materials | Main functions |
|--|---------------------------------------|
| Fused Alumina, Calcined Bauxite, Chamotte, Fire clay | Main Aggregates, Filling materials |
| Clay minerals | Plasticity; Injection |
| Pyrofillite | Plasticity; Expansion (500/1300°C) |
| Silica, Fine sand | Expansion (600/1000°C) |
| Kynite | Expansion (>1200°C) |
| Fine calcined Alumina / Fume silica | Sintering/Mullite formation/Expansion |
| Zirconium/Chromites | Special additives/spalling/Corrosion |
| Silicon Carbide, Carbon | Corrosion resistance |
| Silicon Nitride | Erosion resistance |
| Metallic powders | Erosion resistance/Sintering |
| Coke, ultra fine carbon | Drilling |
| Tar/Resin/Special Oils | Binders |

Chapter 2

LITERATURE REVIEW

LITERATURE REVIEW

Hubert et.al [6] studied the effect of ageing on the property evolution of tap hole clays. They observed that during ageing of the tap hole clay an increase in the molecular mass of the binder takes place above with a decrease of the low weight fraction by evaporation. An increase in the degree of aromaticity and a slight oxidation of the binder was also observed. Those effect results in an increase of asphaltting leading to better gelatin of the bitumen. Overall, it increases the strength of tap hole.

Schntz et .al [7] studied the Development of pollution free tap hole mixes from Non-Tar/Non-Resin Tap hole mixes .They developed anthracene oil-a new binder system fractionated oil obtained from coal tar. This anthracene oil content less than 50ppm benzopyrene which is enviro3nmentally accepted. However the use of anthracene oil required some additional additives like metallic boron.

Samukawa et. al [8] studied the effect of carbon sources on the properties of tap hole clay . They used three different carbon sources, viz. nanocarbon powder (Carbon A) pulverized graphite (Carbon B) and porous carbon (Carbon C) as the source of carbon for use in the tap hole mixes.

The effect of three different carbon sources was observed through AP, BD, Corrosion index tests. They observed for obtaining a higher value of strength, density and corrosion index. Carbon A with nano range particle size should be used. However, an increase in either carbon B and C resulted in good / easy drillabilty but lower strength and density.

lida et. al [9] studied the drill ability of two different blast furnace tap hole mix having varying SiO_2 and Al_2O_3 and correlated the drilling behavior with different physical parameter. They observed that high overall Young's modulus of the mud material increase the drilling time and wear loss of Carbide tool bits. They proposed that an increase in the overall Young's modulus probably cause an increase in the fracture toughness and strength of the mud material.

Schutz et. al [10] reported the development of a hybrid binder system based on tar-phenol system for tap hole clay mixes .They noted that this hybrid binder had similar plasticity had good shelf life, rapid hardening behavior was absent and improved gas release properties. The sintered tap hole clay mass showed positive expansion due to the presence organic compound.

Masakazu et. al [11] studied the applicability of high-density tap hole mix to blast furnaces. They used coal tar as binder along with a carbon based spherical grained plasticizer. It was observed that the binder plasticizer combination helped in increasing the corrosion

resistance, strength and density. This combination gave rise to longer tapping time. The binder requirement was observed.

Kitazawa et al [12] studied viscoelastic behavior of tap hole clay for understand the filling behavior of tap hole clay during pushing of new clay in the tap hole at a pressure 39.2 MPa. They introduced a factor "Time Constant" which is the time for 1/e of the total displacement is left. This factor indicates how much retardation takes place until the displacement reaches the end point. The test results showed that due to the existence of above time constant, the Marshall test and other extrusions tests performed under similar condition may provide a different result.

Komebani et al [13] studied the effect of ferrosilicon nitride on the property development tap hole clay material. They observed that reaction between Fe and Si_3N_4 become favorable above 1200°C and above 1400°C , reaction between Fe, Si_3N_4 and Al_2O_3 takes place leading to the formation of SiC, FeSi and AlN and the evolution of CO and N_2 gas.

Perez et.al [14] studied the development of non polluting binder for tap hole clay mix. The binder was developed to replace tar and resin because both of them either contain benzo pyrene and formaldehyde which are carcinogenic. They observed that the developed tap hole clay with newly developed binder had lower thermal expansion as compared tap hole clay with either tar or resin. The compressive strength was good even upto 1450°C which indicated good sinteribility of tap hole clay The plasticity variation with time for newly developed binder was comparable to that of tar and resin. The adhesive strength was better as compared to tar and resin. It was concluded that the developed liquid could be a substitute for tar and resin

Lopes et.al [15] studied the behavior and the influence of ferro silicon nitride on the final properties of tap hole mud refractories.and found that Ferrosilicon nitride by itself is not directly responsible for the grain in performance. Factors such as blast furnace operational condition, pig iron temperature, plugging and operating procedures are also very important and need to be carefully controlled. However Ferro silicon nitride improves the matrix strength and thus prevents slag penetration and friction reduction

Chapter 3

EXPERIMENTAL PROCEDURE

EXPERIMENTAL PROCEDURE

3.1 Identification of the raw materials and determination of particle size distribution in the supplied Tap hole clays

In order to identify the different raw materials and their weight fractions in the tap hole clay, it was necessary to remove the organic binder and additives from the tap hole clay. The process involves the following steps: Since the binder is organic in nature, in the first step, organic solvents from four different groups, viz. ketone group (acetone), alcohol group (propanol), aromatic group (tetrahydrofuran) and amine group (ethylene di amine) were tried separately to study the dissolution behavior of the binder. The efficiency of a solvent for binder removal was measured by the weight loss of the clay after washing. This was followed by use of a combination solvent for the binder removal.

3.1.1 Binder removal using pure organic solvent

The supplied tap hole was washed with different organic solvents for the removal of binders in order to identify the raw materials and grading of the different raw materials used in the formulation of the clay. The effect of different solvent (Acetone, Propanol, Tetrahydrofuran and Ethylenediamine) on the efficiency of binder removal was studied by recording the weight loss of the clay on washing the clay with the above solvents. The process involves taking weighed amount clay in a round bottom Teflon bottle and the different solvents i.e. acetone, furan, propanol and ethylenediamine was individually added to separate batches of clay sample and a uniform suspension was prepared by intense and continuous shaking in a mechanical shaker for 4 hours. The ratio of the solid to solvent was kept constant for all type of solvents (2 gm clay per 10 ml solvent) in order to study the effect of solvent type on binder/resin removal. The solvent leached out the binder present in clay masses. The binder rich solvent was filtered out and the solid residue was dried in oven at 60-70°C. After drying, the dry solids were weighed and the weight loss is considered to be the amount of the resin /binder present in the clay.

3.1.2 Binder removal using combination organic solvent

Table 3.1 shows that the observed weight loss is high when aromatic solvents are used. On the basis of this, a combination aromatic solvent consisting of Toluene and tetrahydrofuran is used for binder removal. Different weight fractions of Toluene and Tetrahydrofuran (30:70,40:60, 50:50, 60:40 and 70:30) was used to determine the solvent composition for optimizing the weight loss.

3.2 Granulometry of washed and dried clay

The washed clay was dried in the oven and was sieved for determining the particle size distribution or granulometry. The sieve analysis was carried out with a wide range of sieve sizes 1-3 mm (coarse fraction or CF), 0-1mm (middle fraction or MF) and -200 mesh or $\leq 75\mu\text{m}$ (small fraction or SF) and sieved in a ro-tap sieve shaker to avoid the clogging of sieves as well as to ensure efficient sieving.

3.3 Phase Analysis of washed tap hole clay.

The phase evolution of the washed tap hole clay were studied by X-ray diffraction technique (Philips PAN alytical, Netherland) using Cu K_α radiation at 35 KV and 25 mA in the 2θ range $20-80^\circ$ at a scan speed of $3^\circ/\text{min}$. The XRD study was carried out on both the washed clay as well as on the different size fractions of the washed clay obtained after sieving. The latter was done to quantify the presence of different minor additives (SiC , Si_3N_4 etc) which usually have fine sizes.

3.4 Resin preparation

It is well known that the resins play an important role in deciding the final properties of the tap hole clay. The two types of resins, viz. Resol (RR) and Novolac (NR) are used for the tap hole clay. Commercially they are available having wide variation in setting behavior, storage life and other properties. Although, it is planned to use commercial resins for the compositions that the study will develop, in order to understand the effect of different resin components on the properties of tap hole clay, it was decided to prepare the resin in the laboratory. Although the prepared resin was used only during the initial stage of study, but it was observed that the prepared resin although being similar in properties in that of commercial resin, it had low self life- probably due to the absence of stabilizers. Nonetheless, the prepared resin was helpful in understanding the effect of different resin ratio (RR:NR) on the properties of developed clay. The following sections, therefore discusses the procedure for resin preparation as well as the study on the optimization of the resin ratio

3.4.1 Procedure for resin preparation

Two types of resin are prepared i.e. Resol (liquid) (R: R) and Novolac (solid) (N: R)

Resol : 50 gm of phenol is added to 60 ml of formalin and 1.06 gm of NaOH. Then it was mixed properly and heated at constant temperature i.e. $80-90^\circ\text{C}$ till the bubbles come out from the heating mixture. The mixture was cooled 5-10 min in room temperature and then kept with an air tight cover in freeze for experimental purpose.

Novolac: 50 gm of phenol is added to 31.80 ml of formalin and 5 ml of HCl .Then it was mixed properly and heated at constant temperature i.e. 80-90⁰ C till the bubbles come out from the heating mixture. The mixture was cooled 5-10 min in room temperature and then kept in freeze with an air tight cover for experimental purpose.

3.4.2 Optimization of resin ratio for the developing tap hole clay using washed tap hole clay raw material

The washed clay was mixed with different ratios of RR and NR resins for testing the binding property of the resin. From the weight loss behavior and the literature data the maximum resin limit was set at 15 wt% and the minimum resin limit was set at 12 wt%. The above limit was decided on the basis of the different literatures and patents available on tap hole clay. It may also be noted that the weight loss of the clay during washing with organic solvents (assumed due to the removal of resin binder) was between 10-16%, which is close to the resin limit set in this study. It is found that a 60:40 ratio of resol:novolac resin showed the best binding properties. The washed clay was mixed with resin and hot compacted between 70-80⁰ C in a steel die at a compaction load of 65 Kg/cm². The compacts were kept in a sillimanite crucible and packed with petroleum coke and fired at 1200⁰ C/2hrs in normal atmosphere furnace. The sintered compact was characterized with respect to AP, BD, CCS, and PLC, drillability and slag test.

3.5 Batch preparation

Five different compositions (Trial 1 to Trial 5) of tap hole clay were prepared following the compositions of Standard-1 and Standard-2 materials. These batches were mixed with different resin ratio (40:60, 50:50 & 60:40), sintered at 1200⁰ C, 1300⁰ C & 1400⁰C for 2hrs (as discussed above) and tested for AP, BD, CCS, and PLC, drillability and slag test.

3.6 Characterization of sintered specimens

3.6.1 Permanent linear change (PLC)

Permanent Linear Change (PLC) is the dimensional change observed in tap hole clay (expansion or shrinkage) during heating of the clay. Ideally tap hole clay should have some expansion characteristics in order to fill any gaps present inside tap hole to avoid any cracks generated in tap hole material as well as to provide a tight packing. If PLC value is too high, cracks are produced in the new mud, resulting in a collapse of some parts. Sometimes slag or hot metal enter in these cracks, resulting in very hard sintered clay inside tap hole there by creating drilling problem. Similarly, for the clays having negative PLC value, having

shrinkage takes place during sintering which again produces crack in new mud resulting in collapse or penetration of slag or hot metal in these cracks and cause drilling problem.

Test procedure

The test sample length (of the compact tap hole clay mass) is measured between two end faces and the sample is slowly heated in the furnace and held at 1200⁰ C for 2 hr and cooled naturally. The length is again measured between two end faces after firing. The PLC is calculated as follows.

$$PLC=100(L_1-L_0)/L_0$$

Where L₀=Initial length between the two end faces of the test sample.

L₁= length between the two end faces of the test sample after heating.

3.6.2 Volatile matter test (VM)

This test gives amount of volatile organic material (binder) present in the tap hole clay. Volatilization of binder under hot condition causes defect. So it is very important to find the amount of binder present in the tap hole clay.

Test procedure

Test sample is crushed to powder (60 Tyler mesh size). The powder sample is weighed and kept in a crucible and it is placed inside the furnace. The temperature is slowly raised upto 900⁰ C and held there for seven minute; cooled naturally and weighed again. The VM is calculated as follows.

$$VM = 100(W_1-W_0)/W_0$$

W₀=Initial weight of the powder sample

W₁= weight of the powder sample after heating

3.6.3 Apparent Porosity (AP)

It gives an idea about the texture development in a tap hole clay at high temperature. For getting uniform casting rate and high corrosion resistance, tap hole clay must have low porosity and dense structure at high temperature (1200⁰ C).

Test procedure

The test sample is fired at 1200⁰C in reducing atmosphere. The weight of the fired sample was taken. This gives dry weight "D". The weighed test sample was placed in an empty vacuum desiccators containing the immersion liquid and the pressure in the desiccators was reduced to about 25 mm Hg. The immersion liquid was slowly admitted into the sample till

the sample is covered with liquid. After immersion, the suspended weight (H) and the soaked weight (S) of the sample was taken.

$$\text{AP (\%)} = (S-D) / (S-H) \quad \text{and} \quad \text{BD} = D/(S-H)$$

3.6.4 Cold Crushing Strength (CCS)

This test also gives information about the strength of clay which depends on texture develop inside tap hole clay and quality (purity) of raw materials used in manufacturing. e.g for two types of tap hole clays using the same quality and quantity of binder, the clay with better quality refractory aggregates will give higher CCS.

Test procedure

In this test, the test sample is the compact clay mass is fired at specified temperature for specified time (1200°C/2hr) under reducing atmosphere. The measurement of the surface area of test sample on which load has to be applied is taken. The load is applied hydraulically. CCS value will be the failure per unit area of the sample.

Chapter 4

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

4.1 Washing of as received tap hole clay

The washed clay was dried and weighed to know the weight loss of the clay during washing. The weight loss was considered to be equivalent to the amount of resin added to the clay. Table 4.1 shows the effectiveness of the different solvents on the wash ability characteristics of clay.

Table-4.1: Effect of solvent type on the washing efficiency

| Solvent | Propanol | Acetone | Furan | Ethylenediamine |
|-------------------|-----------------|----------------|--------------|------------------------|
| Weight change (%) | -11.67 | -12.72 | -12.17 | 3 |

However, literature shows that the most effective solvent for resin is a mixture of toluene and tetrahydrofuran. Thus it was decided to study the weight loss behavior of the clay after washing in the different compositions of toluene and furan and the results are shown in Table-4.2. It is observed that the weight loss increases with toluene content up to 60vol% and then decreases. So 60:40 volume ratio of toluene: furan is considered as the best combination solvent for binder removal.

Table-4.2: Effect of Toluene: Furan (v/v) on the weight loss behavior of clay during washing

| Toluene :Furan (v/v) | 3:7 | 4:6 | 5:5 | 6:4 | 7:3 |
|-----------------------------|------|-------|-------|-------|-------|
| Weight Loss (%) | 13.1 | 13.95 | 14.68 | 16.02 | 13.76 |

4.2 Estimation of the Resin/ binder content of different tap hole clay

The as supplied clay were washed with the optimized solvent (toluene: furan 60:40 v/v) in order to find out the resin content of the different tap hole clay. The binder content of different clay (tabulated from weight loss data) is listed in Table -4.3. It is observed that the Standard-1 contains the highest amount of resin in compared with the other three types. The Standard-2 clay has the minimum resin content. The above study further indicates that the resin content in the tap hole mix ranges from 10-16%.

Table -4.3: Binder content of different taphole clay

| Clay studied | Standard-1 | Standard-2 | Standard-3 | Standard-4 |
|----------------|------------|------------|------------|------------|
| Binder content | 16.02 | 12.87 | 13.65 | 10.13 |

4.3 Particle Size distribution of washed dried clay

The washed clay was dried in the oven and was sieved for determining the particle size distribution or granulometry. The sieve analysis was carried out with a wide range of sieve sizes 1-3 mm (coarse fraction or CF), 0-1mm (middle fraction or MF) and -200 mesh or $\leq 75\mu\text{m}$ (small fraction or SF) and sieved in a ro-tap sieve shaker to avoid the clogging of sieves as well as to ensure efficient sieving. The results for the different clays are shown in Fig. 4.1 – 4.4. The results indicate that while the maximum size of the particles for Standard 1 and Standard 2 are about 3000 μm that for Standard 3 and 4 are 2000 μm . Further, the median particle size for the four types of clay is:

Table-4.4 Median particle size for the four types of clay

| Clay studied | Standard-1 | Standard-2 | Standard-3 | Standard-4 |
|----------------------|-------------------|-------------------|-------------------|-------------------|
| Median particle size | 500 μm | 250 μm | 500 μm | 500 μm |

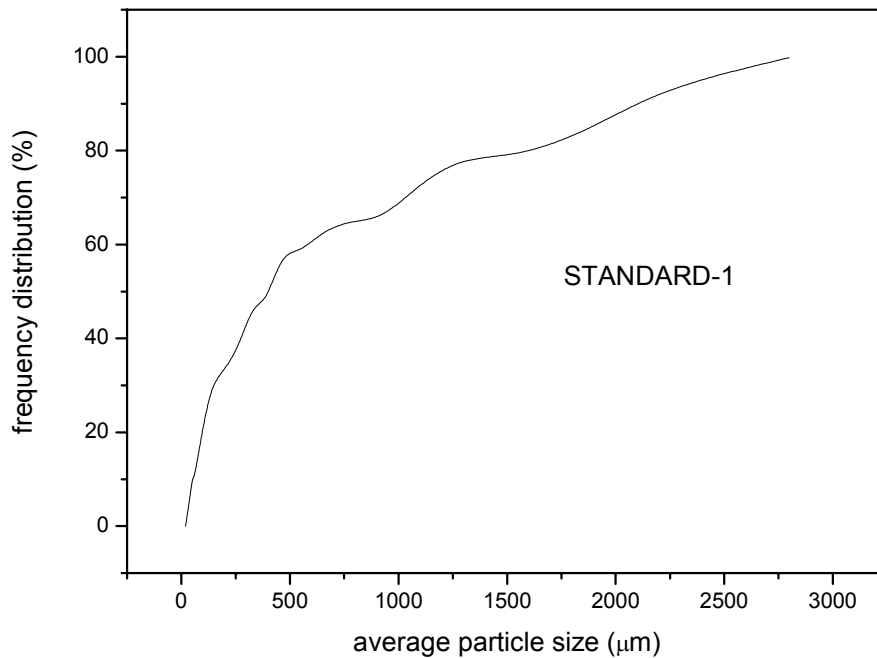


Figure-4.1 Particle Size Distribution of washed dried clay (Standard 1)

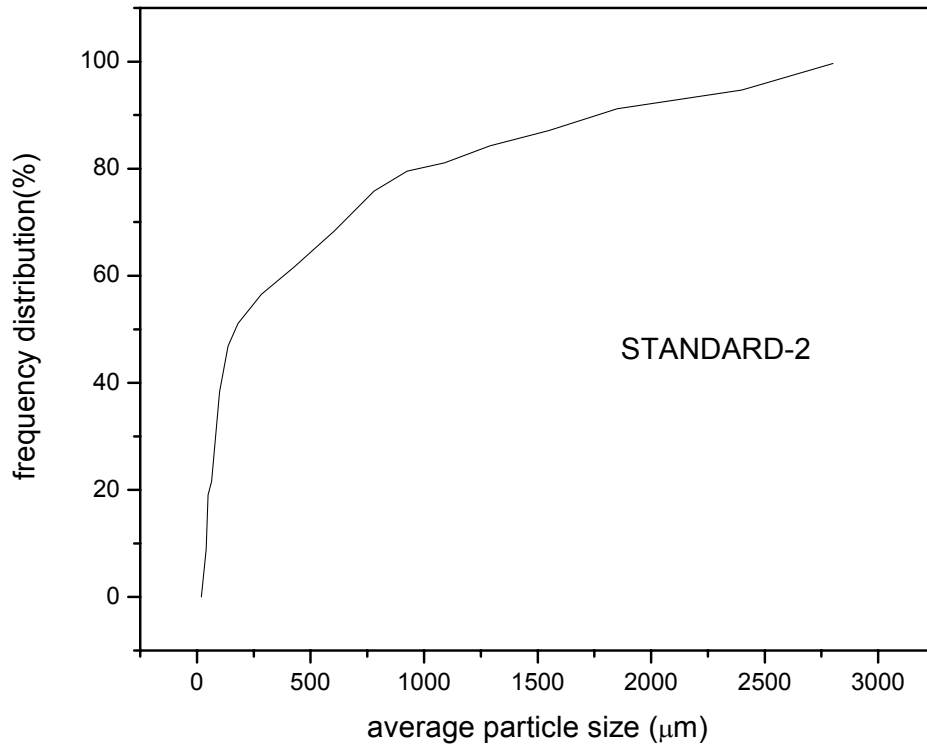


Figure-4.2 Particle Size Distribution of washed dried Standard 2 clay

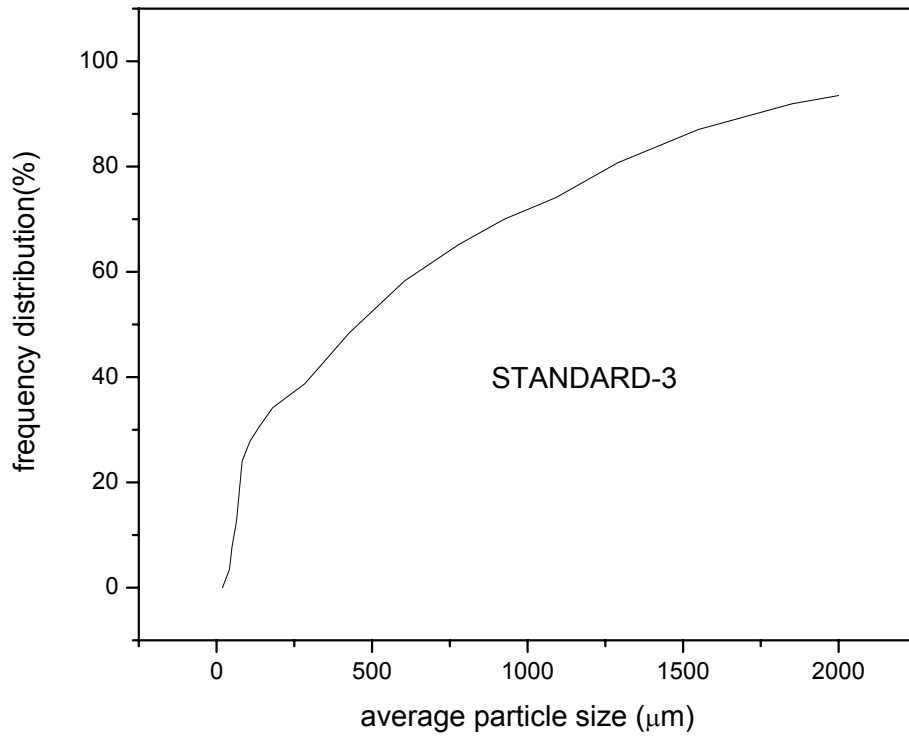


Figure-4.3 Particle Size Distribution of washed dried Standard 3 clay

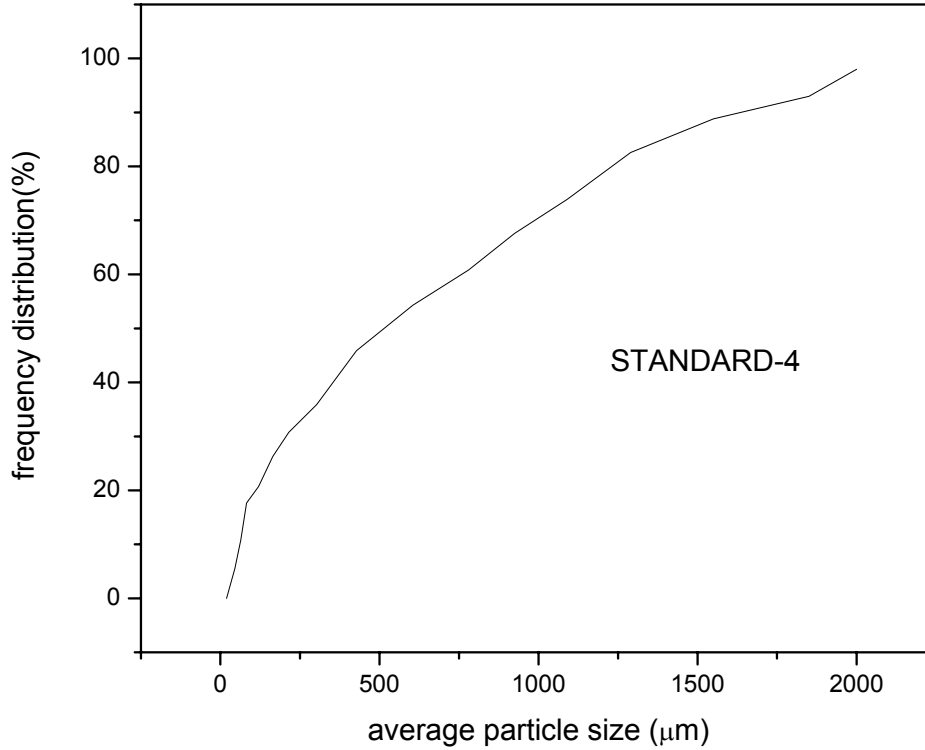


Figure-4.4 Particle Size Distribution of washed dried Standard 4 clay

The weight fraction of different sizes i.e coarse, medium and fine had been calculated from the above particle size distribution and the same is tabulated in 4.5

Table-4.5 Quantitative fractional analysis of four different standard clays

| Type of Clay | Coarse Fraction (%) (1-3mm) | Middle Fraction (%) (0-1mm) | Small Fraction (%) ($\leq 75\mu\text{m}$) |
|--------------|--------------------------------|--------------------------------|--|
| Standard-1 | 30 | 60 | 10 |
| Standard2 | 20 | 40 | 40 |
| Standard-3 | 20 | 60 | 20 |
| Standard-4 | 25 | 50 | 25 |

It is seen from Table-4.5 that on an average the clays use between 19-30% coarse, 40-60% medium and 10-39% fine fractions.

4.4 Phase analysis of Tap hole clay

The phases present in the as received tap hole clay was determined from X-ray analysis. The different phases present in the clay was identified by matching with their standard JCPDS files which were Kyanite (74-2217), Graphite (75-2078), Silicon nitride (82-0701), Quartz (83-0539), Pyrophyllite (74-1193), Corundum (71-1683), Silicon carbide (73-1664).

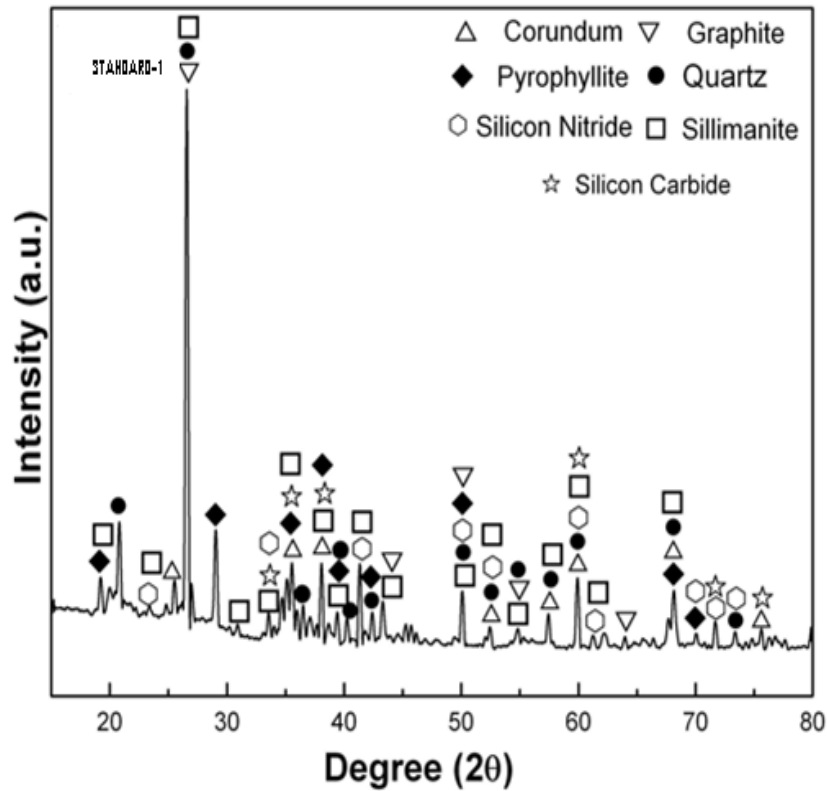


Fig. 4.5 XRD pattern of washed Standard -1 tap hole clay

Figure-3 shows the XRD pattern of the clay Standard-1. The different phases has been identified in the washed clay are Corundum, Quartz, Graphite, Pyrophyllite, SiC, Sillimanite, The XRD patterns of the other three types of standard clay viz. Standard-2, Standard-3, Standard-4 were similar to that of obtained for Standard-2 and hence the XRD patterns of those clays have not been reproduced. However, some clays have some exception like Kyanite in place of Sillimanite in Standard-2 which also contains Si_3N_4 . A detailed semi quantitative phase analysis has been carried out and the results are tabulated in Table 4.6.

Table-4.6 Semi quantitative analysis of different size fraction of washed Tap hole Clay

| Type of clay | | Corundum | Quartz | Kaolinite | Kyanite | Pyrophyllite | Sillimanite | Graphite | SiC | Si ₃ N ₄ |
|--------------|---|----------|--------|-----------|---------|--------------|-------------|----------|-------|--------------------------------|
| Standard 1 | C | 10.42 | 12.08 | -- | 49.61 | 7.38 | -- | 14.21 | 2.11 | 4.19 |
| | M | 6.69 | 15.07 | -- | 45.31 | 6.63 | -- | 17.68 | 3.25 | 5.38 |
| | F | 11.33 | 14.90 | -- | 49.96 | 16.00 | -- | 22.56 | 0 | 2.13 |
| Standard 2 | C | 9.76 | 16.59 | | - | 20.66 | 20.90 | 19.82 | 7.81 | - |
| | M | 10.83 | 14.32 | | -- | 12.42 | 28.19 | 22.32 | 6.50 | -- |
| | F | 11.33 | 20.60 | -- | | 16.00 | 29.50 | 22.56 | 0 | |
| Standard 3 | C | 0.00 | 26.52 | 16.85 | -- | -- | 19.25 | 18.89 | 18.50 | -- |
| | M | 7.48 | 33.63 | 14.67 | -- | -- | 15.07 | 29.15 | 0.00 | -- |
| | F | 33.62 | 26.52 | 6.76 | -- | -- | 15.19 | 14.82 | 0.00 | -- |
| Standard 4 | C | 11.68 | 29.01 | 6.69 | -- | -- | 13.51 | 28.50 | 10.62 | -- |
| | M | 10.19 | 27.00 | 4.77 | -- | -- | 18.37 | 32.61 | 7.06 | -- |
| | F | 0.00 | 0.00 | 32.07 | -- | -- | 49.44 | 18.48 | 0.00 | -- |

Table 4.6 provides the weight percentage of different components as obtained in different size fraction which were Coarse (1-3mm), Medium (0-1mm), Fine ($\leq 75\mu\text{m}$). An analysis of Table-4.6 reveals that these different components had different role. Corundum and Quartz provided the corrosion and wear resistance, Kyanite, Pyrophyllite and too some extent Sillimanite are not only the sources of Al_2O_3 and SiO_2 but they also provide expansion to the clay when heated. Kaolinite gives plasticity, acts as a source of Al_2O_3 and SiO_2 but they are also responsible for shrinkage of the tap hole clay. Graphite provides the non-wetting behavior and drillability while SiC and Si_3N_4 gave high temperature strength and later also acted as a sintering aid. Table 4.7 gives the overall composition of four standard clays. This Table is produced by multiplying the percentage of each component with its size fraction and summing up the percentage for all the three size fractions i.e coarse, medium and fine. For example, for standard 1 clay Table-4.7 gives the percentage of quartz to be 18.49. Table 4.5 shows that the coarse, medium and fine for standard 1 clay is 30, 60, 10. Table 4.6 provides the quartz amount for coarse, medium and fine to be 16.59, 14.32 and 20.60 respectively. Thus, the total amount of quartz in standard 1 clay is $(16.59 * 0.30 + 14.32 * 0.60 + 20.60 * 0.10 = 15.63)$. This explains the different compositions obtained for different clays which is reproduced in Table 4.7.

Table - 4.7 Composition of four different washed tap hole clay

| Components | Standard-1 | Standard-2 | Standard-3 | Standard-4 |
|-----------------|------------|------------|------------|------------|
| Quartz | 13.09 | 15.63 | 29.11 | 18.92 |
| Silicon Carbide | 3.19 | 6.24 | 5.92 | 5.77 |
| Corundum | 9.22 | 10.56 | 8.81 | 8.57 |
| Graphite | 15.13 | 21.60 | 23.55 | 27.88 |
| Pyrophyllite | 8.39 | 15.25 | -- | -- |
| Silicon Nitride | 5.29 | 4.57 | -- | -- |
| Sillimanite | -- | 26.13 | 17.25 | 27.63 |
| Kyanite | 45.7 | -- | -- | -- |
| Kaolinite | 13.09 | | 15.35 | 11.22 |

4.5 Processing of resin and trials on the washed components of the standard clay

4.5.1 Batch composition of Resol and Novolac for different resin ratio

The following Table (Table-4.8) gives the weight of two different resins, viz. Resol and Novolac for different resin ratio both for 12% resin as well as for 15% resin. For any resin ratio, the mixing sequence of resin and clay (or the components) are as follows:

At first, half of the clay or washed components are mixed with Novolac for 10 minutes in the mixing bowl. This is followed by the addition of the Resol and further mixing for 10 minutes. The remaining components are added, mixed for another 10 minutes and the entire mixture is heated between 60-70°C for 5-10 minutes so that the resin becomes viscous fluid and mixing is uniform.

Table 4.8 Batch composition of Resol and Novolac for different resin ratio

| Resin ratio | Amount of tap hole clay | Resol | | Novolac | |
|-------------|-------------------------|-------------|-------------|-------------|-------------|
| | | Maximum 15% | Minimum 12% | Maximum 15% | Minimum 12% |
| 40:60 | 10gm | 0.6 | 0.48 | 0.9 | 0.72 |
| 50:50 | 10gm | 0.9 | 0.6 | 0.9 | 0.6 |
| 60:40 | 10gm | 0.9 | 0.72 | 0.6 | 0.48 |

4.5.2 Results on the Trials carried out with Washed Components of Standard Clay and Prepared Resin

This trial was conducted with two aims in mind: Firstly, what should be the composition of Resol to Novolac for ideal mixing and proper binding of clay to obtain a good pressed compact. Secondly, how the properties vary with resin ratio and the data obtained from the Trial will be useful in determining the optimum resin ratio for tap hole clay. The two different resins were mixed with the washed components of standard clays (1 to 4) as per Table-4.5. It was observed that for resol:novolac 40: 60 and 50: 50 the binding of the clay components was not proper in the green stage and no compact could be made out of it. Proper mixing and good binding was observed for resol : novolac 60: 40. Hence, the trials were carried out with this resin ratio. The following Table provides the data on the physical properties of tap hole clay after firing at 1200°C for 2 hrs.

Table 4.9 AP, BD, CCS and PLC of the Four Standard Clays

| Clay Properties | Standard 1 | Standard 2 | Standard 3 | Standard 4 |
|--------------------------------|-------------------|-------------------|-------------------|-------------------|
| A.P | 32 | 27 | 41.6 | 37 |
| BD | 2.52 | 3.69 | 2.95 | 1.9 |
| CCS (kg/cm²) | 99.5 | 154.86 | 44.2 | 88.49 |
| PLC (%) | 1.6 | 2.1 | 2.3 | 2.3 |

4.6 Indigenously Proposed Trial Batches Similar to Standard 1 and Standard 2

New trials batches were prepared in the light of Standard 1 and Standard 2 Tap hole clay batches. These two as received batches were taken as the references because they provided the best property. Five different batches were prepared keeping Standard 1 as the reference composition. It is to be noted at this page all the four batches (with Standard 1 as references) or the other two batches (with Standard 2 as reference) were not prepared simultaneously. Firstly, one batch was prepared, its properties evaluated and depending on the difference in properties between the Standard and the developed batch, further modification of the batch was made in an attempt to overcome the shortcoming of the previous batch. Table 4.10 provides the base composition of Standard 1 and the five developed compositions of the new batches. The following Table provides the data on the physical properties of tap hole clay after firing at 1200⁰C for 2 hrs. at a resin ratio (R:N) 60:40.

Table 4.10 AP, BD, CCS and PLC of the Five Trials Considering Standard 1

| Composition | Standard 1 | TR-A | TR-B | TR-C | TR- D | TR-E |
|------------------------|-------------------|-------------|-------------|-------------|--------------|-------------|
| Quartz | 13.09 | 19 | 19 | 22 | 19 | 19 |
| SiC | 3.2 | 8 | 8 | 8 | 3.5 | 3.5 |
| Corrundum | 9.2 | 10 | 10 | 7 | 10 | 10 |
| Graphite | 15.13 | 25 | 25 | 25 | 25 | 25 |
| Pyrophillite | 8.39 | -- | -- | | | -- |
| Silimanite | | 38 | 30 | 38 | 30 | 38 |
| Kaolinite | | - | 8 | - | 8 | - |
| Silicon nitride | 5.29 | - | - | | 4.5 | 4.5 |
| Kyanite | 45.7 | | | | - | - |
| 1200(60:40) | | | | | | |
| PLC | 1.3 | 1.9 | 0.5 | 0.4 | 1.5 | 0.9 |
| AP | 28 | 25 | 36 | 32 | 40 | 26 |
| BD | 2.6 | 2.5 | 2.0 | 2.1 | 2.0 | 1.9 |
| CCS | 110 | 110 | 88.5 | 88.5 | 143.8 | 60 |

Table 4.11 AP, BD, CCS and PLC of The Five Trials Considering Standard 2

| Composition | Standard 2 | TR-F |
|------------------------|-------------------|--------------|
| Quartz | 18.5 | 25 |
| SiC | 4.49 | 5 |
| Corrundum | 9.81 | 10 |
| Graphite | 24.7 | 25 |
| Pyrophyllite | 15.82 | -- |
| Silimanite | 23.33 | 20 |
| Kaolinite | | 15 |
| Silicon nitride | | - |
| Kyanite | | |
| 1200(60:40) | | |
| PLC | 2.3 | 1 |
| AP | 28 | 38 |
| BD | 2.7 | 2.0 |
| CCS | 120 | 77.43 |

The ideal value of the for each Standard is given. It is seen that the optimum composition are Trial-E and Trial-F which have close value to ideal.

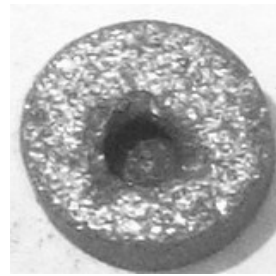
4.7 Drillability

The drillability of Tap hole clay characterized the ease of drilling of the clay after it has been set. The ease of difficulty of the drilling depends on the composition. Presence of high amount of clay causes good densification and drilling may be difficult. Presence of abrasive material lika Al_2O_3 or SiO_2 also increases the difficulty of drilling. The results of the drilling test carried out on five different batches of Tap hole clay based on Standard 1 Tap hole clay and one based on Standard 2 Tap hole caly. Fig (A to F) shows the drill hole. It is seen that drilling is smooth without clay but due to Graphite flakes and SiC, loose pieces were coming out drilling. Figure B shows with higher Corundum and lower Quartz while C is the figure for lower Corundum and higher Quartz. It is clear that drill hole is smooth for higher Corundum

and Quartz. Figure d and E shows the effect of Ferrosilicon Nitride. High amount of Ferrosilicon Nitride causes difficulty in drilling and some chipping is required.



[A]



[B]



[C]



[E]



[F]

Fig 4.6 Drilling behavior of six different Standards

Chapter 5

CONCLUSIONS

CONCLUSIONS

Following conclusions can be drawn from the present study on development of Tap hole clay.

- (1) By optimizing the solvent composition near complete removal of binder/ resin could be achieved.
- (2) The resin composition were also optimized and it was found that the suitable resin is 60% Resol and 40% Novolac.
- (3) The effect of Kyanite could be replaced by changing the corundum and Silimanite composition.
- (4) Graphite and SiC aided in drillability but the sintered clay was not storage.
- (5) Kaolinite caused shrinkage and drilling was also poor.
- (6) A composition of Sillimanite and Ferrosilicon nitride gives a promising result with respect to AP, BD and PLC but it need to be further optimized for CCS and drillability

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