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Physical Sciences

SPECTROSCOPIC AND CHEMICAL EVALUATION OF CLAY MINERALS AND THEIR SUITABILITY FOR THE MANUFACTURING OF ORGANIC CLAY, MEDICINAL CLAY AND PILLARED CLAY

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The levels of trace elements concentration of the clay minerals of Pakistan have been determined. Inductively Coupled Plasma (ICP) spectrometer was used for the determination of trace elements. The samples of the clay minerals were digested in the ETHOS microwave oven at 180 ± 5°C. The trace elements (As, Co, Cu, Cr, Cd, Fe, Mn, Ni, Pb, Se and Zn) in the clay minerals of Pakistan fall within the global range. Except as all the trace elements fall within the technical specification of the medicinal clay. The chemical analysis also shows that (SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, and K_2O) these are within the technical specification of the medicinal clay. Therefore, at present they can be used for external use only. The trace elements (As, Co, Cu, Cr, Cd, Fe, Mn, Ni, Pb, Se and Zn) of clay mineral as well as the activated clay minerals were determined and it is observed that during activation Na, K and Ca ions are leached out. The presence of trace elements of transition metals which are used as catalysts in organic synthesis clearly demonstrate that the catalytic activity of clay minerals is due to these elements. If any of these elements is more than 1% in these clays minerals the clay will act as catalysts without activation. If the quantity of these trace elements is very small and leached out during activation the clay become inactive which is not explained by some workers. Pakistani clays are suitable for making pillared clays. At 550°C, the clay minerals are dehydroxylated and they act as Lewis acid and work as a catalyst in place of $AlCl_3$. It is observed that the clay minerals make complexes with ionic or non ionic surfactant very easily. These complexes make stable suspension in water and oil. It was observed that alkyl group gives a very good organic clay with a swelling property and stable suspension and is superior to the imported clay.

Key words: Spectroscopic evaluation, Clay mineral, Medicinal clay, Pillared clay, Catalyst, Organic clay.

Introduction

There are many medicinal, industrial and chemical uses of clay minerals, all of which depend on one or more of the unique properties of this group of minerals. These minerals have a sheet structure. They form flat, platy hexagonal crystals, white in color when pure. They naturally occur as very fine particles. Water can be absorbed between particles and can hold particles together. Particles slide over each other to form a plastic clay mass that can be absorbed between particles and can be molded and will retain shape when dry. Platy particles suspended in a liquid will link together to coat and protect a surface when dry. They can be compressed into tablets to be used as medicine (Attapulgite is sold as intestopan), melts at high temperature, thermal resistant, electrical insulator. Found in large deposits in several places and is therefore inexpensive.

Large volumes of Na-clay minerals and Na-exchanged, Ca-Mg clay minerals and fuller's earth are directly used in foundry, oil well drilling, iron ore, feed palletizing industries also in civil engineering to impede water movement.

Large quantities of Ca-Mg clay minerals are used directly in iron foundries, in agricultural industries and for filtering and decolorizing various types of oils. A significant portion of Ca-Mg clay minerals used for decolorizing has been acid treated. Large volumes of fuller's or acid earths are commercially used for oil and grease absorbents, as carrier for insecticides, and for decolorizing of oil and fats. Significant volumes of Na-clay minerals are used for various purposes in the manufacturing of many, industrial, chemical and consumer products, such as medical, pharmaceutical, cosmetic, paint (organic clay), building-brick, sewer pipe, roofing tile, gypsum products, pottery-ceramics, radioactive waste disposal, glaze, lubricants, fertilizers, detergents, mortar, catalysts, pa-

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per coating, seed coating, adhesives, water purification and other miscellaneous (Odom 1984).

Spectroscopic evaluation of clay minerals led to an enormous increase of knowledge of natural clay minerals. The chemical constitution of the clay mineral remains as important today as ever it was in its mineralogical description. It is well-known fact that a small difference in the chemical composition of clays can greatly influence the chemical and physical properties (Newman 1987), measuring this difference may be quite demanding on the analytical techniques.

In this study the clay minerals of Pakistan has been subjected to spectroscopic analysis as well as chemical analysis and their suitability for the manufacturing of the medicinal clay used in pharmaceutical and chemical industry, organic clay being used by the paint, ink, paper coating and greases. Pillared clays are used for the development of the catalysts required for the organic synthesis and industrial manufacturing. At present Pakistani clay minerals are not being used for medicinal purposes, as a catalyst in organic synthesis.

Experimental

The clay samples were digested in the ETHOS-Plus microwave system which consists of a programmable 1000-W microwave oven with fume extraction system, 12 sample holder, pressure transducer, computer console, and 12 double-wall Teflon decomposition vessels. The vessels have a capacity of 100 ml with pressure and temperature limits of 200 psi and 260°C, respectively.

Method. Clay samples (1.0 g) were accurately weighed. They were directly added to PTFE digestion vessels followed by the addition of 9 ml of 63% HNO_3 (m/m) and allowed to sit for 10 min to subdue exothermic reactions. After adding 3.0 ml of conc HCl vessels were assembled and loaded onto rotating turntable. The vessels were heated at a temperature of 180± 5°C for a period of 10 min. After digestion, vessels were allowed to cool to at least 70°C in the microwave for safety reasons and to facilitate the condensation of any volatile elements in the digest and to minimize the loss of analytes through any aerosol passing out of the vents. The turntable was then removed and placed in a fume hood to vent and open the vessels. The digests were then transferred to 100 ml volumetric flask and diluted up to mark with deionized water. The samples were then stored in a refrigerator at 4°C. The clay samples solutions after digestion were further diluted ten times before running in the ICP-OES.

The samples were analyzed by the Varion Vista-MPX CCD simultaneous ICP-OES model 1998. The ICP was first standardized by running standard solutions of 1, 10, 20, 30 and 50 ppm of the elements analyzed. The standard solutions were prepared by using metal standard solutions purchased from SCP chemical Co, Canada and are traceable to National institute of standards and technology (NIST) primary standards. Each of the elements in the samples was analyzed at multiple frequencies in the ICP for accuracy and automatic results validation. Results are given in Table 1 and 3.

Chemical analysis was carried out by the standard chemical method (Bennet and Hawley 1965). Results are given in Table 2a and 2b.

X-Rays diffraction (XRD) of the clay samples were taken by using Siemens D5000 X-Ray diffractometer. (Fig 1and 2).

The viscosity of the 30-40% clay solutions in water was measured by the RVT Brookfield viscometer. Results are given in Table 4.

Activation. Finely ground clay (about 10.0 g) was treated with conc. Slowly HCl (200 ml), which was added slowly with constant stirring, the mixture was allowed to stand overnight with occasional stirring. The clay was washed 4-5 times with distilled water till the washing becomes neutral, then dried and calcined at 500°C.

Results and Discussion

Medicinal clay minerals. There is an increasing use of Na-clay minerals in the preparation of medicine, pharmaceuticals and cosmetics. Various forms of clay have been used in medicine from time immemorial either as external or internal remedies. As an external agent kaolin is useful for its protective influence and power of absorbing moisture. As a desiccant dusting powder, it is some time applied to weeping eczemas, freely discharging ulcers, and similar conditions. A paste of kaolin in olive oil is used to protect skin around ileostomy or cecostomy opening from the digestive enzymes. Internally kaolin has been used as an adsorptive in symptomatic treatment of various forms of entrities. It is thought that kaolin provides protective coating for the irritated mucosa, and thereby decreases discomfort. It may also diminish the loss of water and electrolytes until specific therapy can be instituted.

The clay minerals used for medicinal purposes are generally water washed having high brightness in some cases must also be high in magnesium and the toxic metals such as lead must be less than 10 ppm and arsenic must be less than 2 ppm. Paul (1999) published technical specification of the medicinal clays. The trace elements limits of phybiosis by Paul (1999) are given in the Table 1 along with trace element analysis of Pakistani

Table 1
Trace elements in clay minerals of Pakistan

Trace elements in clay minerals	Pakistani clay minerals					
	Fire clay mg/kg	China clay mg/kg	Industrial clays (European commission 2001) mg/kg	Bentonite clay mg/kg	Burfab clay mg/kg	Medicinal clay mg/kg*
As	8.3	5.0	10.0	3.00	3.00	< 1
Ba	194.0	45.0	-	36.00	22.00	-
Cd	0.8	0.3	1.0	0.23	0.20	
Co	8.0	7.0	-	8.00	7.00	17
Cr	57.4	19.0	100.0	11.00	22.00	-
Cu	38.0	44.0	60.0	10.30	14.00	<29.7
Mn	99.0	210.0	-	163.00	139.00	-
Ni	27.0	15.0	75.0	10.00	25.00	-
Pb	27.0	4.6.0	75.0	2.00	26.00	13 to 22
Se	6.0	120.0		10.60	6.00	< 1
Zn	18.0	1237.0	120.0	747.00	16.50	-

(Paul 1999)

clay minerals. The elemental analysis of Pakistani clay minerals was undertaken by (ICP-OES Inductively coupled plasma, optical emission spectroscopy) the results are shown in Table 1. Literature survey showed that the trace elements present in the clay minerals of Pakistan have not been studied before.

All these elements are also present in European and American clays (Table 1) (European commission 2001). Some of these elements are essential for our body and derived from food. Some elements are needed by body in greater amount such as calcium and magnesium. The trace elements like chromium, cobalt, copper, manganese and selenium are needed in smaller quantities but they can be toxic in excess.

Arsenic is present in Pakistani clay minerals is 4-5 mg/kg. Minute traces of arsenic are found in vegetable and animal forms of life. It is a constant element of cell life and is present in eggs (Thomas 1984). Many household and garden pesticides contain various forms of arsenic. All of these are toxic if ingested or inhaled in sufficient quantity. An accumulation of arsenic in the body will cause disorders of alimentery tract, nausea, vomiting, diarrhoea, dehydration, neuritis and paralysis of wrist and ankle muscles. United States Environment Protection Agency (USEPA 2002) has set the limits of arsenic to 1 ppm or less in drinking water. It can cause skin damage or problem with circulatory system, and may have increased risk of getting cancer.

Barium compounds are usually used in paint industries, to kill pests and used to color fireworks. Poising occasionally comes from using the soluble salts in place of insoluble sulfate. USEPA (2002) has set the limits of 2 ppm or less for barium in drinking water. It causes increase in blood pressure. Discharge of drilling wastes, discharge from metal refineries and erosion of natural deposits are the main causes of the presence of barium in drinking water. Barium is quite high in Pakistani clay minerals.

Cadmium is used industrially in electroplating and in atomic reactors. Its salts are poisonous. United State Environment Protection Agency has sets the limits of cadmium in drinking water upto 0.5ppm. The cadmium determined in Pakistani clays is 0.2 to 0.9 which is within the limits of EPA. Increased amount of cadmium causes kidney damage. Corrosion of galvanized pipes, erosion of natural deposits, discharge from metal refineries, run off wastes from batteries and paints are main causes of cadmium presence in water. It is also used as a stabilizer in PVC pipes used for drinking water in Pakistan.

Cobalt can be utilized by humans only as the part of vitamin B_{12}. Average intake are 0.3mg per day. Very high doses (29.5mg per day), which were used in the treatment of certain anemias, have proved to be toxic. In Pakistani clays the quantity of cobalt is within the limits of medicinal clay standards.

Copper is associated with a number of enzymes. Deficiency has occasionally been observed in malnourished infants. Particularly, if their initial stores were depleted for example, prolonged feeding of cow’s milk alone (which contain less copper than most foods) Although shell fish and liver are particularly rich in copper, the main sources in the average diet are meat, bread, and other cereal products and vegetable. USEPA (2002) has set the limits of copper in drinking water up to 1.3 ppm. Short term exposure of copper could cause gastrointestinal distress. Long term exposure could cause liver or kidney damage. Corrosion of household plumbing systems; erosion of natural deposits are main causes of copper in drinking water. Two samples of Pakistani clays contain copper within the limits of the medicinal clay standards Table 1.

Chromium is involved in the utilization of glucose. It is fairly and widely distributed in foods those with high content include brewer's yeast, meat, wholegrain cereals, legumes and nuts. A safe level of intake believes to be more than 25 microgram per day for adults and between 0.1 and 1.0 microgram per kg per day for children and adolescents. Enviroment Protection Agency has set the limits of chromium in drinking water up to 10 ppm. It can cause allergic dermatitis (USEPA 2000). Discharge from steel and pulp mills; erosion of natural deposits are main causes of chromium in drinking water. With the exception of two samples of clay all the samples of clay have chromium within the limits of drinking water.

Manganese is present in number of enzymes and activates others. Tea is exceptionally rich in manganese and plant products, including nuts, spices and whole cereals are general much better sources of manganese than animal products. An essential element needed for normal bone metabolism. Deficiency in humans has not been demonstrated. Pakistani clays are rich in manganese.

Selenium is needed for an enzyme in the red blood cells, and the main dietary sources are meat, fish and cereal products. The selenium content of plant varies widely with level in the soil, and in some parts of the world. Animals fed on local produce develop symptoms of deficiency or excess. Neither is common in humans. In 2000 USEPA has set the limits of selenium in drinking water up to 5 ppm. It can cause hair or fin-ger nail loss; numbness in fingers or toes; circulatory problems. Discharge from petroleum refineries; erosion of natural deposits; discharge from mines are the main causes of selenium in drinking water. Pakistani clay minerals are rich in selenium.

Nickel as a nickel carbonyl is used in plating metals. It is toxic, when inhaled causing pulmonary edema. Nickel is also used as a catalyst in Ghee making industry. The quantity of nickel in Pakistani clays is less than that of in European and American industrial clays. Pakistan standard for Ghee industry is 1ppm.

Lead is a metallic element and its compounds are poisonous. Accumulation and toxicity occur if more than 0.5mg per day is absorbed. Most cases of lead poisoning occur in children eat the paint and thus develop signs of toxicity. The other sources which contribute the lead to the environment are the smoke released by the vehicle using lead containing petrol as an anti-knocking agent. Bentonite and china clay of Pakistan has the lead within the limits of the medicinal clays. All the Pakistani clays meet the standards set for the industrial clays by European commission for environment to be used for any other purposes than medicinal clays.

Zinc helps the healing of wounds, and is also associated with the activity of wide variety of enzymes. Its deficiency many contribute to growth retadation, hair loss, delayed wound healing, emotional disturbances, etc. It is still under discussion that zinc has its role in sex determination during preganancy.

About one third of the comparatively large amount is present in the bones. Zinc is present in wide ranges of foods particularly in association with protein, and meat and dairy products, which are its excellent sources. About one third of zinc in the diet is absorbed, but is reduced if large amounts of whole cereals rich in dietary fibers and phytic acid are eaten, although the amount of zinc present in the whole grain cereals is enough to of set this. Average adult intakes are 9 and 12 mg per day. High intakes from water stored in galvanized containers have caused toxicity.

National Secondary Drinking Water Regulations (NSDWR), (USEPA 2002) are non-enforceable guidelines regulating contaminants like Al, Fe, Cu, Zn, Mn, Ag that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water (USEPA 2002).

Trace elements in the Pakistani clays meet the industrial standards set by the European Commission Directorate General for environment(ECDGE 2001). But there is slight variation in the standards for the medicinal clay. Chemical analyses of clay minerals of Pakistan listed in Table 2 a and b are within the limits set by the Paul (1999) for the medicinal clays. The Pakistani clay minerals are suitable for external use only such as poultices, masks, baths, creams and lotions.

The term "Medicinal clay" used in health care is relating to a clay mineral that has been extracted solely for the purpose of pharmaceutical or medical usage. It is important to differentiate ordinary clay such as the one used in the manufacture of ceramics, from medicinal clays. Although the material is the same, the methods involved in the extraction process as well as the quality standards associated with its applications are entirely different. At present in Pakistan no clay is extracted solely for medicinal purposes.

Clay catalysts. ICP spectrometric analysis of trace elements present in clay minerals and activated clay minerals are re-

Table 2 a

Chemical analysis of clays

S.	Element	Bentonite						Swat China clay					*Extreme
no.		Clay 1	Clay 2	Clay 3 white	Clay 4	Clay 5	*Medicinal bentonite (%)	China 1	China 2	China 3	China 4	China 5	composition (%)
1	Ignition loss	8.00	10.70	10.00	6.20	10.10	-	11.85	11.40	15.80	7.16	8.60	-
2	SiO_2	57.00	46.68	58.80	53.20	49.65	63.5	46.84	44.20	50.30	46.00	44.50	22.8-90
3	Al_2O_3	23.70	14.75	20.45	11.60	15.56	21.4	36.60	36.65	29.75	32.00	37.00	15.6-23
4	Fe_2O_3	7.50	3.25	0.50	10.00	3.50	3.78	0.70	0.75	0.25	0.62	1.75	5.4-6.2
5	CaO	0.10	1.40	0.70	1.40	0.70	0.66	2.10	4.25	0.70	10.22	5.02	0.4-13
6	MgO	2.26	6.08	5.87	3.54	4.16	2.03	0.67	2.06	0.50	1.00	2.98	11-12
7	Na_2O	0.47	5.40	3.00	2.40	4.80	2.70	0.50	0.54	0.27	1.65		0.1-1
8	K_2O	0.86	0.68	0.60	0.70	0.66	0.310	0.30	0.01	1.80	0.09		3.4-3.7

*Paul 1999

corded in the Table 3. These trace elements (As, Cd, Ni, Mn, Co, Cu, Pb, Fe, Se and Zn) and their compounds have been used as catalysts for the synthesis of organic compounds in the laboratory as well as on industrial scale. It is observed that the increase in any one of these elements or more in the clay minerals increases the catalytic activity of clay minerals. Ehsan *et al* (1999) carried out the analysis of red clay by XRF spectrometer. In this clay iron and titanium are present in substantial quantity(Fe 17-37%, Ti 4.75%) and even after activation the amount of these elements was less effected as compared to the other elements like Ca, Na, K. Ehsan *et al* (1999) synthesized 9, 10 dihydroanthracene by using red clay as a catalyst. We believe that unactivated clays may be treated as potential catalysts. Activated clay catalysts have been used for hydrogenation, polymerization, and hydroformylation for cracking. All of these catalysts have been used at much higher temperature than the catalytic activity we observed for our catalyst for Friedel Crafts benzylation.

The chemistry of the acid activation process and properties and chemistry of the resultant catalysts have been discussed by (Mills *et al* 1950; Thomas *et al* 1950; Hansford 1952; Miliken *et al* 1955; Ryland *et al* 1960). Thomas *et al* (1950) postulated that removal of one of pair of octahedral aluminum ion from montmorillonite, for example, removes two hydroxyl groups and leaves the other of the aluminum in four fold coordination. This tetrahedral aluminum, with its charge balancing proton, form a bronsted site and is the source of the catalytic activity. However, Mills *et al* (1950) have shown the cracking activities of acid treated bentonites from various deposits cover the range from inactive to a level of activity comparable to silica alumina. This range exists despite of almost identical physical properties after acid treatment, for both activable and non activable bentonites. A possible basis for differentiating between these two classes may be found in the observation by Milliken *et al* (1955) that acid activation of raw kaolinite and halloysite, followed by calcinations led to catalysts of inferior quality. However, if calcinations at 550°C precedes the acid leaching step the activity of the catalyst so obtained from either halloysite or kaolinite was greatly improved. Calcination of the kaolin at this temperature should have caused dehydroxyaltion with its accompanying transition to metakaolin.

The spectroscopic analysis of Pakistani clays indicates the catalytic activity is due to the presence of transition metals present in all the clays. If any of these transition elements exceeds more than 1 percent of the clay composition, the clay become active without acid activation. We believe the activity of the clay minerals is due to these transition metals.

X-Rays diffraction (XRD) pattern of the clay before and after activation indicated that both are disordered kaolinite $Al_2Si_2O_3(OH)_4$ and illite trioctahedral KO_5(Al, Fe, Mg,) 3(Si, Al)$_4$O$_{10}$. After acid treatment a change is observed in the proportion of transition metal (Fe, Ti) and Al. X-ray diffraction of laterite is recorded in Fig 1. The (XRD) of activated laterite is recorded in Fig 2. The peak at d = 7.1 of laterite is completely eliminated in the activated laterite. This shows that hydroxlated phase in laterite is totally de-hyroxylated and the de-hydroxylated phase is not completely amorphous (Fig 2).

The treatment with cold conc. HCl has little effect on the composition of the host layer and results in acid treated clay. The acid attack on the clay structure progresses inwards from the edge of the clay platelets leaching alkaline cations, particularly Mg, Ca, K and to some extent Fe. Acid activation causes little damage to the silicate layer and the structure in the centre of the clay platelets remain unaffected. The trace elements in all the clay minerals are affected with even cold acid treatment. This explains if the quantity of the transition trace elements in mineral clays is negligible this will become totally inactive with acid treatment. This explains why some clay minerals have no catalytic activity after activation. The Pakistani clays have all the properties to act as a catalyst itself or to act as a pillar to make a suitable catalyst for the synthesis of organic compounds.

The Pakistani clay minerals contain about 16 times more Fe and three times more Ti than the Indian clay minerals. Sabu *et al* (1993) calcined the clay then dried the catalyst after acid treatment at 110°C. It has been reported that if clay is heated upto 110°C so as to remove most of the interlamellar water until only one layer of water remains at about 5% of total water. This increases the Bronsted acidity in Friedel-Crafts reaction $AlCl_3$ is a Lewis acid that takes up an electron pair to form a co-ordinate covalent bond. Ehsan *et al* (1999) after

Table 2 b

Chemical analysis of clays

S. no.	Elements	Fire clay			Ball clay	High alumina clay	Ball clay	Clay (white)	Clay (black)	*Medicinal clay (%)
		Clay 1	Clay 2	Clay3						
1.	Ignition loss	14.20	12.20	15.30	16.00	13.40	10.40	8.20	7.20	
2.	SiO_2	44.40	47.75	46.00	31.30	33.80	56.20	61.20	58.40	56.70
3.	Al_2O_3	38.25	36.10	34.73	51.18	48.98	32.70	25.00	28.00	23.00
4.	Fe_2O_3	0.75	1.00	0.37	0.12	0.25	0.10	0.75	5.00	5.83
5.	CaO	1.40	0.32	1.40	0.70	0.70	0.15	0.27	1.40	0.45
6.	MgO	0.50	0.52	0.50	0.50	0.50	0.07	0.35	0.50	0.07
7.	Na_2O	--	0.13	0.65	--	0.03	0.09	0.15	--	0.01
8.	K_2O	--	0.26	0.86	--	0.01	0.01	0.26	--	3.6 0

*Paul 1999

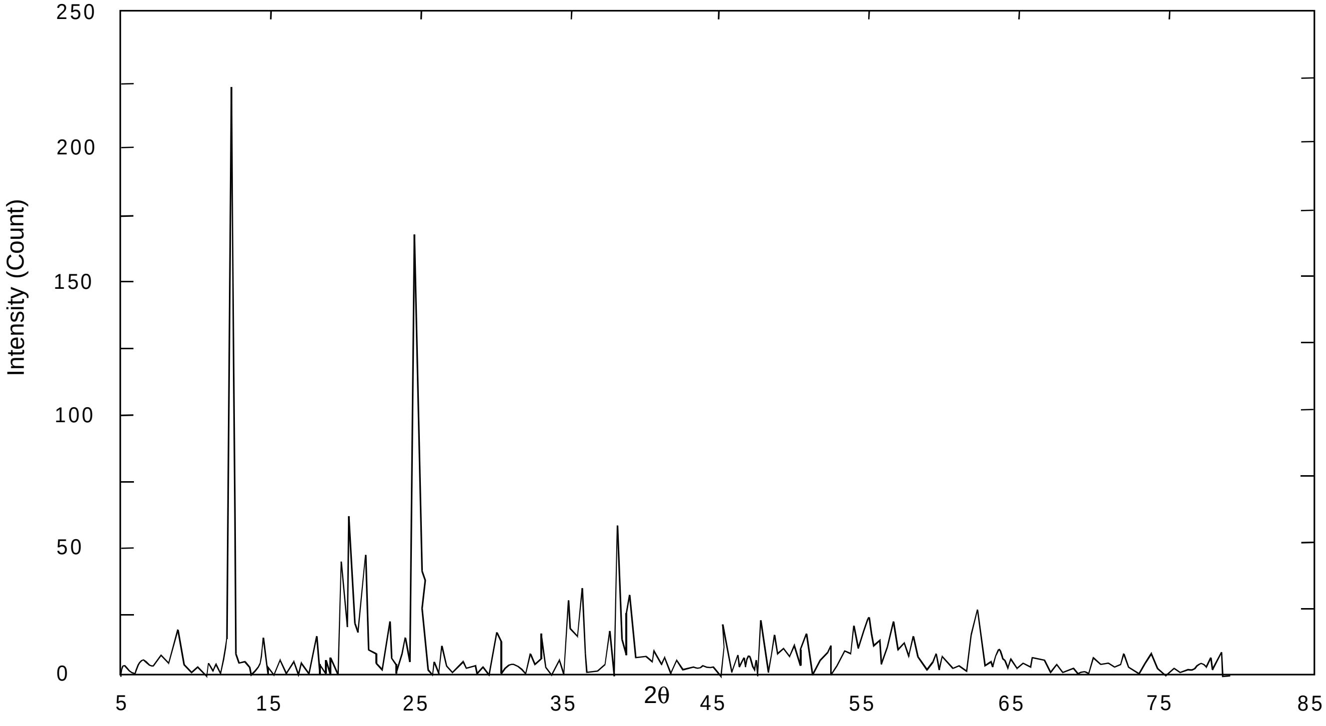

Fig 1. X-Rays diffraction of the clay samples by using Siemens D 5000 X-ray diffractometer

treating the clay with acid calcined it up to 550°C, which results in decrease in the Bronsted acidity but increase in Lewis acidity. This resulted in the formation of L 99 catalyst which is ideal for benzylation.

Commercially marketed clays are montmorrillonite and beidellite. These clays are amorphous and have good swelling property. These are marketed as cation exchanged clays or large polyatomic inorganic ions intercalated into montmorillonite clays. These catalysts are not acting at less than 100°C for Friedel Crafts benzylation.

The L99 has moderate catalytic activity as compared to $AlCl_3$. Hence the poly substitution and polymerization is not possible with L99. This property has enabled us (Ehsan *et al* 1999, 2001and 2002) to synthesize following compounds 9, 10 dihydroanthracene, biphenyl methane, benzyl naphthalene, *o* and *p* hydroxy biphenyl methane, 1-benzyl 2- napthol and 4-

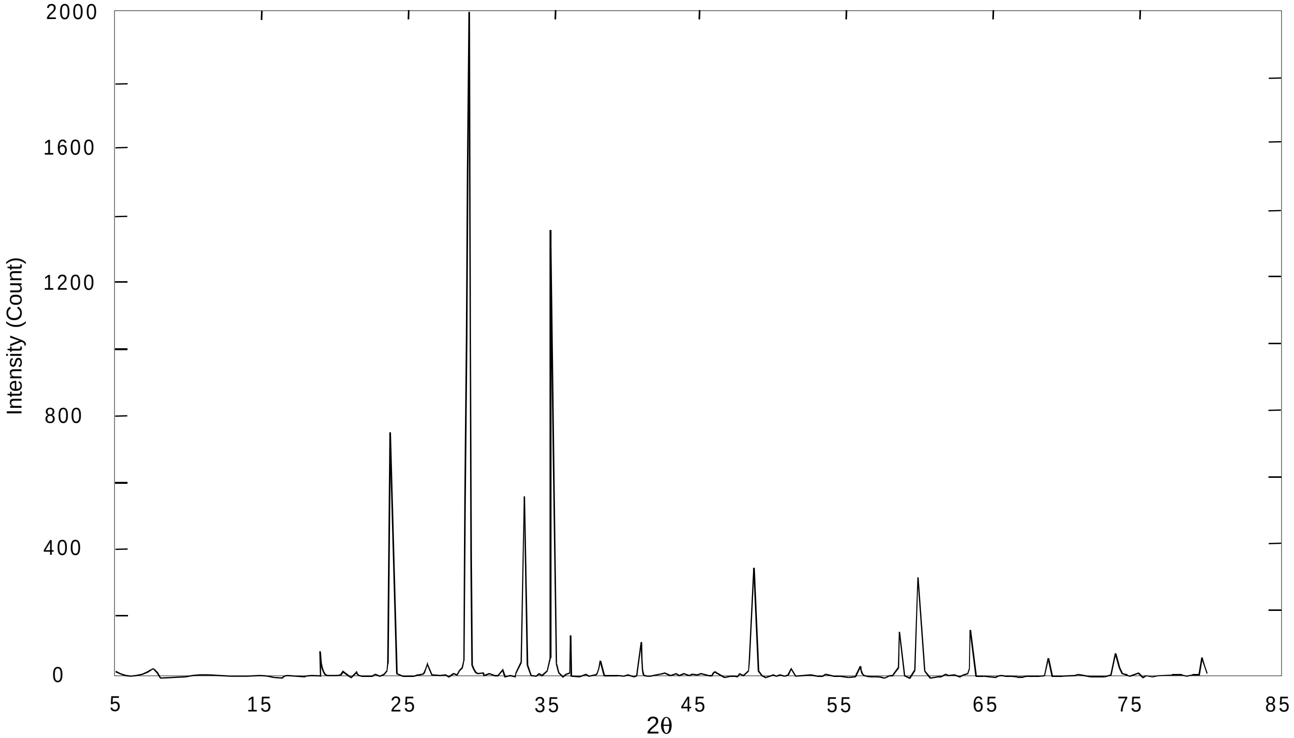

Fig 2. X-Ray diffraction of activated laterites of the clay samples by using Siemens D 5000 X-ray diffractometer

Table 3
Catalytic activity of Pakistani clay minerals

S. no	Trace elements	Bentonite		Fire clay		Laterite		China clay	
		Unactivated	Activated	Unactivated	Activated	Unactivated	Activated	Unactivated	Activated
1	As	3.0	2.4	8.3	7.0	32.0	10.0	5.0	4.00
2	Cd	0.23	0.05	0.8	0.5	9.0	7.0	0.3	0.02
3	Co	8.0	7.0	8.0	3.3	93.0	80.0	7.0	1.2
4	Cr	11.0	11.0	57.4	5.5.0	941.0	785.0	19.0	7.2
5	Cu	10.3	10.0	38.0	126.0	137.0	62.9.0	44.0	12.0
6	Fe	134.0	92.0	170.0	3627.0	-	-	11836.0	5968.0
7	Mn	163.0	162.0	99.0	17.7	308.0	93.0	210.0	48.0
8	Ni	10.0	10.0	27.0	23.0	50.0	34.0	15.0	9.3
9	Pb	2.0	2.0	27.0	12.0	61.0	38.7	4.6	6.0
10	Se	10.6	10.0	6.0	7.0	0.8.0	1.0	120.0	26.0
11	Zn	747.0	747.0	18.0	569.0	165.0	84.6	1237.0	1511.0

benzyl 1- napthol (Fig 3).

Presence of transition metals in the minerals and clay minerals, elimination of basic cations such as Na, K, Ca and Mg and the de-hydroxylation of clay mineral at 550°C is the essential requirement for the development of suitable catalyst.

Organic clay. Natural sodium clay minerals occur in commercial quantities in only few places, but Ca- Mg clay and fuller's earth deposits of considerable size occur on almost every continent. Attempts to change Ca-Mg clay minerals to so called sodium clay minerals are a common practice in the clay industry, especially where naturally occurring sodium clay deposits are rare. The ion exchange is usually performed by mixing soda ash (sodium carbonate) with crude, moist clay using various mechanical methods. A simple determination of hydration characteristics should be given priority in evaluation of clay mineral deposits as so many industrial uses are dependent on this unique property (Table 4). A num-

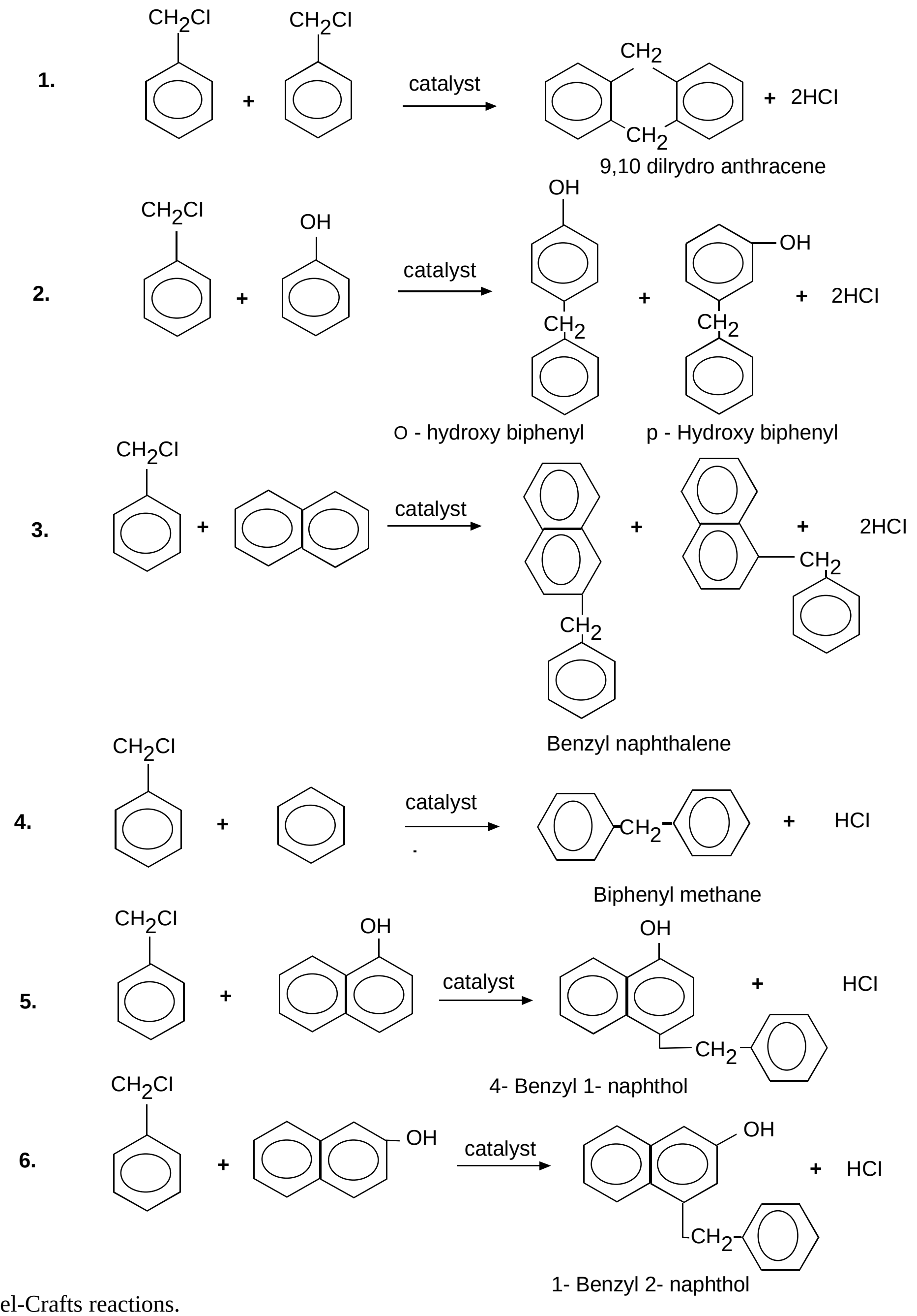

Fig 3. Friedel-Crafts reactions.

Table 4
Viscosity of clays

Sample no	Initial reading	At 30% solid leaching			At 40% solid leaching	
		After 03 h	After 24 h	After 48 h	After 24 h	After 48 h
1	15	15	90	155	200	375
2	15	15	50	65	215	390
3	15	15	120	250	285	605
4	15	15	180	270	330	425
5	15	15	30	45	110	165
6	15	15	65	110	315	450
7	15	15	20	20	370	555
8	15	15	40	40	225	400
9	15	15	15	15	150	150
10	15	15	15	65	130	235

ber of samples of clay minerals were subjected to hydration tests results are recorded in Table 4. Some of the samples swelled significantly. This swelling property showed the suitability for industrial use. The vast majority of naturally occurring clay mineral having Ca-Mg as the predominant exchangeable cations is essentially non swelling.

The property of clays to exchange inorganic cations by organic cations and also the uncharged polar compounds could enter the interlayer space without cation being released, has resulted in the development of useful number of organo-clay complexes (Odam 1984).

Organic-clad clays are widely used for stabilizing the gel properties of lubricating greases. The greases prepared with organic clad clays are said to have superior properties.

Similarly these organic clad clays are used in both oil and water based paints. Natural, Na exchanged Ca and organic clad clays are used in both oil and water based paints. The clays act as suspending and thickening agents and the gel structure is said to improve brush ability and spraying characteristics and to reduce pigment penetration into porous surfaces. They are used in printing inks to control the consistency, penetration and misting during the printing operation. These organic clad clays are not manufactured in Pakistan. At present these are being imported by the paint and grease industry.

As clay minerals make complexes with organic compounds easily. These complexes are prepared with anionic (like alkyl benzene sulfonate, alcohol ethoxy sulfates etc) and nonionic (alcohol ethoxylates, alkyl phenol ethoxylates etc) surfactants. The sedimentation test was carried out and it was observed that they are stable suspension in oil and water Table 4. Complexes with long chain alkyl ammonium ions showed the best swelling and sedimentation properties. They are better in texture and are suitable for both water and oil paints when compared with imported clays, their properties are better than the imported clays.

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