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CHARACTERIZATION OF COAL AND WASTES FROM ZONGULDAK COAL WASHERY AND EFFECT OF CLAYS ON COAL FLOTATION

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T.C. YÜKSEKÖĞRETİM KURULU
DOKÜMANTASYON MERKEZİ

To My Parents,
and my wife, Tasneem Zahra
and our son, Mohammad,
and our daughters, Batool and Fatima

Approval of the Graduate School of Natural and Applied Sciences.

for Prof.Dr. Alpay Ankara

Director

I certify that this thesis satisfies all the requirement as a thesis for the degree of Doctor of Philosophy.

Prof.Dr. Günhan Paşamehmetoğlu

Chairman of the Department

We certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Doctor of Philosophy in Mining Engineering.

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ABSTRACT

CHARACTERIZATION OF COAL AND WASTES FROM ZONGULDAK WASHERY AND EFFECT OF CLAYS ON COAL FLOTATION

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In this study, the qualitative and quantitative mineral composition of Zonguldak washery wastes, coal and black water have been determined, with an emphasis on the characterization of clays which harmfully affect various processes. The petrographic analysis of wastes revealed an average of 58 % (by volume) clay minerals in addition to silicates, coal, carbonates, sulphides and magnetite. The XRD analysis of all the samples showed qualitatively and semi-quantitatively, the presence of three clay minerals, illite, kaolinite and chlorite. The washery wastes were abundant in illite (47 %) whereas coal and black water samples showed the dominance of kaolinite (58 %) and illite (65 %), respectively.

For semi quantitative XRD analysis, coal samples were pretreated to remove organic carbon and also subjected to low temperature ashing (LTA) for verifying the presence of three clays.

Loss on ignition analysis of all the samples revealed that organic carbon ranged from 5-63 % where as carbonates were 3-6.5 %.

Mineral matter of coal found by acid digestion, LTA and Parr formula were 39.8, 42.2 and 38.2 %, respectively. The sulphur content was 0.48 %.

The zeta potential measurements of clean coal gave isoelectric point at pH 4.1. The pure kaolinite had more negative zeta potential than chlorite and illite and no point of zero charge (pzc) value was obtained for kaolinite whereas illite and chlorite gave pzc's at pH 2.5 and 3.0 respectively.

The zeta potential of clean coal by using electrolytes showed that only Al^{3+} cations reversed the sign of the charge. The use of depressants and dispersants on coal increased the negative zeta potential.

Three pure clays namely kaolinite, illite and chlorite from Turkey and clean coal samples were floated as artificial coal-clay mixture; illite had the worst, chlorite the worse and kaolinite the least harmful effect by depressing the coal.

The direct flotation of 35.1, 39.9 and 67.1 % ash coals with kerosene oil, Pamak 4 and oleic acid revealed that Pamak 4 gave 20 % higher yield than kerosene oil at the same ash level, indicating its future potential.

The reverse single stage flotation with Flotigam ENA of 35.1 % ash coal successfully brought 62 % yield with 16.5 % ash in concentrate, and two stage flotation by combining direct flotation using Pamak 4 followed by the reverse flotation of the concentrate gave lower ash product (12 %) with a yield of 55 %.

Key Words: Washery Wastes, Clay Minerals, XRD Analysis, Low Temperature Ashing, Zeta Potential, Coal-Clay Flotation.

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ÖZ

ZONGULDAK LAVVARI KÖMÜR VE ATIKLARININ ÖZELLİKLERİNİN BELİRLENMESİ VE KİLLERİN KÖMÜR FLOTASYONUNDAKİ ETKİSİ

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Bu çalışmada, çeşitli işlemleri olumsuz şekilde etkileyen killerin belirlenmesine ağırlık verilmek üzere Zonguldak lavvarının katı atıkları ile kömür ve lavvar suyunun mineral içeriği nitel ve nicel olarak tesbit edilmiştir. Petrografik analiz, katı atıklarda ortalama hacimce % 58 oranındaki kil minerallerinin yanında silikatlar, kömür, karbonatlar, sülfürler ve manyetitin bulunduğunu göstermiştir.

XRD analizleri tüm örneklerin illit, kaolinit ve klorit olmak üzere üç çeşit kil minerali içerdiğini göstermiştir. Lavvar katı atıklarında illitin (% 47), kömür ve lavvar suyunda ise sırasıyla kaolinit (% 58) ve illitin (% 65) çoğunlukta olduğunu göstermiştir. Yarı-nicel XRD analizleri için kömür örnekleri karbonu uzaklaştırmak amacıyla ön işleme tabi tutulmuş ve kil minerallerinin varlığını göstermek için düşük sıcaklık küllendirmesi (LTA) yapılmıştır.

Ateş kaybı analizleri, bütün örneklerde % 5 - % 63 arasında organik karbon ile, % 3 - % 6.5 arasında karbonatın varlığını göstermiştir..

Kömür örneğinin asitle özümleme, düşük sıcaklıkla küllendirme ve Parr formülü ile bulunan mineral madde miktarı sırasıyla % 39.8, % 42.2 ve % 38.2 olarak bulunmuştur. Kömürün kükürt içeriği ise % 0.48'dir.

Temiz kömür ile yapılan zeta potansiyel ölçümleri, kömürün eş elektrik noktasının (IEP) pH 4.1 de olduğunu göstermiştir

Sıfır yük noktası (pzc) olmayan kaolinitin illite göre daha negatif zeta potansiyele sahip olduğu, illit'in ve kloritin sıfır yük noktalarının sırasıyla pH 2.5, ve pH 3.0'de oluştuğu anlaşılmıştır. Temiz kömürde elektrolitlerle yapılan zeta-potansiyeli ölçümleri, Al^{+3} katyonunun kömürün yüzey yükünün işaretini değiştirdiğini göstermiştir. Dağıtıcı ve bastırıcıların kullanılması ise kömürün negatif zeta potansiyelini arttırmıştır.

Saf kaolinit, illit, klorit ve temiz kömürden oluşan sentetik karışımlar ile flotasyon deneyleri yapılmış, ve kömür için en zararlı kil mineralinin illit, en zararsız kil mineralinin ise kaolinit olduğu tesbit edilmiştir.

% 35.1, %39.9 ve % 67.1 kül içeren değişik kömür örnekleri üzerinde gazyağı, Pamak 4 ve oleik asit kullanarak yapılan direkt flotasyon çalışmalarında, aynı kül içerikli kömür üretiminde Pamak 4'ün gazyağına göre % 20 daha fazla verim sağladığı gözlenmiştir. Bu toplayıcı gelecek için ümitli görünmektedir.

Flotigam ENA kullanarak % 35.1 küllü kömür ile yapılan tek basamaklı ters flotasyon deneyi sonucunda % 16.5 kül içerikli temiz kömür, % 62 lik bir verimle kazanılmıştır. Pamak4 kullanarak yapılan düz flotasyon ve onu takip eden ters flotasyondan oluşan iki aşamalı flotasyon ile % 12 küllü temiz kömür % 55'lik bir verimle kazanılmıştır.

Anahtar Kelimeler: Lavvar Atıkları, Kil mineralleri, XRD Analizi, Düşük Sıcaklık Küllendirmesi, Zeta Potansiyel, Kömür-Kil Flotasyonu.

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NOMENCLATURE

XRD	X-Ray Diffraction
IEP	Isoelectric Point
pzc	Point of Zero Charge
rom	Run of Mine
HLB	Hydrophile-Lipophile Balance
LTA	Low Temperature Ashing
IR	Infrared
FTIR	Fourier Transform Infrared
DTA	Differential Thermal Analysis
A	Angstrom
J.C.P.D.S.	Joint Committee on Powder Diffraction Search
PDI	Potential Determining Ions
BSS	British Standard Sieve Series
ASTM	American Society of Testing and Materials
COPO	Cool Oxygen Plasma Oxidation
mm	Millimeter
rpm	Revolution per minute
MIBC	Methyl Isobutyl Carbinol
g/t	Grams per tonnes
cm	Centimeter
Kg	Kilogram
L	Liters
ml	Milli liters
mV	Millivolts
tph	Tonnes per hour
Kcal/Kg	Kilocalories per kilogram
SEM	Scanning Electron Microscopy
^{o}C	Degrees Centigrade
m	Meter

CHAPTER I

INTRODUCTION

1.1 General

Turkey has a large bituminous coal mining industry with its centre at Zonguldak coal fields, where four washeries are in operation, namely, Çatalağzı, Kandilli, Amasra and Zonguldak Main Washery. Zonguldak Main Washery has the biggest capacity of washing 1000 tons per day of 0-100 mm coal, established in 1957, to clean coal produced from Üzülmez and Kozlu districts (Özbayoğlu, 1977). The washery consists of three units; the coarse jigging section using Baum jigs treating 100-6 mm coal, the fine feldspar jigs treat 6-0.5 mm and minus 0.5 mm comprising about 15-20 percent of the r.o.m. coal goes to flotation cells for treatment.

In flotation circuit, a mixture of 95 percent kerosene and 5 percent di-ethyl hexanol is added to the pulp just before feeding the flotation cells. The consumption of this reagent is about 600 grams per ton of coal treated. A coal concentrate is obtained with 60 percent recovery containing ash around 16 percent (Özbayoğlu, 1977). Elsewhere recoveries even below this ranging 40 to 50 percent at the same ash levels have been reported (Sezgin, 1973).

Coal flotation has been practiced in Turkey for more than 35 years and of course it met with many problems for obtaining low ash product without sacrificing the recovery. Some of these problems were pointed out by Özbayoğlu in 1977, along with a need for research to solve these problems. As a pioneer, she correlated flotation characteristics of Turkish bituminous coal with physical, chemical and particularly with the petrographic composition. Another investigation in this direction filled the gap by finding flotation characteristics of oxidized coal (Sarıkaya, 1988). Although these researches were of great value to understand the nature of floatability of Zonguldak coal, yet they were limited in scope towards solving the practical problems of washeries encountered due to their high level of impurities particularly clays which resulted in low recoveries and high ash upon washing the coal, as well as the difficulties met later during dewatering and filtration operations.

Clay minerals in coal, constituting 60-80 percent of mineral matter (McClung et al., 1979) and shales swell in presence of water, resulting in high proportion of slimes on disintegration which cause considerable loss of recoveries in flotation due to their coatings on mineral and bubble and increased reagent consumption (Brown, 1954; Jowett et al., 1956; Burdon et al., 1976; Mishra, 1978; Arnold and Aplan, 1986a). Other investigators (Yancey and Taylor, 1935; Neczaj et al., 1974; Lynch et al., 1981; Arnold and Aplan, 1990) have found no loss of coal due to slimes but water carry over mechanism was thought to be mainly responsible. In order to resolve the controversy, Arnold and Aplan (1986a) investigated the effect of clays on coal flotation by using artificial mixtures of pure coal and clays. They used bentonite, illite and kaolinite, most commonly occurring clays in U.S.A. coal (Gluskoter, 1967; O' Gorman and Walker, 1972; Rao and Gluskoter, 1973) and found that bentonite was the most harmful clay for coal flotation. They could not match their results with actual system as the coal used in their study was not well characterized and therefore, exact role of clays could not be assessed by them.

Recently (Garcia et al., 1991; Tarazona et al., 1992) on characterization of coals from Asturian central basin (NW Spain), it was found that major clay minerals in decreasing order of abundance were illite, kaolinite, mixed layers illite-smectite and chlorite.

In Turkey washeries are facing such problems and Zonguldak coal washery recently switched over to flocculation in place of flotation for fine coal below 0.5 mm. In view of the difficulties in floating fine, high ash Zonguldak coal, research work into characterization of clays and their effect on flotation was undertaken in this study.

1.2 Statement of Problem

In general the object of this study is to characterize the clays of Zonguldak coal washery and to investigate their effects on coal flotation. Hence the following specific research areas were identified for experimental investigatation.

1. Clays should be well characterized in the washery wastes and coal, in respect to their type and amount present.
2. After characterization, their amount in terms of mineral matter should be determined.
3. As different clays affect coal flotation differently, their effect should

be determined by floating artificial mixtures of pure coal and clay.

4. Zeta potential measurements of pure coal and clays to be carried out to correlate the effect of clays on coal flotation and zeta potential.

5. The effect of clays, determined by floating the artificial coal/clay mixtures, should be matched with actual system. Flotation Feed (below 0.5 mm), containing 35.1 percent ash floated under the same conditions should be designated as the actual system. A comparison of the two is expected to reveal the effect of clays due to slime coatings and due to the water carry over mechanism.

6. Coal flotation with ionizing collectors such as oleic acid and Pamak4 (a combination of linoleic, oleic and rosin oil acids), regarded up till now as only of scientific interest should be carried out on the basis of their better activity compared to kerosene oil (hydrophile-lipophile balance "HLB" value of 17 for oleic acid and 14 for K. oil) as reported in literature on surfactant science and technology (Myers, 1988). A comparison of these two systems of direct flotation should give a better insight in to the use of ionizing collectors, particularly for flotation feeds consisting of fine, high ash coals. A success if achieved, may be a useful technique for dealing with other fine high ash coals (e.g. 39.9 % and 67.1 % ash).

7. Reverse flotation for coals containing high ash and sulphur is usually done in the two stages, in which pyrite is floated with xanthate in the second stage while coal is depressed with carboxymethyl cellulose

(CMC) or dextrin (Miller, 1973; Laskowski et al., 1985).

Single stage reverse flotation has been a dream for researchers to float high amount of clays associated with coal. Some partial success by floating quartz in coal-quartz artificial mixtures with quartenary amines was claimed (Stone Street and Franzidis, 1989). Flotation studies involving actual system (flotation feed) with amines should be attempted in order to find a way more suited to coals containg high amount of clays, not amenable to direct flotation very efficiently.

8. Two stage flotation a combination of direct flotation using ionizing collectors in first stage and then floating the clays by using amines in second stage (Reverse flotation) while depressing coal with dextrin, may not be very attractive during normal flotation practice of coal but may have some benefits for difficult to float coals where all other available techniques fail.

9. Use of dispersants, depressants and electrolytes in coal flotation have not shown encouraging results (Arnold and Aplan, 1986a; Arnold and Aplan 1986b). However to explore their effects on zeta potential of coal and flotation of coal, and coal/clay mixture comprises a part of this study.

CHAPTER II

CHARACTERIZATION OF COAL AND WASHERY WASTES: THEORETICAL ASPECTS

2.1 General

Coal is a black or brownish black combustible solid derived from a heterogenous mixture of plant remains and associated mineral matter that have undergone chemical and physical metamorphic changes by biological and geological processes. It is composed principally of carbon, hydrogen and oxygen with lesser amounts of nitrogen and sulphur, ranging in rank from anthracite to lignite and brown coal (Aplan, 1988) with massive variations in chemical and physical properties through these ranks. Luckie (1988) asserted that there is no such thing as coal; there are coals. Zonguldak has high volatile bituminous coal, sometimes with a very high percentage of mineral matter (Toprak, 1984). The coal consists of ash 10-40 %, volatile matter 29.5-33.8 %, carbon 86.2-86.7 %, hydrogen 5.1-5.7 % sulphur 0.4 to 0.9 %, oxygen 5.6-6.3 % and has calorific value 8180-8280 kcal/kg (T.K.İ. Kurumu, 1973).

The complications do not end with characterizing the coal material because coal seams also contain a broad range of mineral matter. So in fact, a coal preparation engineer has to deal not with coal (and its properties) that comes from the coal seam per se, but with raw coal which includes overbreak of roof and floor materials incorporated in to the coal during mining. The massive variability of the amount and nature of coal, the ash forming minerals and pyrite will dictate what may be expected in the preparation process (Aplan, 1988). Intergrown minerals including clays, pyrite, siderite and fine grained quartz are the principal source of ash in washed coal. Clay minerals account for 60-70 % of all mineral matter intergrowth and the most frequent types are kaolinite (low swelling but high ash fusion point) and illite (prone to swelling). These two minerals can indicate the degree of metamorphism as kaolinite decreases in proportion with increase in temperature and pressure where as illite increases and alters to chlorite with further increases (Falcon, 1978a).

2.2 Methods of Characterization of Coal Refuse

Jenkin and Walker (1978) described the methods used for mineral matter analysis in coal, which was responsible for its ash determined by heating the coal at 700 °C to 850 °C in muffle furnace according to ASTM procedure. The mineral matter can be calculated from Parr Formula: (Parr, 1932; Tsai, 1982).

$$\text{Mineral Matter} = 1.08 \text{ ash} + 0.55 \text{ sulphur}$$

The mineral matter can also be found by demineralizing coal with alkali treatment (Wang et al., 1986) or by acid digestion using HCl and HF (Bishop and Ward, 1958). Alternatively low temperature ashing (LTA) by oxygen plasma at 150-200 °C is a standard technique for obtaining the mineral matter in coal and coal refuse, in order to characterize them for clay minerals. (Augenstine and Sun, 1974;

Miller et al., 1979; Tsai, 1982). Gluskoter (1965) found that on the average, the LTA mineral matter is 1.1 times that calculated by using the Parr Formula.

Optical microscopy and scanning electron microscopy (SEM) are widely used petrographic methods to characterize the mineralogical components of coal in thin and polished sections (Jenkin and Walker, 1978) and the procedures used for analysis are identical to sedimentary petrography (Milner, 1962) as described in books (Kerr, 1959; Hartshrone and Stuart, 1970; Hutchison, 1974).

The clays are the most frequently occurring inorganic constituents in coal and x-ray diffraction (XRD) is the best technique for their identification (Jenkin and Walker, 1978). Gluskoter (1967) used it for determining clay minerals in Illinois coal and found illite, kaolinite, illite -montmorillonite and chlorite. O'Gorman and Walker (1971) used XRD and Infrared (IR) as complementary methods to each other for mineral matter determination in some American coals. Jenkin and Walker (1978) applied Fourier Transform Infrared (FTIR) spectroscopy to coal and coal refuse for their mineral matter determination. Some recent studies (Garcia, et al., 1991; Tarazona et al., 1992; Acharya, 1992) used XRD alone or combined with other methods to characterize their coals.

2.3 Methods of Characterization of Shales

Clay stones, clay shales or slates in highly metamorphosed form are termed as phyllite or mica schists (Potter et al., 1980) and constituted the waste materials of Zonguldak washery. According to Pettijohn (1975) average clay mineralogy of shales is clay minerals 58 %, quartz 28 %, feldspar 6 %, carbonates 5

% and iron oxides 2 %. Figure 2.1 gives types of various clays based on their structure and describes their properties and names (Stumm and Morgan, 1981).

Mineralogy and texture of shales are determined petrographically. For clay mineralogy, bulk mineralogy and crystallinity, XRD is used. Samples are disaggregated, then sedimented on slides or packed in holders for XRD examination. Ideally mineralogy can be determined by SEM (Potter et al., 1980).

Although Differential Thermal Analysis (DTA) is important among techniques enabling identification of clays (Rowland, 1955; Mackenzie, 1957; Grim 1968), thermogravimetric analysis (Dual, 1951; Brown 1972), and IR (Brown, 1972) are also useful; yet the XRD is considered as the most reliable one (Tschirley, 1981). Brindley (1951) was the pioneer for XRD application to the identification of clay minerals and recognizing their structural groups and varieties. Brindley (1955) found that structurally similar minerals but having different chemical composition may show characteristic differences in lattice parameters.

2.3.1 Petrographic Microscopy

The microscope is a simple direct observation tool and was therefore selected for analysis of mineral matter in coarse wastes of Zonguldak washery.

The mineralogical analysis may be entirely quantitative or qualitative. The analysis is based on count of grains, from which volume percentages can be obtained and converted to weight percentages using the specific gravity. In most work 500 to 600 grains is a more usual number to be counted (Cady, 1965). Hutchison (1974)

Structure	Remarks	Names
A. Two-Layer Clays		
T O T O T O	Little isomorphous substitution Small cation exchange capacities (CEC) Nonexpanding	Kaolinite Dickite Nacrite Halloysite (Interlayer water)
B. Three-Layer Clays	1. Expanding (Smetites ofr Montmorillonites) Substitution of a small amount of Al for in T-sheet and of Mg, Fe, Cr, Zn, Li for Al or Mg in O-Sheet.	Montmorillonite Nontronite Volkhonskyite Hectorite Saponite Sauconite Vermiculite
T O T M^{+m}, nH_2O T O T	Large CEC ($M = Na^+, K^+, Li^+, Ca^{2+}$,............) Swell in water or polar organic compounds	
M^{+m}, nH_2O T O T	2. Nonexpanding (Illites) About 1/4 of Si in T-sheet replaced by Al, similar O-sheet substitutions Small CEC $M^{m+} = K^+$	Poorly crystallized Micas (mussovite, biotite, phlogopite)
C. Chlorites		
T O T O (B. ucite) T O T	Three-layer alternating with brucite Brucite layer positively charged [some Al(III) replacing M(II)], partially balances negative charge on T-O-T (mica) layer Low CEC, nonswelling	
D. Fibrous Clays	Different type of structural units consisting of double silica chains (tetrahedra) joined to one-dimensional O-layers and containing interstitial water.	Attapulgite Palygorskyite Sepiolite

Figure 2.1. Clay Minerals and Their Structures (Stumm and Morgan, 1981).

recommended point counting on a flat sawed surface or thin section for modal analysis of mineral components in rocks. A polarizing microscope with Swift automatic point counter stage unit as described by Hutchison (1974) is used.

The criteria used for identification of minerals and microcrystalline aggregates are generally based on changes in colour (pleochroism) on stage rotation, refractive index (related to density), birefringence (difference of highest and lowest refractive indexes) and morphology. For particular species such as quartz, feldspar, mica, carbonates and iron oxides, useful differentiating criteria are given by Cady (1965).

2.3.2 X-Ray Diffraction

As already mentioned, XRD was the best method for clay minerals identification in coal and wastes and therefore chosen for analysis of samples collected from the washery. The method not only identifies but also furnishes quantitative estimates of minerals in natural clayey materials (Brindley and Brown, 1984) as well as the mineralogical characterization of clay fraction of solid (Whittig, 1965).

2.3.2.1 Clay Preparation Techniques for XRD Analysis

Clay is a material less than about 1 micron (2 micron is upper limit). Sedimentation and disaggregation procedures to prepare samples for XRD examination are covered in detail by (Tanner and Jackson, 1948; Jackson, 1956; van

Olphen, 1963; Kunze, 1965; Brindley and Brown, 1980).

The clay particles may be bound together by iron oxides and/or by organic matter and carbonates and much consideration is required to the removal of such coatings. Iron oxides can be removed by sodium dithionate ($Na_2S_2O_4$) solution buffered at neutral pH with sodium bicarbonate ($NaHCO_3$); sodium citrate is added as a complexing agent (Mehra and Jackson, 1960). Organic matter can be removed by oxidation with 30 % H_2O_2 (Jackson, 1956). Efficient use of H_2O_2 requires an acid medium, and hence prior treatment of carbonates is required. Alternatively Troell (1931) proposed the use of sodium hypobromite to oxidize organic matter. The removal of calcium carbonate is done by sodium acetate buffer adjusted to pH5 with acetic acid (Grossman and Mitchell, 1961). Alternatively HC1 is used to remove carbonates (Brindley and Brown, 1980).

Kunze (1965) pointed out that the above pretreatments have minimum effect on the constituents other than those to be eliminated and therefore were used for pretreating samples of coal and coal refuse to remove organic matter before XRD analysis.

The clay minerals have a platy morphology and easily orient for XRD examination (Brindley and Brown, 1984). However, most investigations required oriented mounts and unoriented (randomly oriented) mounts.

The unoriented mounts, are necessary to obtain complete diffraction data for spacing and intensities. They are obtained by packing dry clay sample in an aluminum holder (Carroll, 1970).

The oriented mounts (less than 2 micron) are prepared as glass slides and show 001 series of basal reflections with little or no evidence of hkl reflections. This type of mounts are very useful for clay mineral identification as each basal spacing is related to the type of layer structure. They are analyzed as air dried, glycolated and heat treated specimens. The glycolated specimen reveals information about clays having interlayer swelling on treatment with water or organic reagents (Brindley and Brown, 1984). The heat treated specimens are examined by heating to about 550 °C which renders them dehydrated giving changes in XRD pattern of clays (Brindley and Brown, 1984). Leonard and Weed (1967) heated the specimens between 300-400 °C. (See Appendix A for X-ray diffraction principles and identification of clay minerals).

CHAPTER III

EFFECT OF CLAY SLIMES ON COAL FLOTATION

3.1 Introduction

The most important group of minerals in coal are clay minerals which on the average account for some 60-80 % of total mineral matter associated with coal (McClung et al., 1979). Shales, silts and schists or slates associated with coal as overbreak materials from roof and floor add to the clay content of coal coming to washery for cleaning ; by their disintegration and swelling in water forming a high proportion of slimes. The presence of ultrafine clay (less than 2 micron) or other slimes may inhibit froth flotation of coal (Brown and Smith, 1954; Jowett et al., 1956; Burdon et al., 1976; Mishra, 1978). Renton (1982) stated that most of the mineral matter (60-70 %) by weight of average low temperature ash) consists of clay minerals interspersed between layers of coal.

Kaolinite and illite are most abundant clay minerals in coal with the mixed layer clays and chlorite occurring in lesser concentrations (Rao and Gluskoter, 1973). The ratio, kaolinite to illite has been shown to vary systematically, depending upon regional depositional setting. Coals containing kaolinite alone are not uncommon, although in most coals kaolinite is found in association with other clay minerals

(Renton, 1982). The mixed layer clay minerals found in low rank coal usually contain smectite interlayers (Jenkin and Walker, 1978). For U.S. coals O'German and Walker (1971;72) found kaolinite as the principal clay mineral in addition to quartz, gypsum, illite and montmorillonite.

The composition of mineral matter fractions of washery black waters was different from coal with illite being dominant clay and montmorillonite and mixed layer clays in large amount with lesser amounts of quartz, calcite, kaolinite and chlorite in minor amounts (Bradley et al., 1980a; Bradley et al., 1980b). The black water mineralogy and coarse refuse mineralogy are controlled by overbreak materials and not that of coal measure itself; these differences could not be explained because the coarse refuse mineralogy of U.S. coals was not determined (Aplan, 1988). The European coals have illite and sericite as dominant and abundant clay minerals, with montmorillonites being rare whereas kaolinite is very common (Stach et al, 1982). The mineralogical composition of Asturian (NW Spain) coal basin (Tarazona et al., 1992) in decreasing order of abundance is clay minerals (illite, kaolinite, mixed layer illite-smectite, chlorite), quartz, carbonates (calcite, siderite, ankerite).

Clays in Turkish coal, coarse refuse and black water are still unknown and therefore, problems due to clays in flotation, heavy media separation, flocculation and dewatering remain to be solved. The Zonguldak washery switched over to flocculation due to these problems and other Turkish washeries are encountering problems due to clays.

3.2 Effect of Slimes in Coal Flotation

The slimes cause loss of recovery either through slime coatings on mineral or bubble and increased consumption of reagents. Many investigators (Sun, 1943; Fuerstenau et al., 1958; Iwasaki et al., 1962) found that slime coatings are heaviest, when the slime is uncharged or oppositely charged to the material being floated. The effect of slime coatings to flotation response is also dependent on the particle size of the slimes (Iwasaki et al, 1962).

Sutherland and Wark (1955) noted that slime coatings are less likely to form in a dispersed system; depending on the clay surface charge (both edges and faces of clay) due to electrostatic attachment of clay to the coal particles. van Olphen (1963) indicated that clay particles may be influenced: face to face, edge to face, face to edge or in combinations. He found that the clay faces are always negatively charged, while the clay edges exhibited an IEP (isoelectric point) at about neutral pH, and presence of inorganic salts and alkalies affected the flocculation behaviour of clay suspension significantly.

The pH has been found (Campbell and Sun, 1970a; Wen and Sun, 1977; Özbayoğlu, 1977) to control the sign of the charge and zeta potential on coal surface and inorganic ions affected depending upon concentration and valency of these ions. Arnold and Aplan (1986a) found that increase in clay content of coal feed gave increase in ash content of froth due to water carry over mechanism. In their investigations they found that kaolinite and illite clays were causing little or no coal depression whereas even 2 % bentonite in flotation feed resulted in significant coal depression through armour coating of bubbles and increased slime coatings. The addition of oil tends to float more ash and pyrite by collecting slime coated particles and addition of clay dispersants such as calgon, lignin sulfonate and sodium silicate tend to depress coal flotation.

In another study, Arnold and Aplan (1986b) found that flotation of coal is lower in distilled water than tap water (containing Ca $^{2+}$, Mg^{2+}, Na^{+}, Cl^{-}, SO_4^{2-}) and presence of clays magnifies the coal depression. In the presence of kaolinite and illite, ions present in the flotation pulp were masking the charge on the clay particles, inhibiting the formation of slime coatings, and hence depression. It was also found that pH did not appreciably affect the flotation recovery of clean coal in tap water and in the absence of clay slimes in the range of pH 3.5-9. At low pH and in the presence of clays, the negatively charged clay faces were attracted to positively charged coal surface forming slime coatings which caused coal depression, especially in distilled water and in presence of bentonitic clay. At neutral pH in distilled water, slime coatings also form due to either (1) the IEP of the clay edge at about neutral pH or (2) attraction of the positively charged clay edge to the negatively charged coal. In alkaline circuit, the clay edges and faces and the coal surface were all negatively charged and no slime coatings formed. No depression was noted with kaolinite clay, and depression in the presence of bentonite was due to armour-coatings of bubbles.

These two detailed studies (Arnold and Aplan, 1986a; Arnold and Aplan 1986b) opened new avenues for research in to the effect of clays on coal flotation after well characterizing the clays to match with the actual systems.

CHAPTER IV

SOME RECENT RESEARCHES IN COAL FLOTATION

4.1 Introduction

Froth flotation is one of the processes used in coal preparation to remove a large proportion of ash forming minerals from coal since coal particles are naturally hydrophobic whereas clays, pyrite and other associated minerals are hydrophilic. However coal is heterogenous material and its components behave in different manner during flotation (Lynch et al., 1981). This process has probably the greatest potential of any fine cleaning devices for treating all of the fine fractions from 28 mesh (0.5 mm) to micron sized particles (Aplan, 1979). Altogether it accounts for about 10 percent of coal cleaned (Burger, 1980a) in U.S.A, whereas in Turkey about 14-18 percent of raw bituminous coal coming to washery is treated by flotation (Özbayoğlu, 1980).

The coal due to its hydrophobicity, can be floated by a frother alone such as methyl isobutyl carbinol (MIBC), heptyl alcohol or pine oil but a non polar collector such as Kerosene and fuel oil is added to increase the hydrophobicity of coal. Low and medium volatile bituminous coals are most readily floated than higher and/or lower rank coals. Anthracite and bituminous coals require oily collectors to float and lignite is non floatable (Wheelock and Markuszewski, 1984) Coal floatability is reduced by weathering and slime coatings (Jowett, 1975). Coal and pyrite pose problems of separating them in flotation as fresh pyrite surfaces appear more hydrophobic than coal (Wheelock and Markuszewski, 1984).

4.2 Electrokinetics in Coal Flotation

When a coal particle (like mineral particle) is immersed in aqueous medium, the surface acquires an electrical charge, either due to dissociation of surface groups or the preferential adsorption of ions. As the system as a whole must be electrically neutral, an equal charge of opposite sign to that of the surface must be present in the surrounding liquid. This gives rise to an electrical double layer (Leja, 1982).

The interphase between the solid and solution phase allows charged species common to both solid and solution. The ions with in the solid are responsible for the surface charge and termed as potential determining ions (PDI). The ions which constitute crystal lattice are PDI for oxides (Glembotskii et al., 1972), bituminous coal (Campbell and Sun, 1970a) and anthracite (Campbell and Sun 1970b). The "zero point of charge" (pzc) for a solid is determined by the concentration of PDI in solution, as at this critical concentration, no transfer of free charges is there and electrical double layer is absent (Aplan and Fuerstenau, 1962). Whenever an oxide exhibits a pzc, its negative and positive hydrocomplexes in solution must be present in equal amount (De Bruyn and Agar, 1962) and so pzc is determined by the pH of its minimum solubility; called IEP by analogy of pzc. At this point zeta potential is zero and H^+ and OH^- are PDI for the species in question. In the absence of specific adsorption of any ionic or polar species and of other sources of charge, the pzc and iep are equal.

In general zeta potential (or electrokinetic potential) determines the electrokinetic behaviour of charged surface and electrolyte solution at the surface of shear (Shaw, 1970). The sign and magnitude of zeta potential indicates the nature of adsorbed ions and the relative magnitude of potential in the solid phase (Mackenzie, 1971). The absolute value of zeta potential is unkown except at pzc (Leja, 1982).

The zeta potentials from mobility data using Smoluchowski equation $V/E = D\zeta / 4\eta$ were calculated first by Adamson (1976). In this equation "V" is the velocity of particle, "E" the applied field strength gradient, "ζ" the zeta potential, "η" the viscosity and D the dielectric constant (permittivity). The mobilities of coal particles are determined generally either at various pH values or at various concentration of salts and organic reagents. In flotation systems, the adsorption of surfactants by electrostatic forces is directly related to electrokinetic characteristics (Leja, 1982).

4.2.1 Surface Negativity and Effect of pH on Zeta Potential of Coal

All coal samples and their lithotypes have negative zeta potential in distilled water (Campbell and Sun, 1970a; Campbell and Sun 1970b; Wen and Sun, 1977; Özbayoğlu, 1977; Wen and Sun, 1981; Padberg and Muller, 1986; Sarıkaya, 1988). Aplan (1976) stated that of all pH values to above 5, coal is usually negatively charged. The surface negativity of coal is due to its anisotropic nature (Chander et al., 1975), consisting of two parts, one formed by rupture of ionic or covalent bond (hydrophilic) and the other by the rupture of van der Waals bonds (hydrophobic). The negative charge is due to the presence of hydrophilic sites (-COOH and -OH group). Thus the zeta potential of coal is a function of this reactive oxygen group.

Özbayoğlu (1977) determined IEP's of vitrain durain and fusain as 4.1, 4.5 and 3.06 respectively and of whole coal at pH 4.05. Sarıkaya (1988) found IEP of unoxidized coal at pH 4.2.

4.2.2 Effect of Reagents on Zeta Potential of Coal

Wen and Sun (1977) found that dodecylamine shows maximum hydrophobicity of oxidized coal with electrolytes at its IEP around 6.5 to 7.0. Wen and Sun (1981) also found that oily collectors adsorb maximum by the oxidized coal at its IEP at a pH 6.5 - 7.0 in the presence of ferrous hydroxide. Sarıkaya (1988) indicated IEP's of oxidized coal at pH 9.3 to 10.9.

Özbayoğlu (1977) found that the heptanol (seven carbon atoms of hydrocarbon radical) lowers the electrokinetic potential continuously with increase in concentration (decrease in zeta potential means better floatability).

Özbayoğlu (1977) and Sarıkaya (1988) while exploring the effect of electrolytes on zeta potential of Zonguldak coal found that only Al^{+++} ions reverse the charge on negatively charged coal surface, converting it to alumina like surface by electrostatic forces. Wen and Sun (1977) also found that Fe^{3+}, Fe^{2+} and Al^{3+} ions only gave charge reversal points. Arnold and Aplan (1986b) showed that SO_4^{2-} ions on mineral matter (largely clay) increase the negative charge and Ca^{+2} ions, reduce overall negative charge of the particles in pH range of 2.5-10.

Myers (1988) mentioned that an increase in electrolyte content will cause a decrease in adsorption of surfactants on to oppositely charged surface and increase in adsorption of likely charged molecules. The presence in solution of polyvalent cations such as Ca^{2+} or Al^{3+} will generally increase the adsorption of anionic surfactants. He also pointed out that certain inorganic ions such as calcium which reduce the stability of many ionic surfactants, act by spreading as a monolayer or as a lens on the interface and displace the stabilizing surfactant species.

4.3 Coal Flotation Reagents and Their Adsorption

A mineral processing engineer is primarily interested in phenomena of positive adsorption, meaning that a substance accumulating at a liquid solid or gas/solid interface, often is a monomolecular film (Jirgenson and Straumanis, 1962). Coal being naturally hydrophobic, exhibits a high contact angle. Sun's (1954) surface component theory stated that floatable components of coal were oil avid and water repellent where as non floatable components were water avid and oil repellent.

4.3.1 Adsorption of Collectors and Frothers on Unoxidized Coal

Sun (1954) found that generally flotation of unoxidized coal is little affected by the presence of small amount of water soluble oxidation products of coal. Oils with low solubility, classified as non polar collector are used in coal flotation, and added as droplets or dispersed as emulsion. Dispersion of water in a soluble and added as droplets or dispersed as emulsion. Dispersion of water in a soluble hydrocarbon oil is a critical issue and emulsification of oils prior to flotation is very effective in flotation process (Franzidis and Anderson, 1986). The droplets of oil adhere to coal and increase its hydrophobicity (e.g. contact angle of vitrain increased from 57^{o} to 82^{o}). Kerosenes are most effective collectors for coal flotation (Brown, 1962). Özbayoğlu (1977) found that adsorption of Kerosene was maximum on Piriç coal from Turkey due to increased vitrinite content and hence hydrophobicity. Wojick et al (1991) found that increase in flotation efficiency results due to increase in concentration of non polar collector.

Moxon et al (1988) obtained maximum yield of coal by floating it with dodecane (Chain C_{12}) and they claimed that non ionic frothers (e.g. polyalkane oxide) gave better coarse coal recoveries in Australian coal preparation plants than MIBC.

Sarıkaya (1988) found MIBC as better frother than pine oil for floating Zonguldak unoxidized coal at pH 7.4. Amyl, hexyl, heptyl and octyl alcohals are other frothers used for coal flotation. Cresylic acid is also an attractive frother (Mitchell and Leonard, 1968). Chernosky (1963) found MIBC as superior frother than others on yield - selectivity - cost basis; which is a short chain alcohal (carbon chain C_5) and Sun (1952) had also found it better frother than either pine oil or cresylic acid on the basis of stability index.

Stone Street and Franzidis (1988; 1989) used quaternary amines to reduce entrainment of fines and develop a reverse flotation process for cleaning high ash South African coal. They used quartz and coal artificial mixtures for flotation and were only partially successful, despite the amines ability to adsorb on coal as action of amines as collector on coal.

4.3.2 Adsorption of Depressants on Coal

The mechanism of depression probably involves the masking of coal surface and competition with collector for adsorption sites (Smith, 1988). In coal flotation it is possible to depress either coal or gangue. Non electrolytes and salts of inorganic acids are used generally in flotation of coal. The former will depress coal while the later are more effective on gangue minerals. Two non electrolyte groups consists of (a) carbo-hydrates, dextrin and starch etc., which are high molecular weight compounds, containing strongly hydrated polar group (b) Tannins such as quebracho composed of complex molecules and thiosulphates. These organic depressants (Smith, 1988) are categorized as polyglycol ethers, polysaccharides (starch, carboxymethyl cellulose, dextrin and gums). Perry and Aplan (1985; 1988) found that polysaccharides used for depressing pyrite, also depressed coal.

The two major salts of inorganic acids used in coal flotation are sodium silicate and sodium cyanide. Sodium cyanide is used for depressing pyrite and sodium silicate for depressing calcite and silicate minerals as well as dispersing clays and shales. Since high ash slurries contain clays and silicates, standard dispersants such as sodium silicate, sodium hexa metaphosphate, lignin sulphonates and other polymeric surfactants may also be considered for depression of clays and silicates. Arnold and Aplan (1986a) found that clay dispersants calgon, lignin sulphonate and sodium silicate all depressed coal and hence lost the benefit of their advantageous use.

Miller and Deurbrouck (1982) used a two stage flotation process for desulphurizing coal. They used kerosene and MIBC in first stage of conventional flotation and the froth product obtained was conditioned with dextrin (coal depressant) and pyrite floated with xanthates.

Laskowski et al (1985) used a single stage direct flotation for desulphurizing high sulphur Canadian coal, using Kerosene oil, MIBC and CMC (depressant) under alkaline conditions. He obtained better selectivity and claimed it a simpler solution than two stage reverse flotation process. An earlier study by Boateng and Phillips (1977) used a single stage process for desulphurizing coal by floating it with kerosene oil as collector, pine oil as frother and lime as depressant for pyrite: claiming 90 % removal of pyritic sulphur.

4.3.3 Surfactant Structure and Emulsion Performance

A surfactant must exhibit sufficient surface activity to ensure significant adsorption at oil-water interface. A quantitative way of correlating chemical structure of surfactant molecules with their surface activity is hydrophile-lipophile balance (HLB) system. The HLB number of surfactant is calculated from its chemical structure and this number is matched with the HLB of the oil phase to be dispersed (Myers, 1988). Becher (1965) calculated HLB numbers of some commonly used oil phases and found that oleic acid has HLB = 17 compared to HLB = 14 of Kerosene oil. Therefore a surfactant containing oleic acid should be more active and selective than Kerosene oil used conventionally uptill now for coal flotation. The use of ionizing collectors is considered as of scientific interest only (Sun, 1954) in coal flotation.

CHAPTER V

MATERIALS AND REAGENTS USED

5.1 Materials

Samples were collected from Zonguldak main washery consisting of raw coal (run of mine) and flotation feed (below 0.5 mm) for flotation experiments whereas the waste materials from jigs, flotation circuit and thickener tank (overflow) were sampled for clay characterization work. Turkish clays namely kaolinite, illite and chlorite in pure form were used in flotation and electrokinetic measurements.

5.1.1 Coals

The clean raw coal samples were collected by hand picking from the feeder of r.o.m. (run of mine) coal. All other coal samples were obtained from the cyclone underflow in the flotation circuit, during the normal operation of washery. Table 5.1 gives the location of samples and their nature, used for experimental work.

Table 5.1. Location and Nature of Coals Used

Location of Samples	Nature of Coal
Zonguldak Washery Feed	Hand Picked (from raw coal)
Zonguldak Washery Feed	Hand Picked (from vitrain bands)
Washery Flotation Feed (Cyclone Underflow)	Below 0.5 mm.
Washery Flocculation Feed (Cyclone Underflow)	Below 0.5 mm (high ash)
Washery Flocculation Feed (Cyclone Underflow)	Below 0.5 mm (very high ash)

5.1.2 Waste Materials

Refuse materials were collected comprising a total of seven samples as given in Table 5.2.

5.1.3 Turkish Clays Used

Pure clays from Turkey were used and their particulars are given in Table 5.3.

Table 5.2. Nature and Location of Waste Samples

Location of samples	Nature of Sample	Designation
Washery old dump	0-100 mm old waste	Sample A
Washery fresh dump	0-100 mm new waste	Sample B
Coarse jig tailing	100-18 mm waste	Sample C
Coarse jig middling	18-6 mm waste	Sample D
Fine jig tailing	6-0.5 mm waste	Sample E
Flotation tailing	Minus 0.5 mm waste	Sample F
Thickener Tank overflow	--------	Sample H

Table 5.3. Turkish Clays Used

Clay Type	Variety and Preparation	Supplier	Location
Kaolinite	ESK 404S, Kaolin 64.6 % passing 5 micron, 81 % Kaolinite; XRD pattern obtained showed mainly peaks of Kaolinite and quartz (Fig.5.1).	Esan-TURKEY	Eskişehir TURKEY
Illite	Crushed in jaw and rolls to minus 10 mesh, then ground to minus 325 mesh Tyler in porcelain ball mill. XRD pattern showed peaks of illite and quartz (Fig.5.2).	MTA-TURKEY	ORDU-TURKEY
Chlorite	Concentrated after magnetic separation, crushed and ground in porcelain mortar grinder to minus 325 mesh. XRD pattern showed mainly chlorite peaks (Fig.5.3).	Prof.Dr Zeki Doğan (I.T.Ü.)	ULUDAĞ-TURKEY

The mineralogical composition of Kaolinite is as follows;

Kaolinite = 81 %; Micaceous materials = 15 %;

Feldspar = 1 % and other minerals = 3 %

The XRD pattern obtained for the Kaolinite clay is shown in Fig. 5.1. Where as XRD patterns of illite and chlorite are shown in Figs. 5.2 and 5.3.

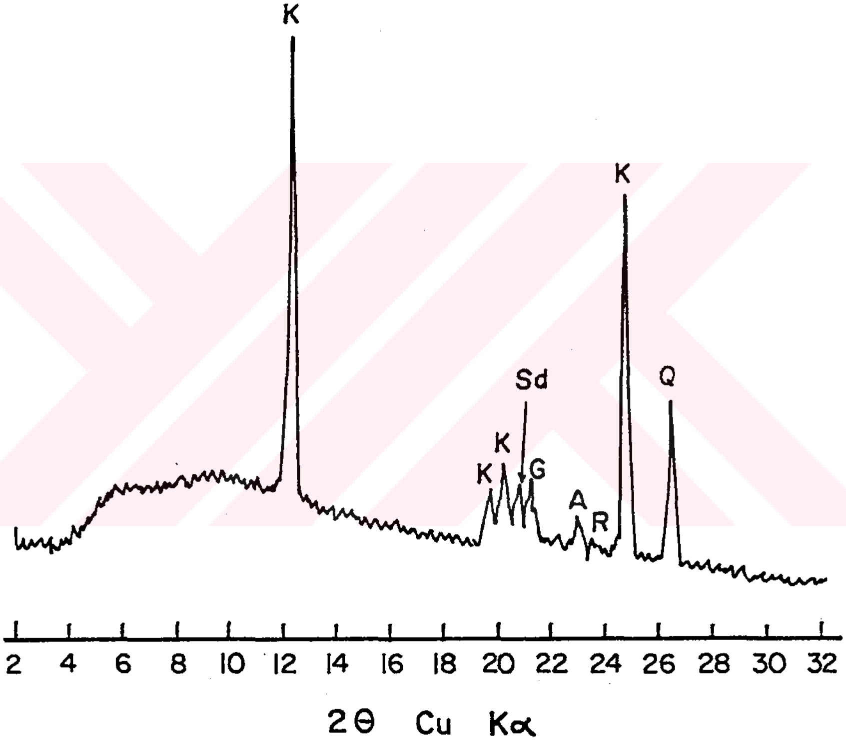

Figure 5.1. XRD Pattern of Kaolinite (unoriented mount) K= Kaolinite; Sd=Siderite; G=Goethite A=Anhydrite; Q=Quartz ;R=Green Rust

5.2 Reagents

The reagents used in this research can be categorized according to the experimental work carried out. Generally reagents used were of analytical grade and solutions were always prepared fresh. Sodium hydroxide and hydrochloric acid both from Merck were used for pH determination. Three standard buffer solutions at pH 4.01, pH 7.01 and pH 9.18 were also used for calibrating the pH meter.

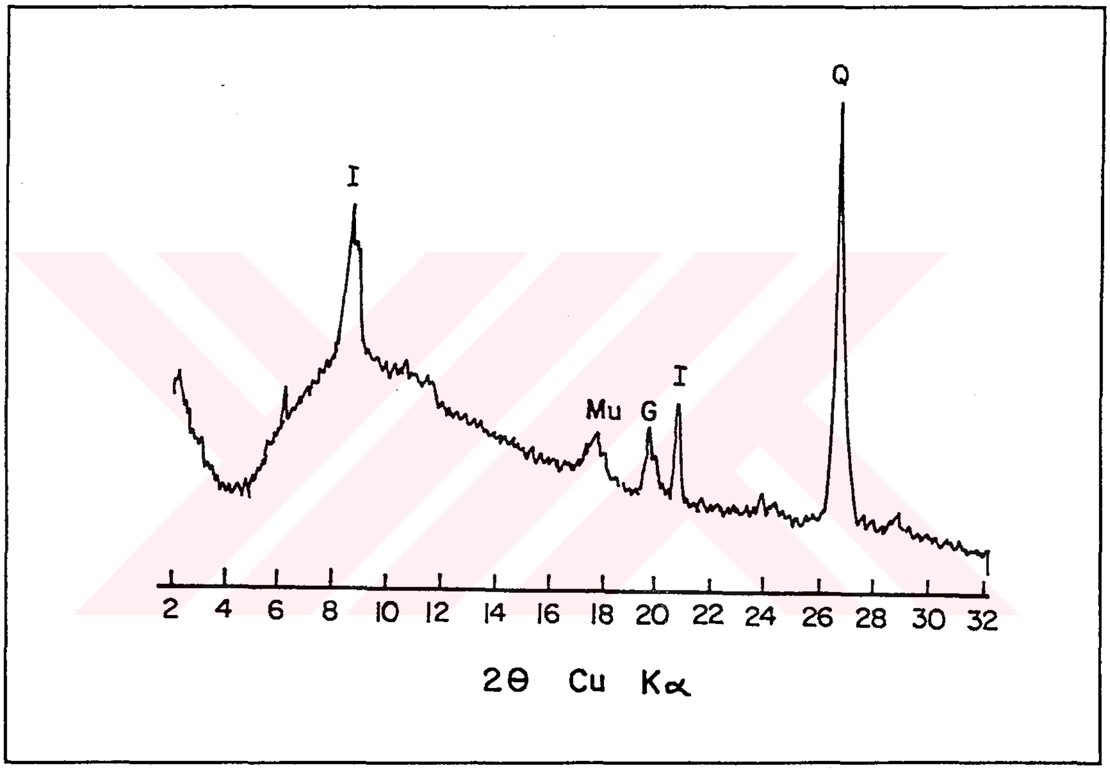

Figure 5.2. XRD Pattern of Illite (unoriented mount) I = Illite; Mu = Muscovite ; G =Glauconite Q = Guartz

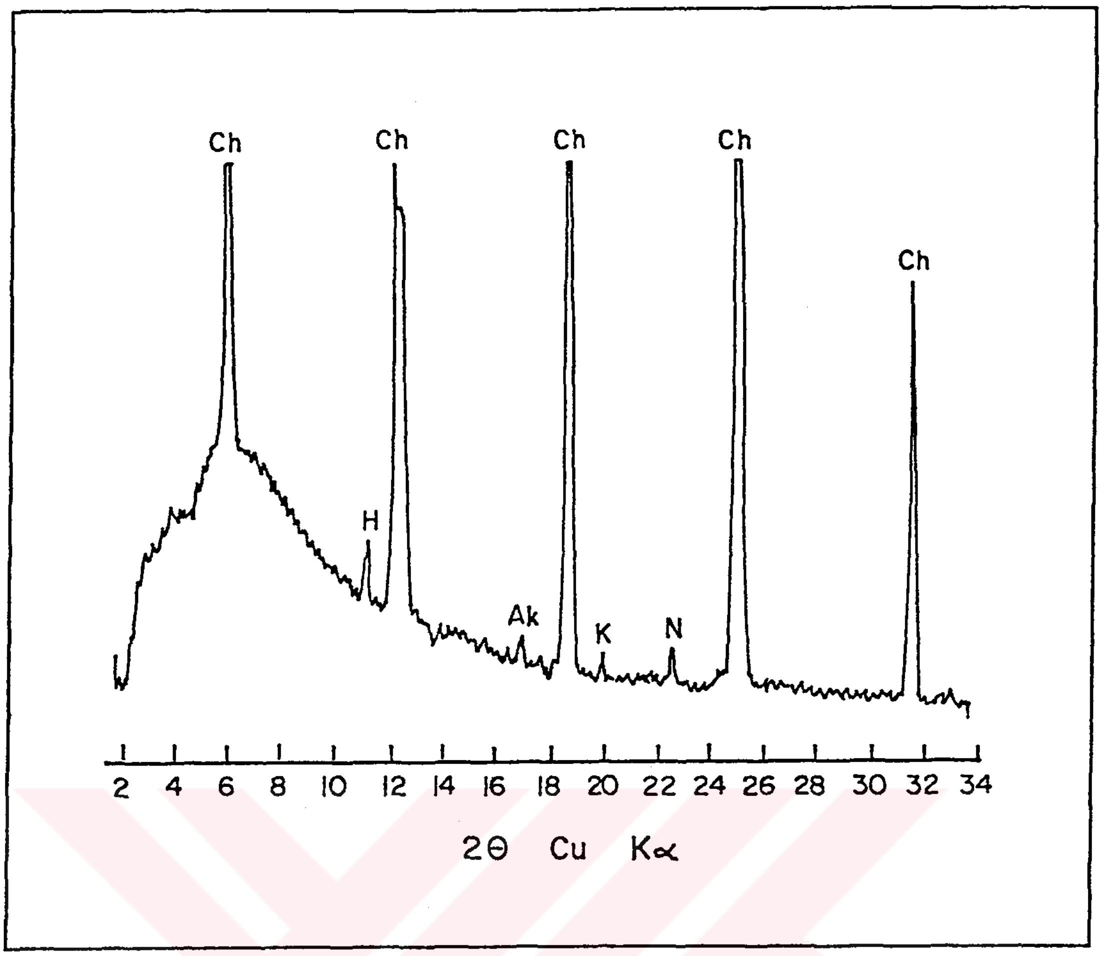

Figure 5.3. XRD Pattern of Chlorite (unoriented mount) Ch=Chlorite; H=Heulandite-Clinoptilolite (Zeolites); A_K=Akaganeite (hydrous iron oxide); K = Kaolinite; N= Natron

5.2.1 Heavy Medium Separation

Tetrabromoethane (bromoform) and acetone from Riedel were used for separation of some minerals for petrographic studies.

5.2.2 XRD Analysis

In XRD analysis sodium pyrophosphate and ethylene glycol from Merck were used for dispersion and glycolation respectively. For pretreatment Merck chemicals, sodium dithionite, sodium citrate, sodium bicarbonate, NaOAc, HOAc and HCl were used. Only H_2O_2 was from local sources.

5.2.3 Electrokinetics

For platinizing the platinum electrodes, platinizing solution (chloroplatinic acid 3 grams + lead acetate 0.02 grams + distilled water 100 ml) was used. Electrolytes from Merck were used and included $MgCl_2$, $CaCl_2$, calcium oxide, $AlCl_3$ and $Al_2(SO_4)_3$. The dispersants and depressants used for this study were namely sodium silicate (modulus $SiO_2/Na_2O = 3.22$ and SiO_2 content of 28.7 %) and sodium hexameta- phosphate (calgon) of Merck; Marsperse CB (sodium lignin sulfonate) of Denver; Aero 633 depressant of Cyanamide; Dextrin of Staley and Tylose C30 (CMC) of Hoechst.

5.2.4 Flotation

Kerosene oil and MIBC were obtained from shell Co. Olive oil (oleic acid) of Denver and Pamak 4 (Linoleic + oleic + Rosin oil) of Hercules was used and found best in a previous research work (Atalay, 1986). Flotigam ENA of Hoechst, Armoflote 18 (a quartenary amine) and Armoflote 21 (alkyl amine acetate) of AKZO were used.

5.2.5 Other Reagents

For demineralization of coal, HCl and HF of Merck were used.

For sulphur determination by oxygen bomb calorimeter, barium chloride ($BaCl_2$) solution and ammonium hydroxide of Merck were used.

CHAPTER VI

EXPERIMENTAL PROCEDURES

6.1 Sample Preparation

The experimental work described in this chapter consists of two distinct phases of samples preparation and procedures for analysis and testing.

As regards sample preparation, it is divided as initial preparation as described in this section and their subsequent preparation according to the methods of analysis and testing. As each technique e.g. XRD, electrokinetic, used some standard methods of sample preparation for analysis and testing which need to be described in a systematic manner.

Similarly procedures and equipments used for techniques used in this research such as petrography, XRD, loss on ignition, electrokinetics and flotation are very different from each other and need description of their equipment and procedures employed in view of the existing standard ones.

The coal samples obtained from Zonguldak were as lumps of about 5-10 cms. Half of the material was crushed by hammer and jaw crusher and rolls subsequently down to 28 mesh which was controlled by screen. The minus 28 mesh material obtained was then divided into samples of about 100 grams each by means of riffles and kept in double plastic bags to avoid any oxidation.

The other part of this sample was used to obtain clean coal by crushing with hammer each piece of coal and then carefully picking up a particular petrographic band (rich in vitrain) by visual observation. Only about 1.5 kilograms material thus obtained was subjected to crushing in jaw and rolls down to 28 mesh. The minus 28 mesh material obtained was divided into about 50 grams samples by riffles and reserved in double plastic bags for future work.

Flotation feed (designated as sample G) collected as cyclone underflow was allowed to settle for a week, then decanted and dried in oven at 60 ^{O}C. The material which is below 0.5 mm was then passed through riffles to obtain about 50 grams samples: kept in double plastic bags.

The waste samples A to F and H as given in Table 5.2 were divided in to three groups for initial sample preparation. The samples A to E (jigs tailings) after air drying were crushed in jaw and rolls to give minus 28 mesh material. Sample F (flotation tailings) was treated similar to sample G. However sample H (thickener overflow was sedimented for a month, decanted and dried in oven at 60 ^{O}C, giving only about 20 grams of sample for experimental work.

6.1.1 Sample Preparation for Chemical Analyses

For ash analyses, all samples were ground to minus 72 mesh BSS, as required by ASTM procedures D271-48. A porcelain pestle and mortar was employed for grinding the samples by hand for ash analyses.

The sulphur and percentage mineral matter analyses were carried out on samples prepared by grinding to minus 325 mesh Tyler in a Pascal agate mortar grinder.

6.1.2 Sample Preparation for Petrographic Analyses

The four waste materials, samples B, C, D and E were hand picked in pieces of 2 x 4 cms size for thin section preparation according to standard, procedure (Milner, 1962). For preparing polished sections, hand picked 2 x 4 cms pieces were crushed to 1 cm in jaw crusher and screened to -6 mesh + 10 mesh (BSS) fractions as recommended by Stach et al (1982).

6.1.3 Sample Preparation for X-Ray Diffraction Analyses

The samples used for XRD study were samples A to H, a total of eight samples. They were prepared in unoriented and oriented forms. For unoriented form these materials were ground to minus 300 mesh BSS in a Pascal agate mortar and then subjected to XRD analysis in powdered form (Hutchison, 1974).

For preparing the oriented mount, these materials were crushed to about 1 cm in a jaw crusher and then in rolls to less than 1 mm. Each material (about 200 grams) was then immersed in water in a 600 ml beaker and mixed with a blender.

The sample was then dispersed using a few drops of sodium hexameta-phosphate (Kunze, 1965; Hutchison, 1974; Brindley and Brown, 1984) and allowed to settle particles greater than 2 micron according to Stokes Law for a predetermined time (Tanner and Jackson, 1947; Jackson, 1956). Then the suspension containing less than 2 micron particles was pipetted. Model HNS centrifuge was used at 2500 rpm for 10 minutes to separate particles from water (Jackson, 1956). The wet particles were spread evenly on six standard vycor glass slides (48x48x6 mm) by a dropper for each material (Hutchison, 1974), to serve as oriented mounts for XRD examination.

For low temperature ashing of coal samples for XRD analysis, minus 300 mesh BSS material was sent to Dr. I.A. Korobetskii, Institute of Coal, USSR Academy of Sciences, Kemerovo.

6.1.4 Sample Preparation for Loss on Ignition Analysis

These samples consisted of materials ground to minus 300 mesh BSS in Pascal agate mortar grinder from pre crushed material (minus 0.5 mm) in rolls.

6.1.5 Sample Preparation for Electrokinetic Measurements

The pure coal sample and three pure clays (kaolinite, illite and chlorite) were used for preparing master suspensions for electrokinetic measurements. Each of them was ground to minus 325 mesh (Tyler) in a Retsch centrifugal mill with porcelain cup and balls. About 20 grams of each sample was mixed with distilled and deionized water in a 1000 ml beaker and then treated with ultrasonics for 10 minutes in Sonorex RK100 Bandelin equipment. The suspension was then allowed to stand for a predetermined time calculated from Stokes Law for settling of 10 micron particles. The portion of the suspension containing less than 10 micron particles was pipetted as master suspension for electrokinetic measurements. This was stored in 1000 ml flask and diluted with distilled and deionized water. Small samples of this suspension were taken each time for electrokinetic measurements.

6.1.6 Sample Preparation for Flotation Tests

The representative coal samples ground to minus 28 mesh were used throughout for flotation tests. However clays were ground to minus 325 mesh in Retsch centrifugal ball mill.

6.2 Procedures and Equipment

6.2.1 Ash, Sulphur and Mineral Matter Determinations

6.2.1.1 Ash Determination

Ash analyses were carried out according to ASTM standards D271-48. The samples were ignited to constant weight at 850 ^{o}C for about one hour in Heraus muffle furnace and the residue obtained after ignition was the ash percentage.

6.2.1.2 Sulphur Determination

The sulphur content of flotation feed was determined in a Parr oxygen bomb calorimeter in accordance with ASTM standards D3177-82. (See Appendix B.1).

6.2.1.3 Mineral Matter Determination

The mineral matter of flotation feed was determined by acid digestion (Bishop and Ward, 1958; Miranda et al., 1991) on samples below 325 mesh using HC1 followed by HCI + HF treatment for demineralization (See Appendix B.2).

The amount of mineral matter can also be determined through the amount of low temperature ash obtained by cool oxygen plasma oxidation (COPO) at temperatures around 150-200 ^{O}C (Miller, et al., 1979). The samples of flotation feed were sent for COPO treatment to Russia as mentioned before in section 6.1.3.

A theoretical calculation of mineral matter content is done by Parr Formula (Parr, 1932; Tsai, 1982) from the ash and sulphur content.

Mineral Matter = 1.08 Ash + 0.55 sulphur

6.2.2 Petrographic Analysis

The petrographic analysis of coarse waste samples B, C, D and E in thin and polished sections was performed by MTA. A polarizing microscope with Swift automatic point counter was employed using a point counting technique. Hutchison (1974) has described the use of such equipment and modal analysis by point counting, in a very systematic manner. The accuracy of counting depends on number of points counted, therefore at least 1000 points for each specimen were counted as recommended by Stach, et al. (1982) in order to obtain reliable and reproducible results.

6.2.3 X-Ray Diffraction Analysis

The X-ray diffraction analysis of all the eight samples (Samples A to H) were performed using Jeol, JSDX-100S, x-ray spectrometer diffractometer available in Geology Department. However, for some initial tests on samples A, F and H facilities of analysis at MTA, on Jeol, JDX-8P diffractometer were used. All the analysis were done using Cu Kα radiations with Cu/Ni electrodes and goniometer speed of $1^{o}(2\theta)$ per minute. The slit widths used were 1^{o} D for divergence slide, 0.2 R for receiver slide and 1^{o}S for scatter slide. XRD patterns (traces) were obtained by scanning between 2^{o}-32^{o} (2θ) for both unoriented and oriented mounts and chart recorded automatically (Brindley and Brown, 1984). The identification of minerals was done using standard tables, search manuals (Carroll, 1970; Brown, 1972; Brindley and Brown, 1984) or Powder Diffraction Files (J.C.P.D.S., 1975). The clay minerals were commonly characterized by spacing of 7, 10-15 and 17 A.

The unoriented mounts were analyzed in powder form (minus 300 mesh BSS) after packing in aluminum holders and gave only the XRD patterns of hkl spacing and not the basal spacing (00l) as obtained in oriented mounts.

The oriented mounts were prepared as glass slides (for less than 2 micron material) to obtain XRD patterns of basal spacing (00l) normal to the plane along c-direction (Carroll, 1970). This direction may vary with humidity, dehydration, cation interlayer positions and acid treatment etc. The hk spacings are a and b directions of the unit cell in all minerals and do not vary appreciably with the treatments. The most common is the treatment with polar liquids such as ethylene glycol or glycerol which aids the identification of smectites and various heat treatments that collapse swelling minerals such as kaolinite and hydroxides (Brindley and Brown, 1984). Keeping these facts in mind, the oriented mounts were examined by XRD in air dried, glycolated and heated samples. An automatic chart recording for each XRD pattern on air dried, glycolated and heated oriented mounts was facilitated by using a colour scheme as follows:

(a)	Air dried	green
(b)	Glycolated	blue
(c)	Heated to 350 °C....	red
(d)	Heated to 550 °C ...	black

The samples A to H for qualitative and quantitative XRD analysis were divided in to three groups. The coarse wastes consisting of samples A to E were categorized as group 1 whereas samples F and G were in group 2 (representing coal samples)and finally sample H (thickener overflow) was placed in group 3 (representing black water).

The sequence followed for analysis consisted of initial analysis of unoriented and oriented sample A, F and H, as first series of XRD results. A second series of detailed XRD analysis of coarse waste samples A, B, and E in unoriented mount in addition to sample A was analyzed after loss on ignition at 900 ^oC . In second series oriented mounts of samples A to E and H were also subjected to XRD analysis.

The third series of XRD analysis was designed for samples F and G containing high amount of organic matter i.e. 33 and 63 % respectively. These samples needed pretreatments for removing cementing agents in order to improve the quality of XRD patterns (Whittig, 1965). Therefore iron oxides were removed by sodium dithionate-citrate-bicarbonate method (Mehra and Jackson, 1960), the carbonates and exchangeable cations by sodium acetate buffer at pH 5 (Grossman and Mitchell, 1961) and organic matter by 30 % H_2O_2 treatment (Jackson, 1956). After pretreatments XRD patterns of oriented sample B and samples F and G were obtained. For combined treatments (pretreatment + acid treatment) method of Black (1965) was followed by first removing carbonates, then organic matter and treating the samples with concentrated HNO_3 and HCl at low heat (60 ^oC) for few hours before treating for removal of iron oxides. Samples F and G were combined treated and then subjected to XRD in addition to their XRD examination on pretreated samples.

It is worthwhile to mention here that, only oriented mounts were used for semi-quantitative analysis of clay minerals in all the samples (Brindley and Brown, 1984). Samples F and G contained very high amount of organic matter (33 and 63 % respectively). The pretreatments were designed for soils containing less than 5 % cementing agents (Kunze, 1965). Therefore, reagent amounts for treatment of these samples were proportionately increased. It was found that samples F and G respectively needed 10 times and 20 times the amount of H_2O_2 in order to change the colour of samples to distinctly brown. A comparison of change in colour to brown was facilitated by using blanks with coal suspended in water.

After qualitative identification of clay minerals an important aspect of this research was the estimation of clay minerals quantitatively. Biscaye's (1965) method yields semi-quantitative results calculated from peak area ratios and the weighted peak area percentages. This method was also used by Pierce and Siegel (1969) and Stoffers and Muller (1972) for the sediments. In Biscaye's method, area of 10 A peak (glycolated trace) multiplied by 4 is equivalent to relative amount of illite and the 7 A peak area is multiplied by 2 giving the relative amount of kaolinite plus chlorite. The 7 A peak area is divided between kaolinite and chlorite by a factor K/Ch obtained from the ratio:

3.58 A peak area / (3.58 A + 3.54 A) peak area where 3.58 A corresponds to kaolinite (002) and 3.54 to chlorite (004). (Details in Appendix A3).

Finally two samples of flotation feed (Sample G) sent to Russia, received after low temperature ashing at 140-160 ^{o}C by cool oxygen plasma oxidation (COPO) and separated by C_2H_5OH for clay fraction were analyzed by XRD in unoriented mounts. One of these samples was additionally treated by COPO at 150 ^{o}C.

6.2.4 Loss on Ignition Analysis

This method simply required ceramic crucibles to heat the samples, an oven and muffle furnace (Dean, 1974). All sample A to H were analyzed for moisture, organic matter and carbon dioxide. About 1 gram (below 300 mesh BSS) of each sample was used and heated to 105 ^{o}C for two hours in the oven, and the difference in weight gave the amount of moisture. This sample was again heated to

500 ^{o}C in muffle furnace for 2 hours and the loss in weight gave the amount of organic carbon (organic matter). The sample was returned for, heating to the muffle furnace at 900 ^{o}C for another two hours. The weight loss gave the amount of CO_2 evolved from carbonate minerals. The CO_2 percentage was converted to $CaCO_3$ percentage by dividing it with 0.44.

6.2.5 Electrokinetic Potential Measurements

Electrophoresis was used for determining the electrokinetic properties. The mobilities of coal and clays were determined over a wide pH range whereas coal mobilities in the presence of various electrolytes (metal ions), dispersants and depressants were also determined at their varying ionic strengths. A Rank Brothers Particle Electrophoresis Apparatus, MKII (Cambridge, England) was used for measuring the mobilities. During the measurements, a quartz rectangular cell and platinum electrodes were used after blacking.

6.2.5.1 Procedure and Calculations of Electrokinetic Measurements

The cell was cleaned with chromic acid and then washed with a continuous flow of distilled water. The cell was then flushed with prepared suspension many times before use. After filling the cell with the prepared suspension, the electrodes were inserted carefully, taking care not to trap any air bubbles. Before the application of electrical field to the suspension, it is necessary to wait until thermal equilibrium at 25 ^{o}C is reached in the cell tank. Then a voltage of 100 volts was applied across the cell.

The velocity of the particles was measured at both the front and back stationary levels in the chamber using the two inner surfaces as reference settings for focusing the microscope. By altering the direction of the current after each mobility measurement, polarization effects were minimized. The mobility of particles, defined as the velocity of migration under a constant potential gradient was computed after taking the averages of reading at the front and back levels. Each reported mobility was the mean of mobilities of 20 particles (10 in each level and 5 in each direction) yielding a standard deviation of about 5 %. The nominal zeta potential (ζ) was calculated from the Smoluchowski equation at 25 ^{o}C as $\zeta = 12.83$ U, where U is the mobility; i.e. ζ (mv) = 12.83 (velocity, micron/sec) / (potential gradient, V/cm).

The mobility of coal particles was measured either at various pH values or at various concentrations of salts, dispersants and depressants as mentioned before. The pH of the suspension was adjusted by adding a small amount of HCl and NaOH. Fisher (Accumet Model 230) pH meter was used for the measurement of pH and it was often calibrated by means of buffer solutions at pH 4.01, pH 7.01 and pH 9.18.

6.2.6 Flotation Tests

A Wedag laboratory flotation machine with a 0.5 liters fiber-glass cell, manufactured locally was used for flotation experiments. The speed of the impeller used for experiments was kept constant at 1420 rpm. Distilled water (pH 6.5) was used in the experiments. Agitation and conditioning time were kept constant as 3 minutes each in all the tests.

CHAPTER VII

EXPERIMENTAL RESULTS

7.1 Characterization of Samples

7.1.1 Chemical Properties of Coal Samples

The average results of ash content of coals used are given in Table 7.1.

Table 7.1. Ash Content of Different Coals From Zonguldak Washery

Coal Sample	Average Ash, %
Hand Picked from r.o.m. raw coal	9.8
Hand Picked clean coal (vitrain bands)	4.5
Flotation Feed	35.1
Flocculation feed (High ash)	39.9
Flocculation feed (Very high ash)	67.1

The sulphur content of flotation feed (35 1 % ash) was found (using formula given in Appendix B.1) as=0.48 %.

The percentage of mineral matter in flotation feed determined by acid digestion, low temperature ashing and Parr Formula were 39.8, 42.2 and 38.2 respectively.

7.1.2 Petrographic Analysis of Coarse Wastes

The thin and polished sections subjected to petrographic studies yielded the results shown in Table 7.2.

Table 7.2. Mineralogical Analysis of Coarse Wastes (Refuse) from Zonguldak Washery

Mineral	Sample B (%)	Sample C (%)	Sample D (%)	Sample E (%)
Quartz	7	18	20	14
Feldspar	2	4	2	1
Pyrite	3	3	4	1
Magnetite	1	1	Zero	Zero
Coal	4	3	22	15
Calcite	5	6	4	5
Clay Minerals	68	65	48	64

7.1.3 X-Ray Diffraction (XRD) Analysis

7.1.3.1 Preliminary Analysis

Three samples A, F and H were analyzed in oriented mounts and their XRD patterns (traces) are given in Figures 7.1 to 7.3, where as their XRD patterns in oriented mounts are given in Figures 7.4 to 7.6. Figures 7.7 and 7.8 show respectively their XRD patterns after glycolation and heating.

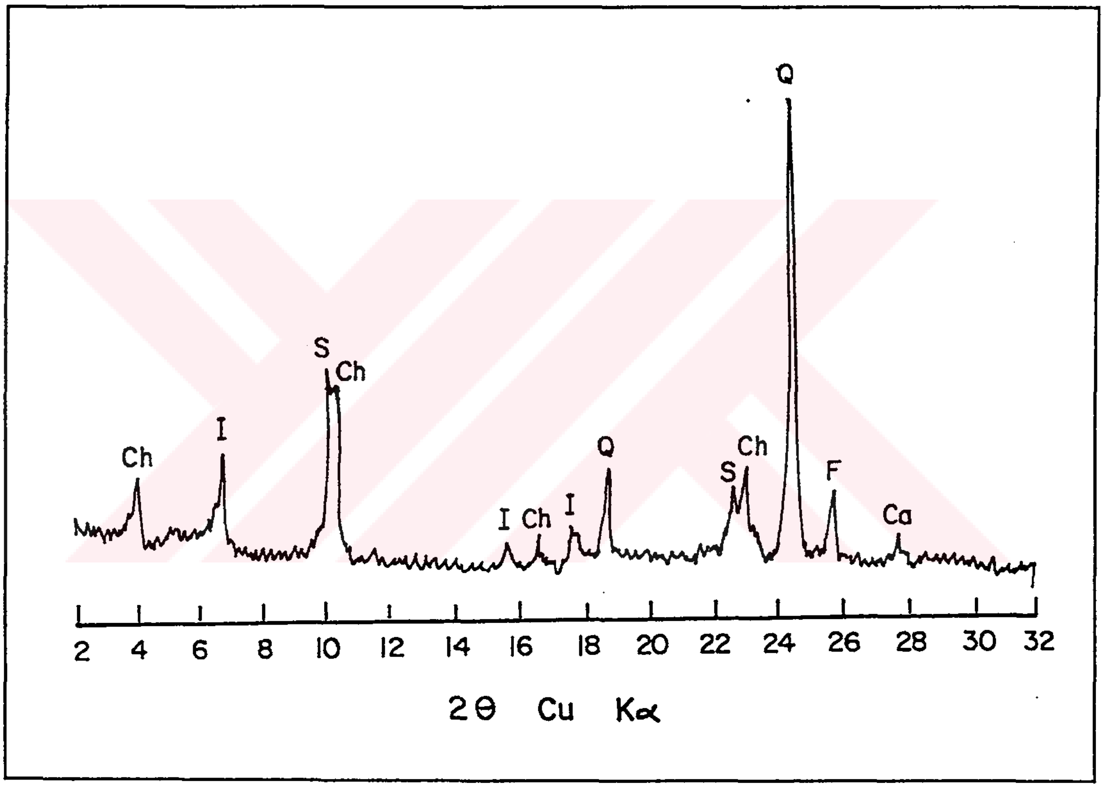

Figure 7.1. XRD Pattern of Unoriented Sample A (0-100 mm Old Waste) (I= Illite, Ch= Chlorite, Q=Quartz, Ca= Calcite, S= Serpentine and F= Feldspar)

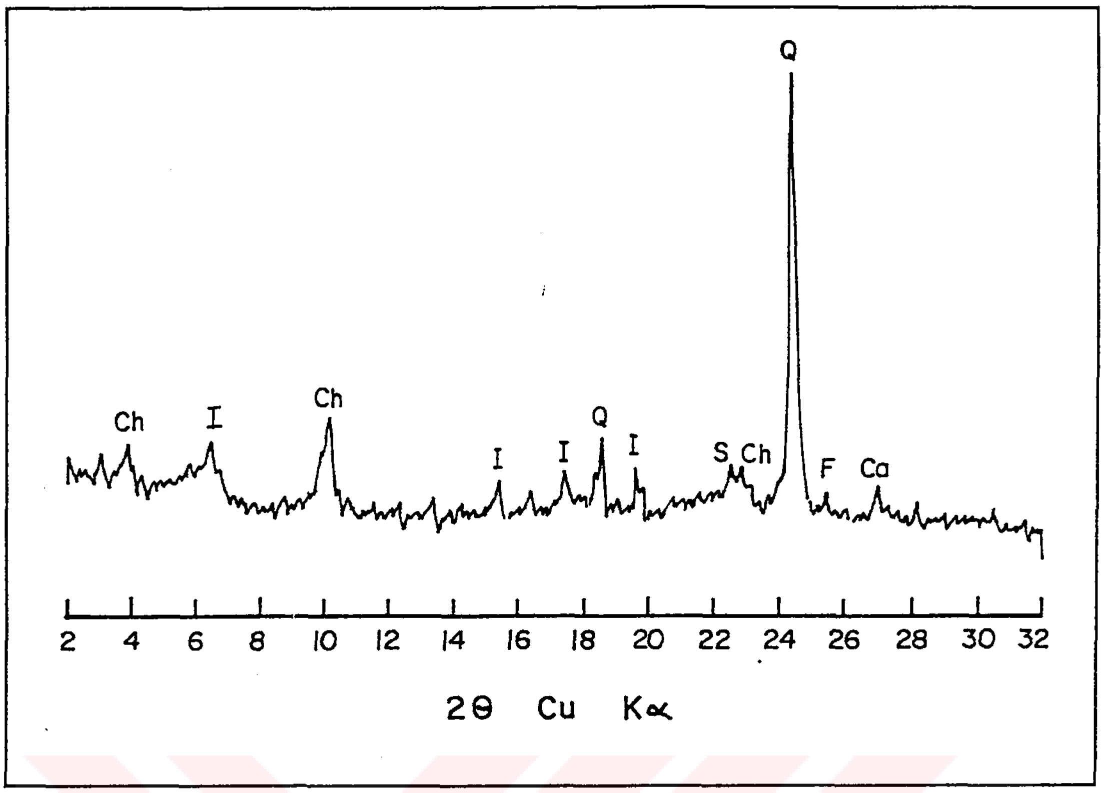

Figure 7.2. XRD Pattern of Unoriented Sample F (Flotation Tailing). (Notions as in Fig.7.1)

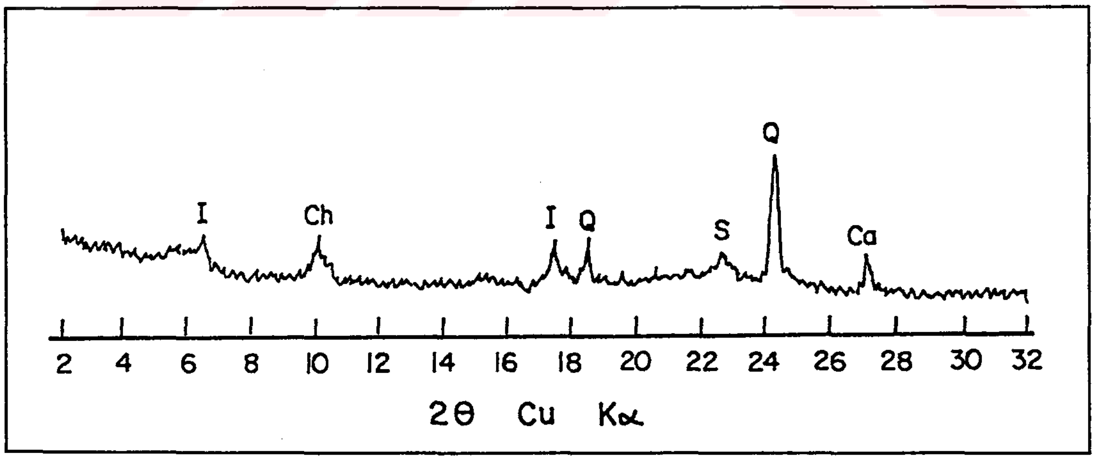

Figure 7.3. XRD Pattern of Unoriented Sample H (Thickener Overflow). (Notions as in Fig. 7.1)

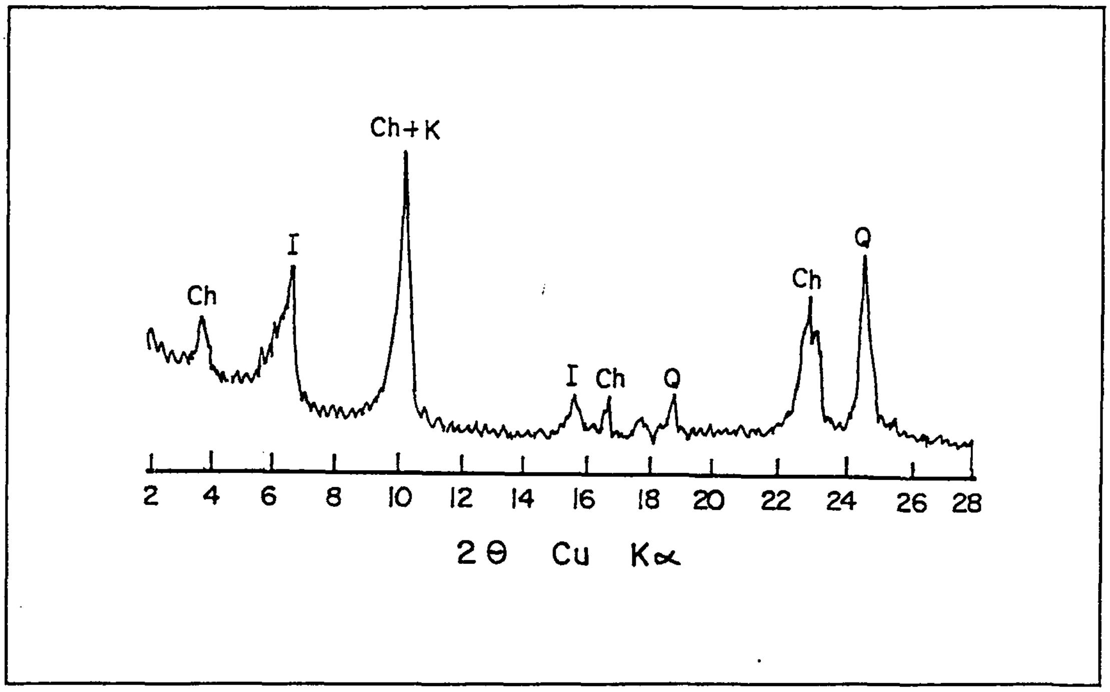

Figure 7.4. XRD Pattern of Oriented Air Dried Sample A. (Notions as in Fig. 7.1. except K= Kaolinite)

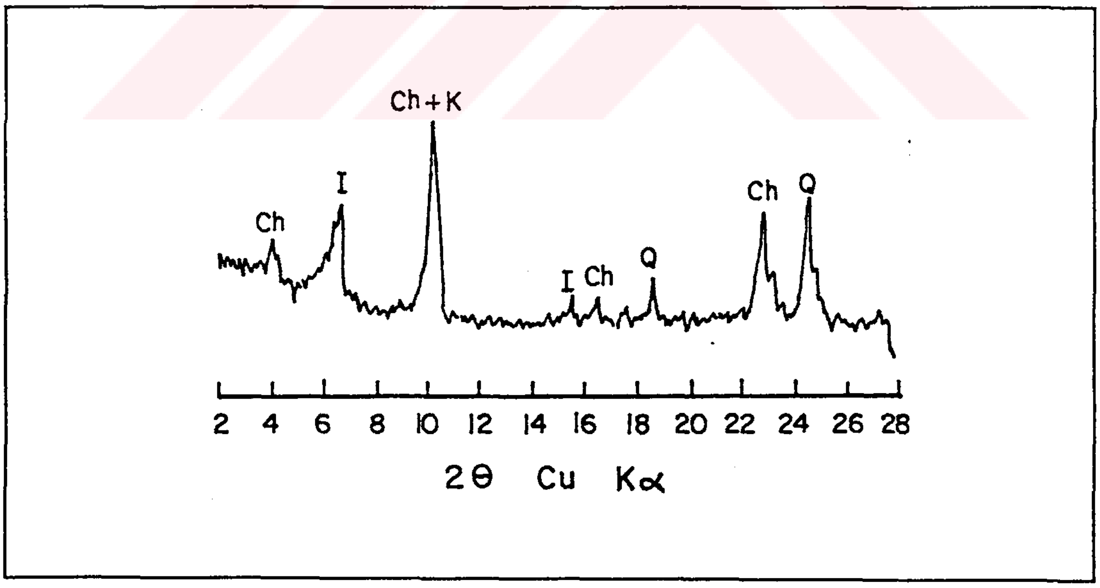

Figure 7.5. XRD Pattern of Oriented Air Dried Sample F (Notions as in Fig. 7.4.)

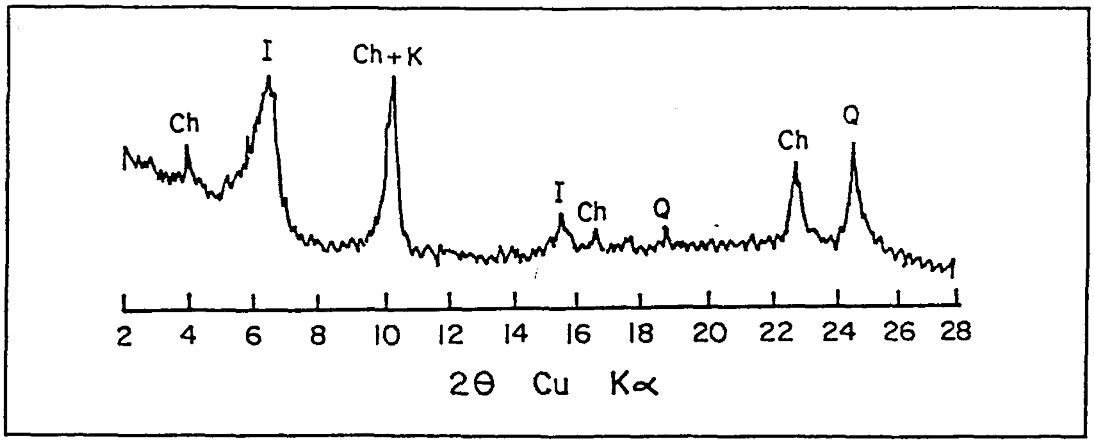

Figure 7.6. XRD Pattern of Oriented Air Dried Sample H (Notions as in Fig. 7.4)

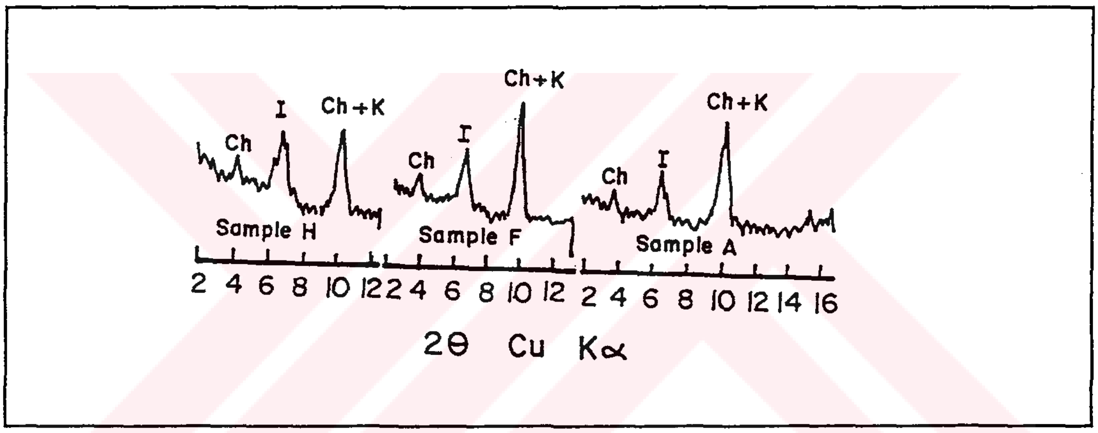

Figure 7.7. XRD Patterns of Oriented Samples A, F and H After Glycolation (Notions as in Fig. 7.4.)

7.1.3.2 Detailed Analysis of Coarse Wastes

Sample B (0-100 mm new refuse) and Sample E (fine jig tailing) were subjected to XRD analysis in unoriented mounts and their results are given in Figures 7.9 and 7.10.

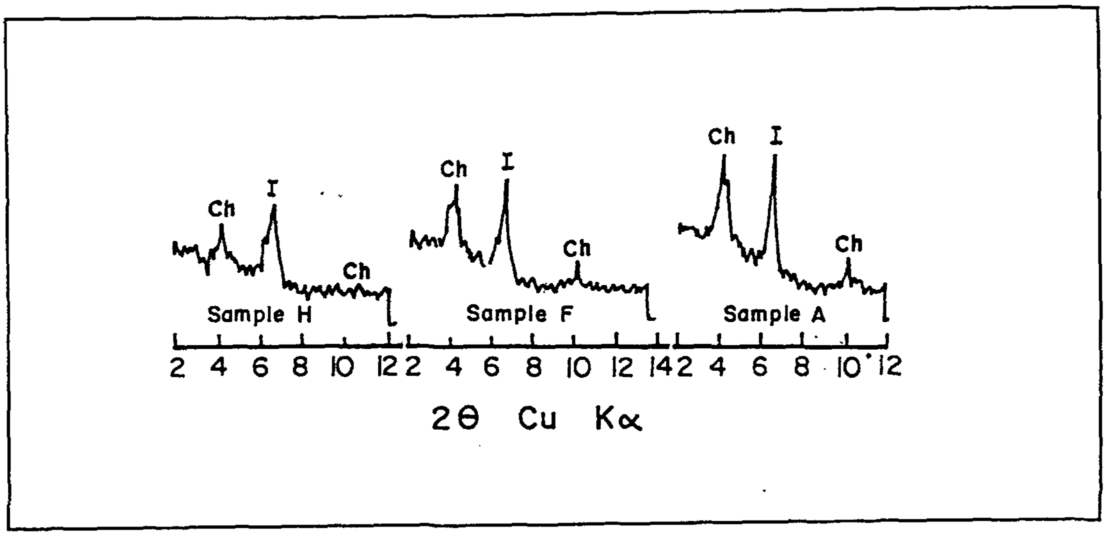

Figure 7.8. XRD Patterns of Oriented Samples A, F and H After Heating to 550 ^{o}C.(Notions as in Fig.7.4)

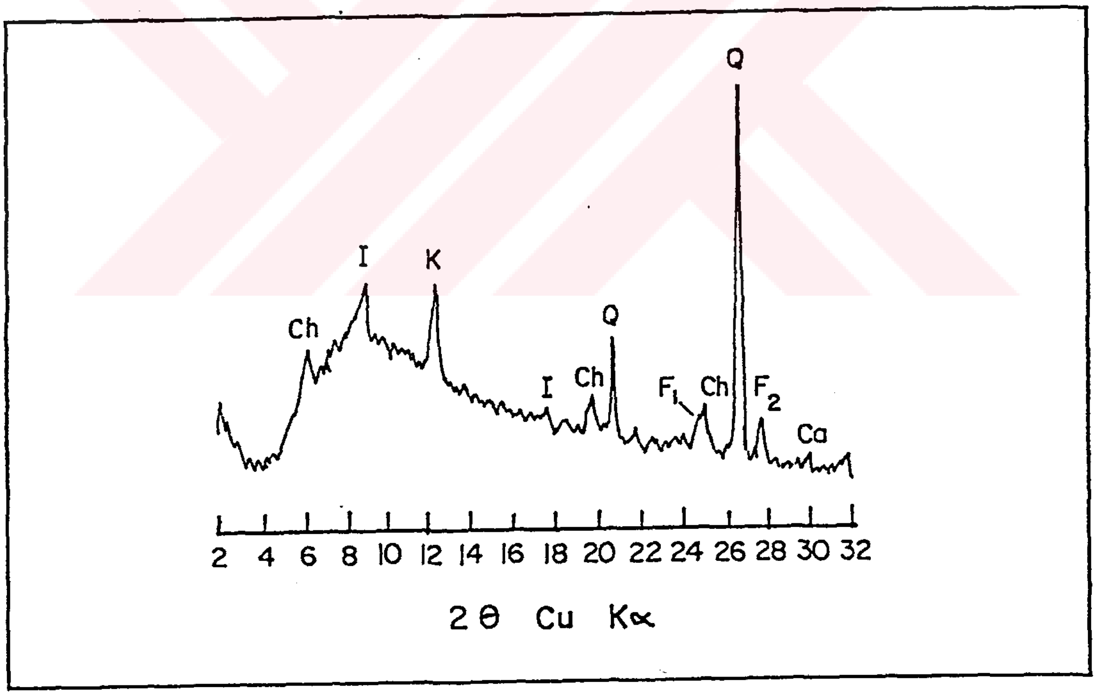

Figure 7.9. XRD Pattern of Unoriented Sample B. (Notions as in Fig. 7.4 except F_1= Orthoclase Feldspar and F_2= Plagioclase Feldspar)

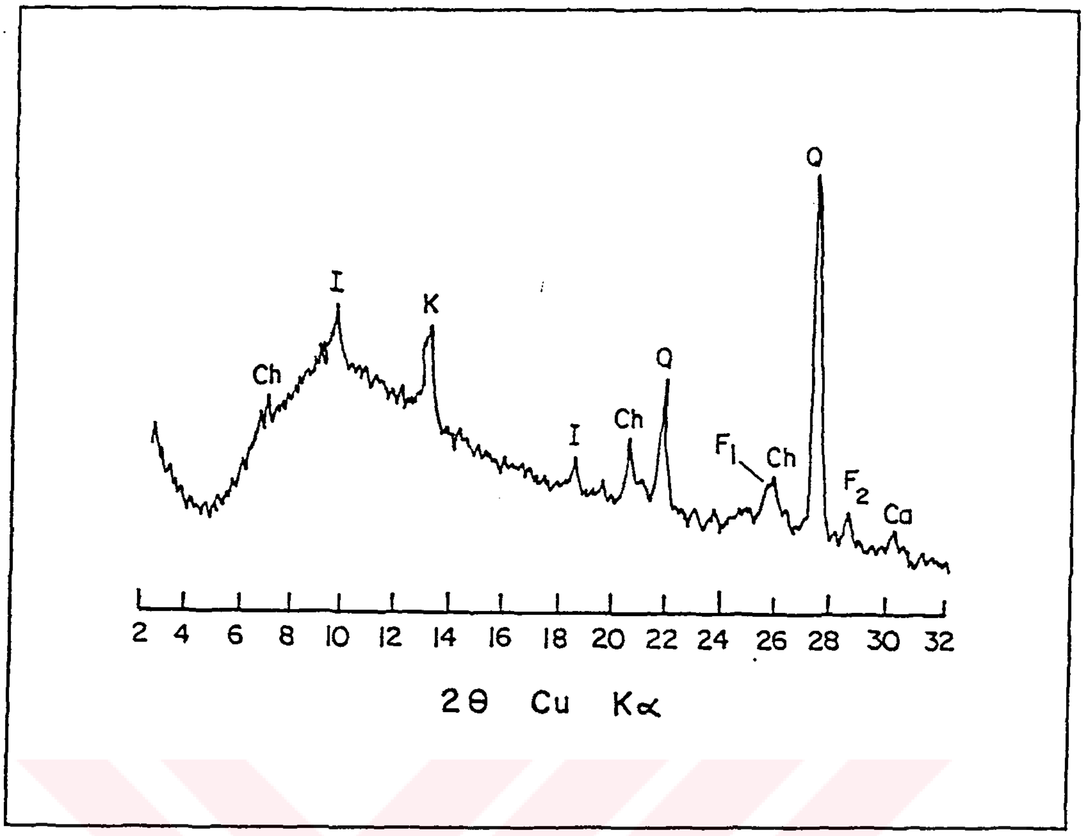

Figure 7.10. XRD Pattern of Unoriented Sample E (Notions as in Fig. 7.9)

Sample A, subjected to XRD in unoriented mount and after loss on ignition analysis (heated at 900 °C) is shown in Fig 7.11.

X-ray diffraction patterns of oriented Samples A, B, C, D and E are given in Figures 7.12 to 7.16.

7.1.3.3 Analysis of Thickener Overflow Sample

The thickener overflow sample designated as Sample H subjected to XRD analysis separately is depicted in Figure 7.17.

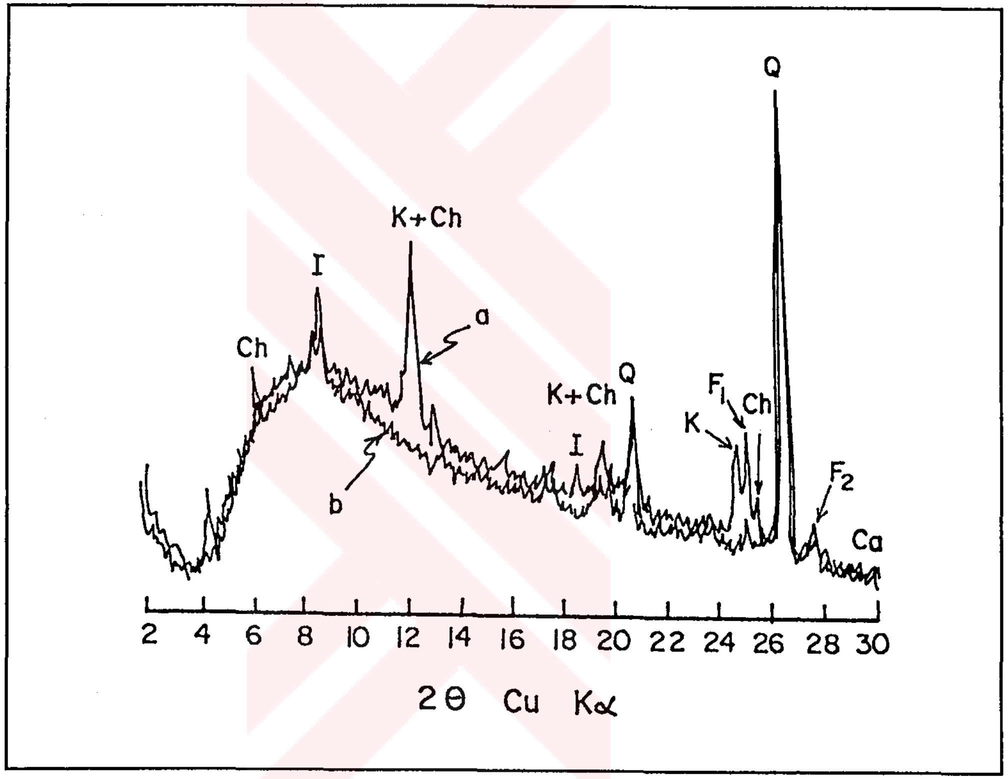

Figure 7.11 XRD Patterns of Unoriented Sample A: (a) Air Dried and (b) After Loss On Ignition at 900 C. (Notions as in Fig. 7.9).

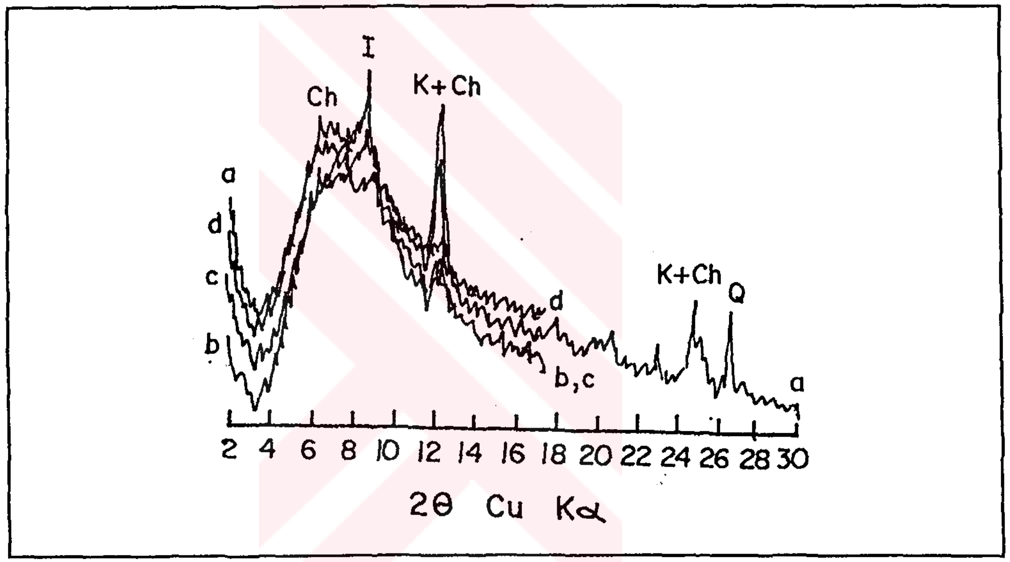

Figure 7.12. XRD Patterns of Oriented Sample A: (a) Air Dried (b) Glycolated (c) Heated to 350 C and (d) Heated to 550 ^{o}C (Notions as in Fig. 7.4).

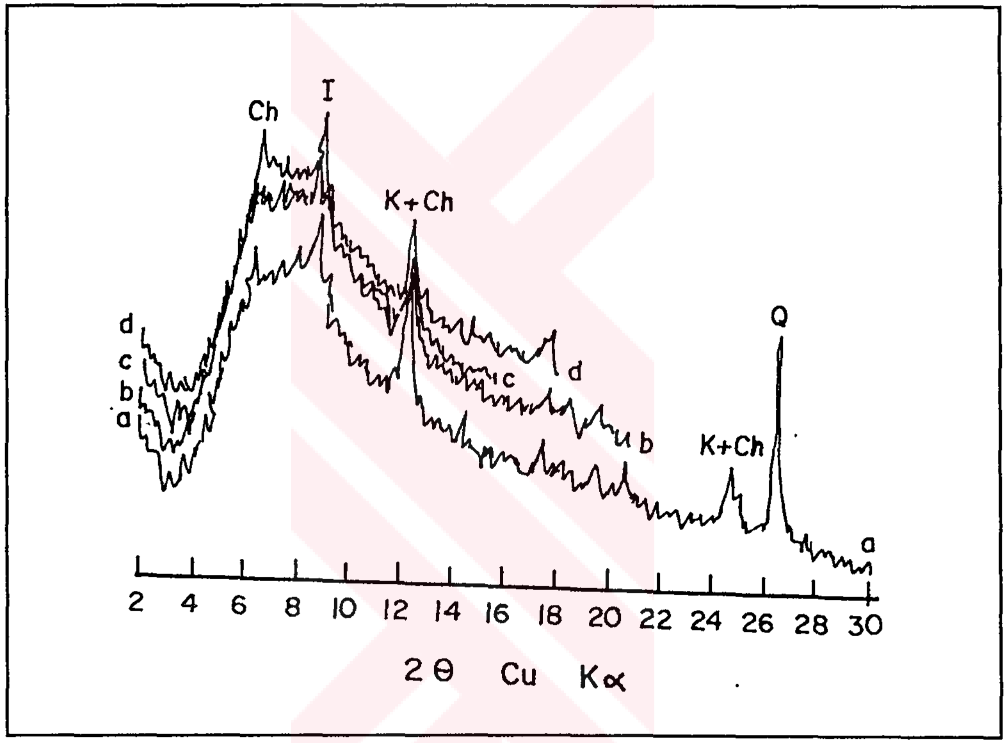

Figure 7.13. XRD Patterns of Oriented Sample B: (a) Air Dried, (b) Glycolated, (c) Heated to 350 °C, and (d) Heated to 550 °C.

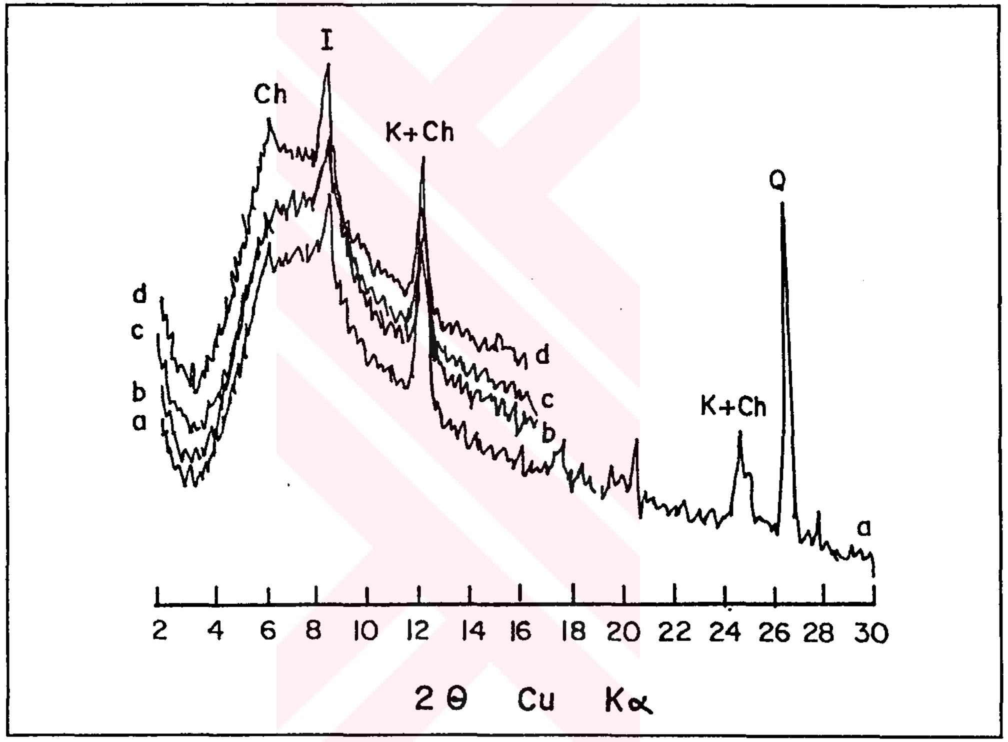

Figure 7.14. XRD Patterns of Oriented Sample C: (a) Air Dried, (b) Glycolated, c) Heated to 350 °C and (d) Heated to 550 °C.(Notions as in Fig. 7.4)

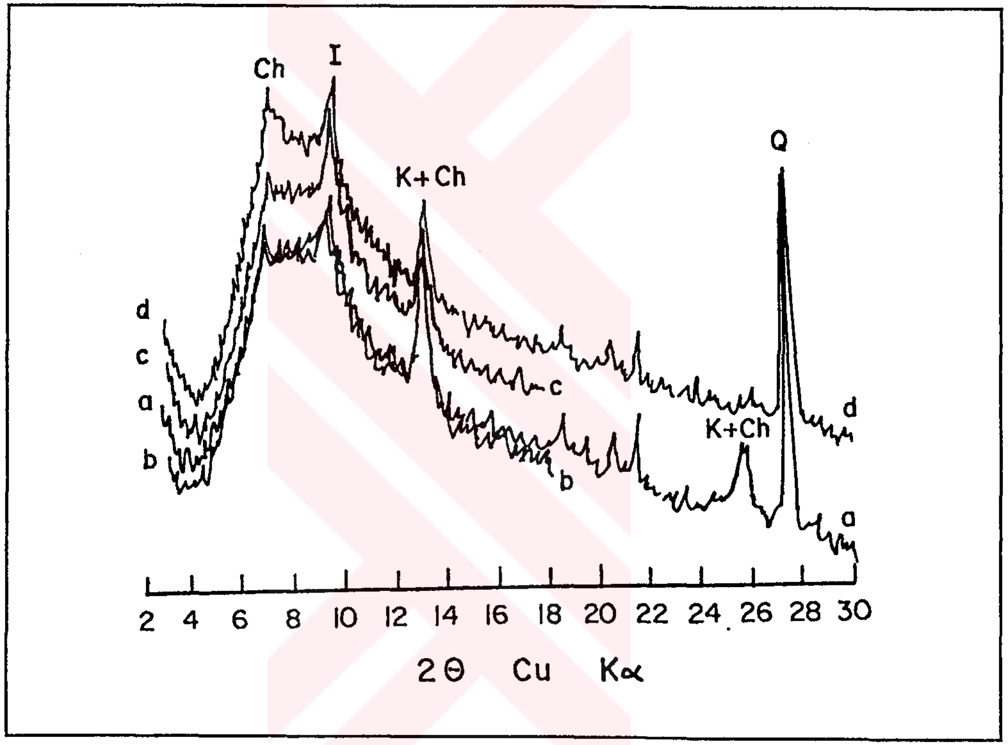

Figure 7.15. XRD Patterns of Oriented Sample D:(a) Air Dried,(b) Glycolated,(c) Heated to 350 ^{o}C and (d) Heated to 550 ^{o}C. (Notions as in Fig. 7.4).

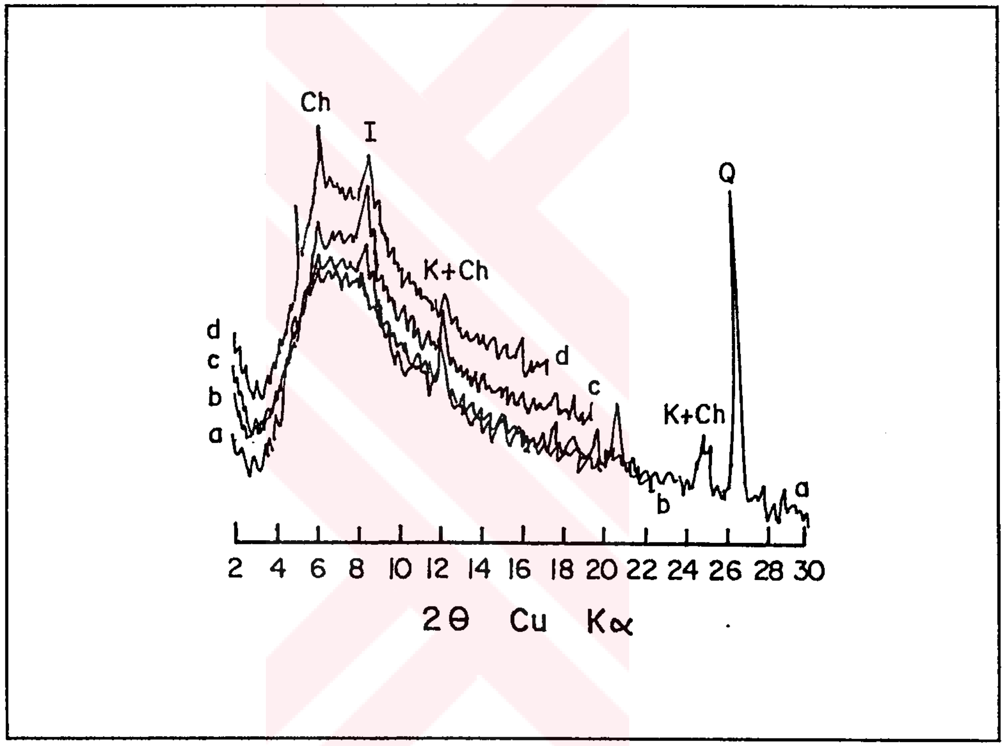

Figure 7.16. XRD Patterns of Oriented Sample E: (a) Air Dried, (b) Glycolated (c) Heated to 350 ° C and (d) Heated to 550 °C (Notions as in Fig.7.4).

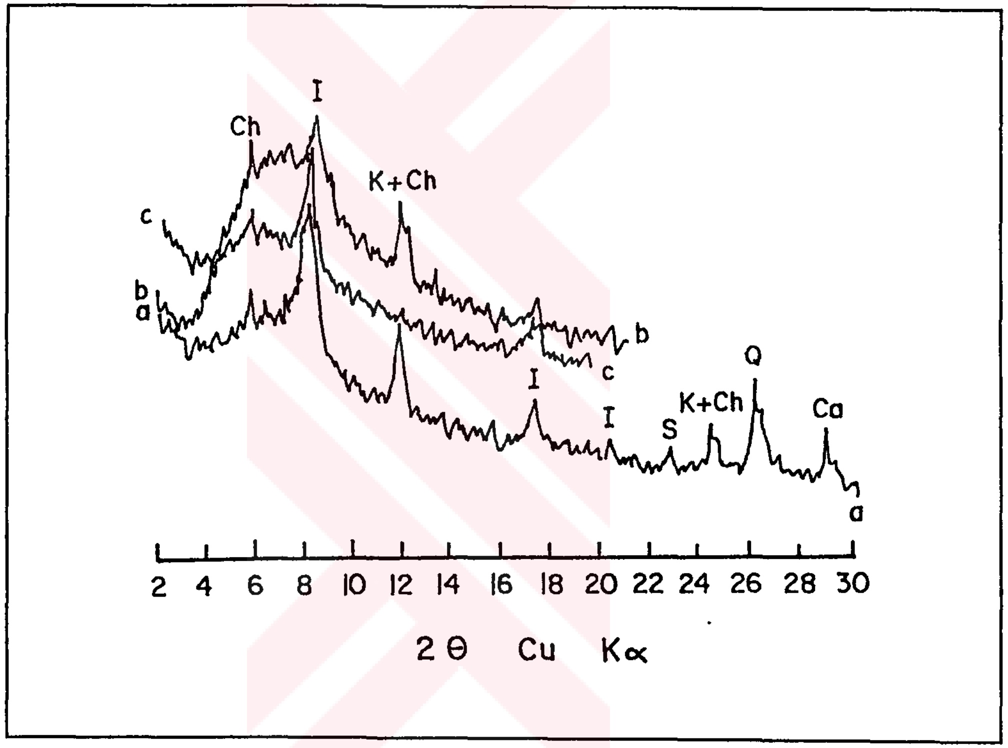

Figure 7.17 XRD Patterns of Oriented Sample H:(a) Air Dried (b) Glycolated and (c) Heated to 550 ^{O}C. (Notions as in Fig. 7.4).

7.1.3.4 Analysis of Pretreated and Combined Treated (pretreated + acid treated) Samples

Sample B (low organic matter) and Sample F (Flotation Tailing) and G (Flotation Feed), containing very high organic matter were pretreated and subjected to XRD analysis as shown in Figures 7.18 to 7.20. The XRD Patterns of combined treated Samples F and G are given in Figures 7.21 and 7.22.

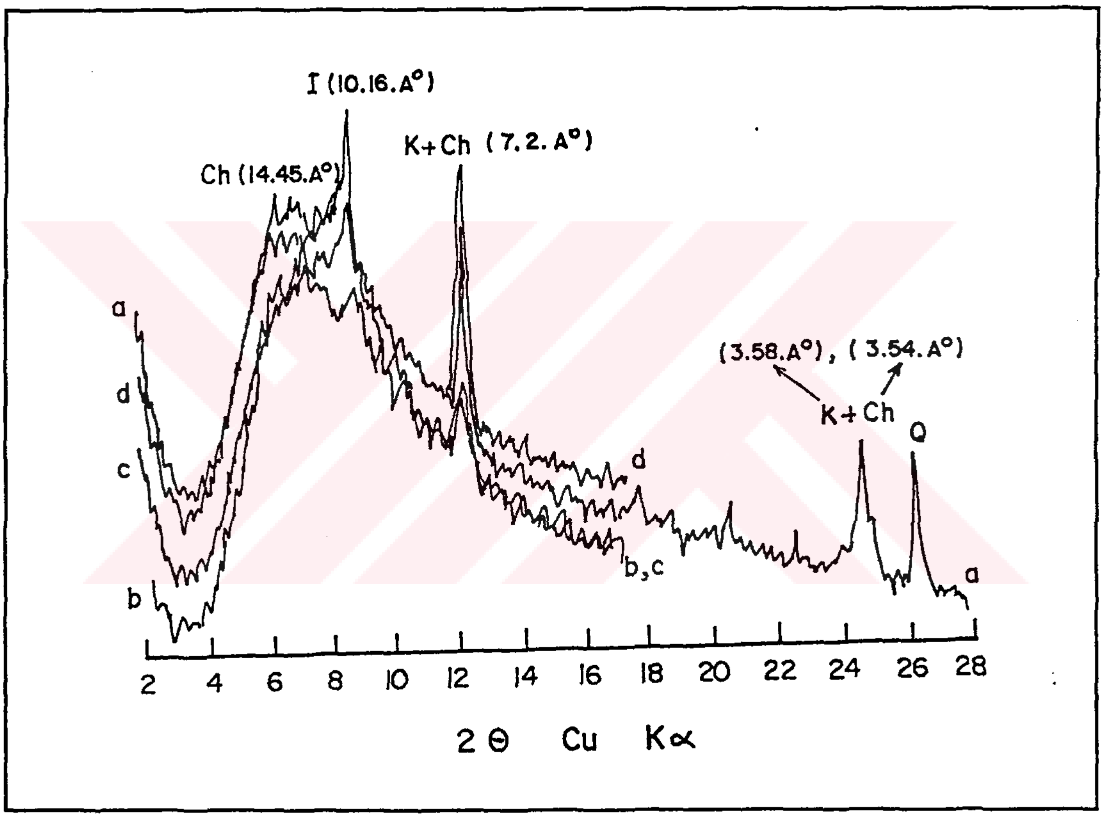

Figure 7.18. XRD Patterns of Pretreated Oriented Sample B: (a) Air dried, b) Glycolated, (c) Heated to 350 ^{O}C and (d) Heated to 550 ^{O}C Notions as in Fig. 7.4)

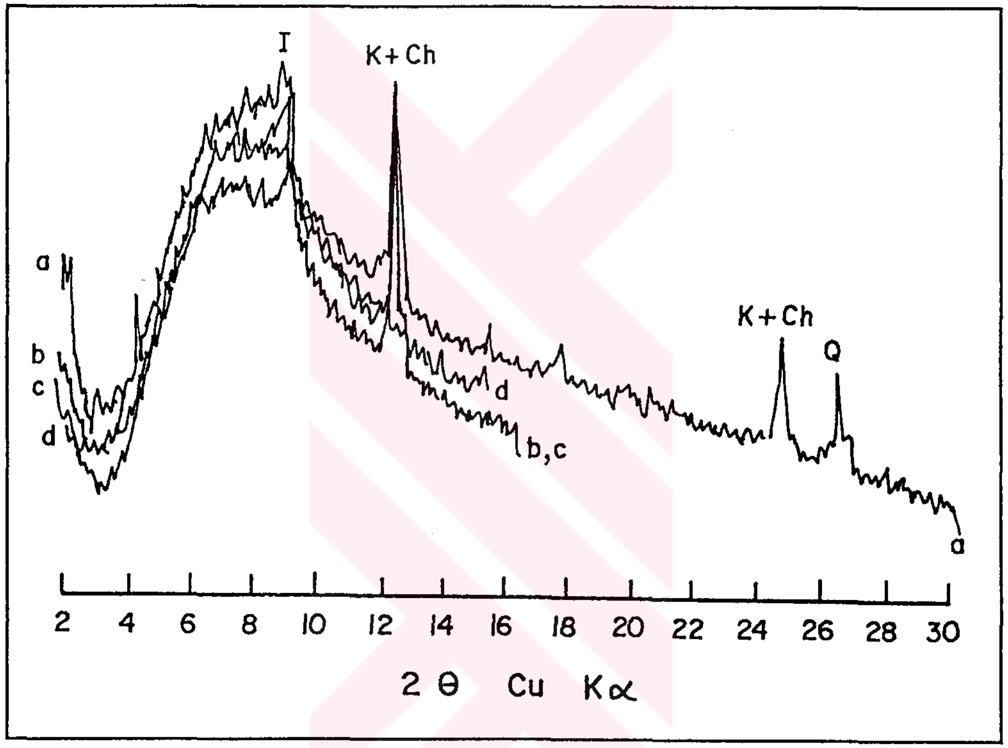

Figure 7.19. XRD Patterns of Pretreated Oriented Sample F: (a) Air Dried, (b) Glycolated, (c) Heated to 350 °C and (d) Heated to 550 °C. (Notions as in Fig. 7.4.)

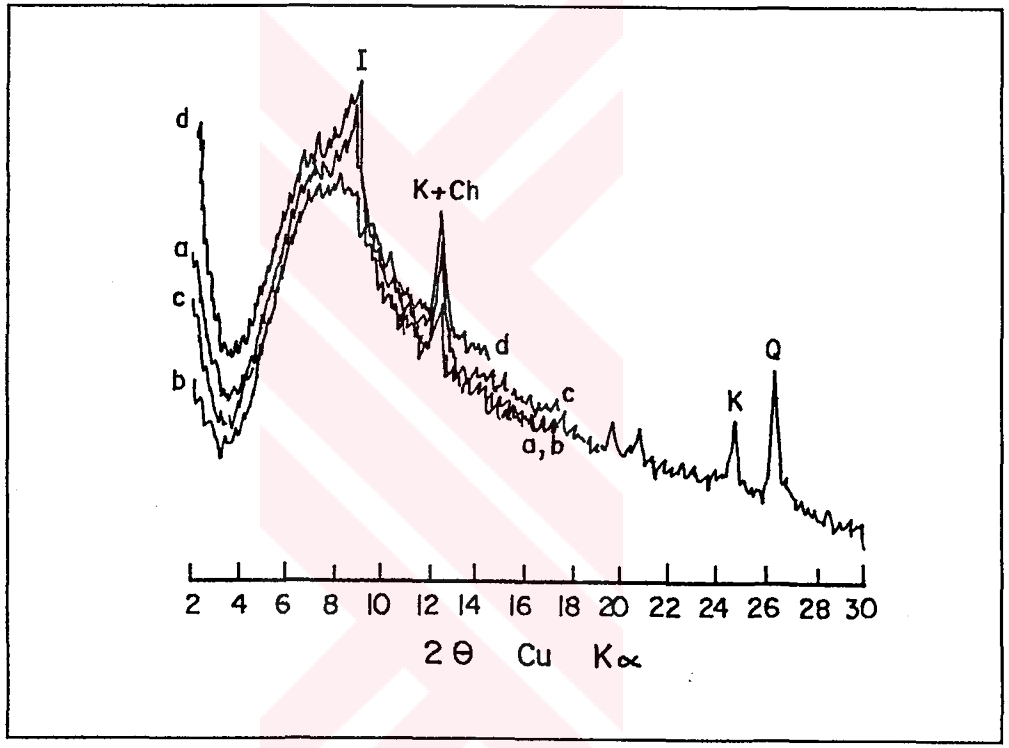

Figure 7.20. XRD Patterns of Pretreated Oriented Sample G: (a) Air Dried, (b) Glycolated (c) Heated to 350 °C and (d) Heated to 550 °C. (Notions as in Fig. 7.4)

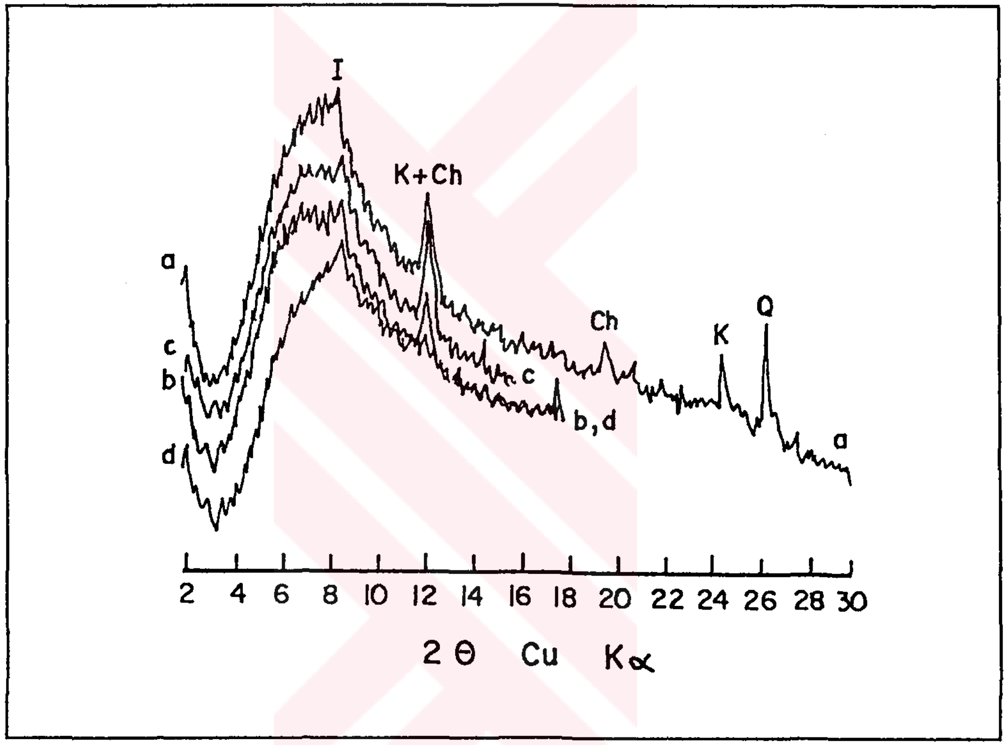

Figure 7.21. XRD Patterns of Combined Treated Sample F: (a) Air Dried (b) Glycolated (c) Heated to 350 °C and (d) Heated to 550 °C. (Notions as in Fig. 7.4).

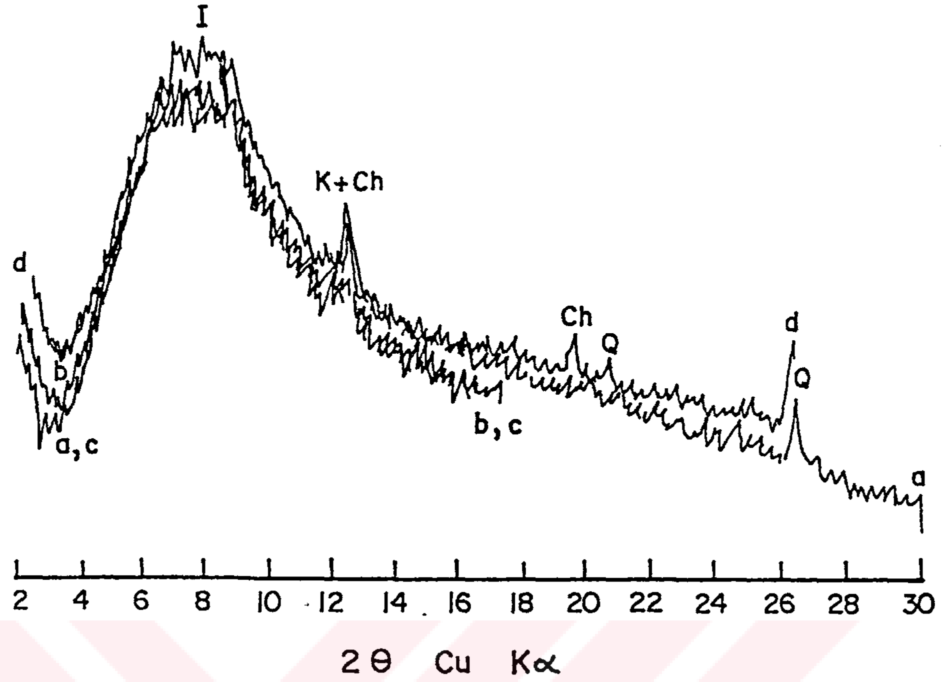

Figure 7.22. XRD Patterns of Oriented Combined Treated Sample G: (a) Air Dried, (b) Glycolated (c) Heated to 350 °C and (d) Heated to 550 °C. (Notions as in Fig. 7.4)

7.1.3.5 Analysis of Flotation Feed (Sample G) After Low Temperature Ashing (LTA)

Two flotation feed samples subjected to XRD after cool oxygen plasma oxidation (COPO) are shown in Figures 7.23 and 7.24. Figure 7.23 was a result of COPO treatment only once, where as Figure 7.24 resulted from separation of low temperature ash after COPO by ethyl alcohol (C_2H_5OH) and again subjecting it to COPO treatment (two times).

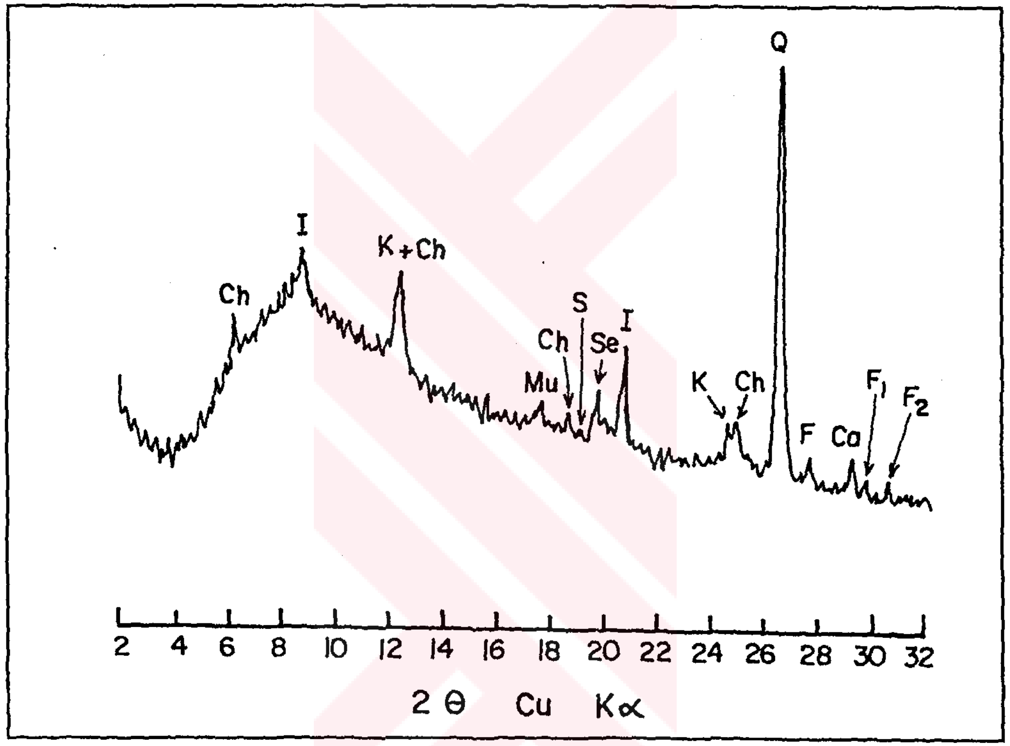

Figure 7.23. XRD Pattern of Unoriented Sample G After COPO Treatment:

(Notions as in Fig. 7.4 except Mu=Muscovite, Se=Sepiolite)

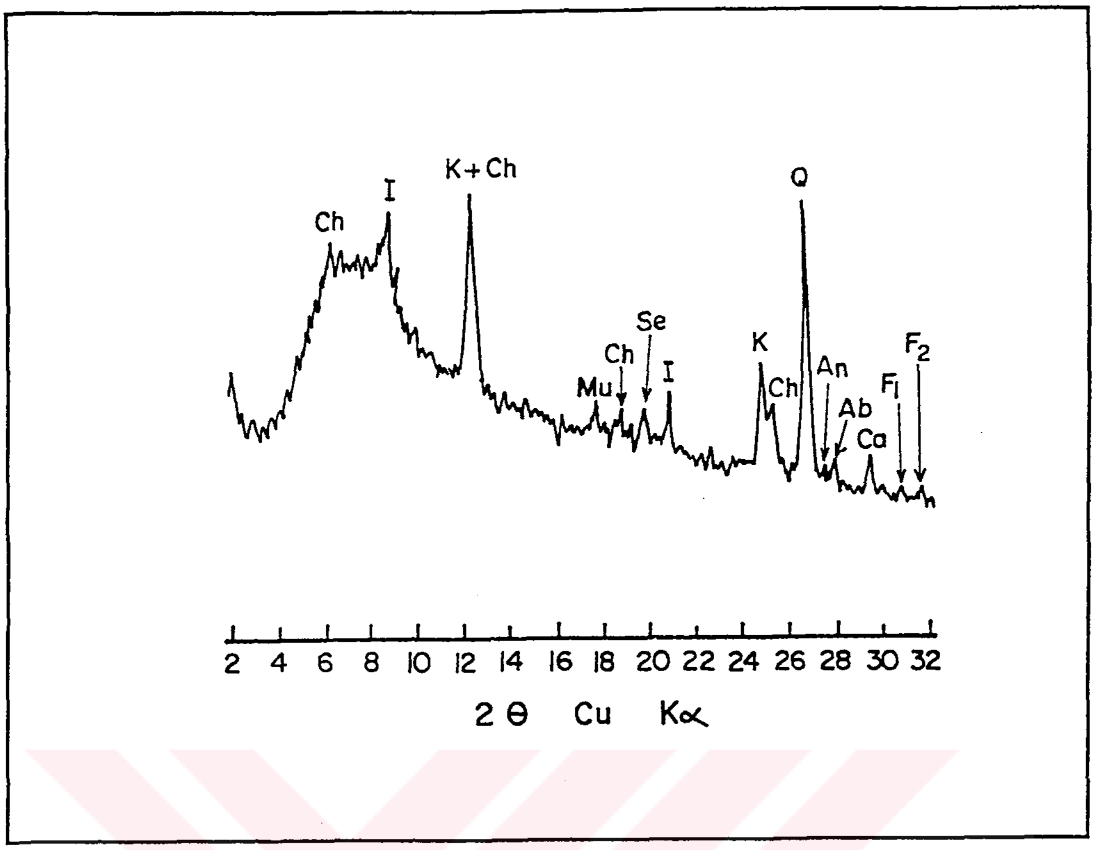

Figure 7.24. XRD Pattern of Unoriented Sample G After Double COPO Treatment. (Notions as in Fig. 7.23 except An = Anorthite and Ab= Albite)

7.1.4 Loss on Ignition Analysis

All the samples (Samples A to H) were subjected to loss on ignition analysis. Their results are shown in Table 7.3.

Table 7.3. Results of Analysis by Loss on Ignition

Sample 1	Percent Loss, 105 ^oC (Moisture, %) 2	Percent Ignition Loss, 105-500 ^oC (Organic Carbon, %) 3	Percent Ignition Loss, 500-900 ^oC (CO_2, %) 4	Percent Total Carbonate* ($CaCO_3$,%) 5
A	0.60	5.59	2.78	6.3
B	0.94	5.97	2.73	6.2
C	0.85	4.96	2.00	4.55
D	1.29	13.86	1.82	4.14
E	1.01	21.29	2.16	4.91
F	1.01	33.25	2.86	6.50
G	0.94	62.85	1.32	3.00
H	0.98	26.72	1.78	4.05

* CO_2 percentage was converted to $CaCO_3$ percentage by dividing the results of column 4 with 0.44

7.2 Flotation Tests

7.2.1 Effect of Clays on Coal Flotation

The effect of pure clays namely kaolinite, illite and chlorite (Table 5.3.) from Turkey was studied on flotation of clean coals (Table 7.1). They were prepared as artifical mixture and floated by using Kerosene oil as collector and MIBC as frother. In these tests, the flotation time, pulp pH and pulp density were kept constant as 1 minute, 6.5 and 10 % by wt., respectively.

7.2.1.1 Effect of Kaolinite on Coal Flotation

The results of flotation tests which examined the effect of kaolinite on coal flotation are shown in Tables 7.4 and 7.5 respectively.

Table 7.4. Effect of Kaolinite on Coal Flotation

Ash in Coal, %	Clay added, %	Yield %	Ash, %	Reagents and Amounts (g/t)
4.5	0	86.7	2.5	K.oil = 340
	5	83.3	3.0	MIBC = 85
	10	79.5	4.0	
	15	76.9	5.0	
	20	72.1	6.0	
	25	68.9	7.0	
4.5	0	97.9	3.0	K. oil = 1020
	5	95.4	4.0	MIBC = 85
	10	91.4	5.5	
	15	87.4	7.0	
	20	83.3	8.0	
	25	79.3	9.0	
9.8	0	85.1	7.0	K. oil = 340
	5	82.5	7.5	MIBC = 85
	10	78.1	8.5	
	15	74.5	9.0	
	20	73.0	9.5	
	25	71.2	10.5	
9.8	0	97.0	8.0	K. oil = 1020
	5	92.0	8.5	MIBC = 85
	10	88.1	9.0	
	15	84.0	10.0	
	20	80.9	11.0	
	25	75.6	11.5	

Table 7.5. Effect of of Kaolinite on Coal Flotation in Presence of CMC

Ash in Coal, %	Clay added, %	Yield, %	Ash, %	Reagent and amount (g/t)
4.5	0	97.9	3.0	K.oil = 1020
	5	85.1	4.0	MIBC = 85
	10	72.5	5.0	CMC = 100
	15	71.0	5.5	
	20	69.9	6.5	
	25	65.2	7.5	
9.8	0	97.0	8.0	K.oil = 1020
	5	91.1	8.5	MIBC = 85
	10	86.5	9.0	CMC = 100
	15	82.4	9.5	
	20	79.3	10.0	
	25	73.0	11.0	

7.2.1.2 Effect of Illite on Coal Flotation

The results of flotation tests which show the effect of illite on coal flotation are shown in Table 7.6.

Table 7.6. Effect of Illite on Coal Flotation

Ash in coal, %	Clay added, %	Yield, %	Ash, %	Reagents and Amount (g/t)
4.5	0	86.7	2.5	K.oil = 340
	5	77.5	4.0	MIBC = 85
	10	73.2	5.5	
	15	68.2	7.0	
	20	64.3	8.0	
	25	59.1	9.0	

7.2.1.3 Effect of Chlorite on Coal Flotation

The results of flotation tests which show the effect of chlorite on coal flotation are shown in Table 7.7.

Table 7.7. Effect of Chlorite on Coal Flotation

Ash in Coal, %	Clay added, %	Yield, %	Ash, %	Reagents and Amount (g/t)
4.5	0	86.7	2.5	K.oil = 340
	5	79.0	3.5	MIBC = 85
	10	76.0	4.5	
	15	73.4	6.0	
	20	70.2	7.0	
	25	66.5	8.0	

7.2.2 Comparison of Artificial Coal /Clay Flotation Systems

The results obtained by floating mixtures of clays and coal with Kerosene oil (340 g/ton) and MIBC (85 g/ton) for one minute are given in Table 7.8.

In the other flotation tests, the actual system was compared with the mixture of three clays (Kaolinite + chlorite + illite). The amount of clays used was determined by semi quantitative XRD analysis of flotation feed. The comparative results of flotation tests are given in Table 7.9.

Table 7.8. Effects of Maximum Amount of Different Clays on Flotation of Clean Coal as Compared to the Flotation Feed

Coal Type	Ash Coal, %	No clay		25 % Kaolinite		25 % Illite		25 % Chlorite	
		Yield %	Ash, %	Yield %	Ash, %	Yield %	Ash, %	Yield %	Ash, %
Clean hand picked	4.5	86.7	2.5	68.9	7.0	59.1	9.0	66.5	8.0
Hand picked	9.8	85.1	7.0	71.2	10.5	-	-	-	-
Flotation Feed	35.1	50.5	15.0	-	-	-	-	-	-

Table 7.9. Comparison of Flotation Systems Using Artificial Coal/Clay Mixture and Flotation Feed

Coal Type	Ash in Coal, %	No Clay		Clays added K =13 % +I=8 % + Ch=4 %	
		Yield %	Ash %	Yield %	Ash %
Clean,Hand Picked	4.5	86.7	2.5	70.1	9.0
Hand Picked	9.8	85.1	7.0	64.1	12.0
Flotation Feed	35.1	50.5	15.0	---	---

7.3 Electrokinetic Potential Measurements

The electrokinetic potential measurements were performed by examining

(i) the effect of pH and (ii) the effect of electrolytes on pure clays and clean coal. Similarly the effects of varying concentrations of different dispersants and depressants were also examined to assess their effect on zeta potentials of coal.

7.3.1 Zeta Potential Determination of Pure Clays

The results of zeta potential determination of three clays by varying the pH are given in Table 7.10.

Table 7.10 Zeta Potentials of Turkish Clays

pH	Zeta Potential (mv)		
	Kaolinite	Illite	Chlorite
2.5	-38.6	Zero	N.D.*
3.0	-32.2	-13.1	Zero
3.5	-29.8	-18.5	-20.1
4.0	-26.1	-22.2	-25.1
4.5	-24.5	-24.0	-26.5
5.0	-31.0	-25.5	-28.5
6.0	-35.2	-28.1	-30.1
7.0	-40.0	-30.0	-31.0
8.0	-42.5	-32.0	-32.5
9.0	-45.0	-33.9	-34.9
10.0	-47.1	-38.1	-36.5
11.0	-49.5	-42.0	-33.9

* Not determined

7.3.2 Zeta Potential Determination of Clean Coal

The results of zeta potential determination of clean coal (4.5 % ash) by varying the pH are shown in Table 7.11.

7.3.2.1 Zeta Potentials of Clean Coal With Varying Amounts of Different Inorganic Electrolytes

The effect of various molar (moles/litre) concentrations of magnesium chloride ($MgCl_2$), calcium chloride ($CaCl_2$), calcium hydroxide [$Ca(OH)_2$], aluminum chloride ($AlCl_3$), aluminum sulphate [$Al_2(SO_4)_3$] was studied on zeta potential of clean coal (4.5 % ash) and the results are depicted in Table 7.12.

Table 7.11 Zeta Potentials of Clean Coal

pH	Zeta Potential(mv)
11.0	-44.8
10.0	-39.9
9.2	-35.0
8.3	-32.2
7.3	-30.5
6.3	-27.8
5.7	-24.9
4.6	-21.1
4.3	-13.3
3.8	+13.6
3.4	+15.0
2.5	+19.6

Table 7.12. Effect of Various Concentrations of Inorganic Electrolytes on Zeta Potential of Clean Coal

Conc. Molar	Zeta Potential (mv)				
	$MgCl_2$ 1	$CaCl_2$ 2	$[Ca(OH)_2]$ 3	$AlCl_3$ 4	$[Al_2(SO_4)_3]$ 5
$1x10^{-3}$	-19.9	-19.4	-26.4	+21.50	+35.1
$5x10^{-4}$	-25.9	-21.1	-29.8	+18.3	+25.5
$1x10^{-4}$	-27.4	-25.1	-29.8	+13.0	+15.7
$5x10^{-5}$	-29.1	-25.9	-30.8	-15.10	-10.7
$1x10^{-5}$	-35.0	-32.0	-33.7	-25.8	-19.5
$5x10^{-6}$	-38.1	-36.0	-37.2	-35.0	-27.0
$1x10^{-6}$	-43.4	-39.5	-41.5	-38.1	-31.0

7.3.2.2 Zeta Potentials of Clean Coal with Varying Amounts of Different Dispersants and Depressants

The effect of various molar concentrations of sodium silicate, Calgon (sodium hexametaphosphate), CMC (Tylose C30), Marsperse CB (Sodium lignin sulfonate), Aero Depressant 633 and dextrin was studied on zeta potential of clean coal and the results are given in Tables 7.13 (a) and (b).

Table 7.13. (a) Effect of Various Concentrations of Dispersants and Depressants on Zeta Potential of Clean Coal

Zeta Potential (mv)				
Conc.Moles/L for 1 & 2	Sodium Silicate 1	Calgon 2	CMC 3	Conc. mg/L for 3
$1x10^{-3}$	-53.6	-37.2	-66.9	5
$5x10^{-4}$	-44.4	-40.2	-65.2	1
$1x10^{-4}$	-37.6	-44.0	-53.5	0.5
$5x10^{-5}$	-35.0	-45.0	-52.5	0.1
$1x10^{-4}$	-32.0	-47.2	-44.8	0.05
$5x10^{-6}$	-28.3	-49.4	-33.1	0.01
$1x10^{-6}$	-27.2	-50.5	-31.9	0.005

Table 7.13. (b) Effect of Various Concentrations of Different Dispersants and Depressants on Zeta Potential of Clean Coal

Zeta Potential (mv)				
Conc.mg/L for 1 & 2	Marsperse CB 1	Aero Depressant 633 2	Dextrin 3	Conc. mg/L for 3
30	-66.0	-46.8	-30.5	5
25	-62.7	-44.5	-32.1	1
20	-55.4	-42.9	-35.3	0.5
15	-52.4	-40.3	-40.0	0.1
10	-46.4	-37.9	-48.5	0.05
5	-41.4	-35.4	-58.1	0.01
1	-39.6	-33.0	-69.5	0.005

7.4 Coal Flotation Tests

The coal flotations with coals containing ash 4.5, 9.8, 35.1, 39.9 and 67.1 % were carried out. These flotation tests were conducted in three sets namely direct, single stage reverse and combined two stage (direct followed by reverse) flotation. A Wedag laboratory flotation machine having a fibre glass cell, manufactured locally, with a constant impeller speed of 1420 rpm was used for flotation experiments. These experiments were performed in distilled water (pH 6.5) with 50 grams of coal to give a pulp density of 10 % by weight, keeping agitation and conditioning time, three minutes each.

The direct flotation was done using clean coals (4.5 and 9.8 % ash) and high ash coals (35.1, 39.9 and 67.1 % ash). Three reagent systems namely Kerosene oil and MIBC, Pamak 4 and oleic acid were used for floating 35.1, 39.9 and 67.1 % ash coals. In some tests effects of CMC, sodium silicate were investigated for 35.1 % ash coal. Pamak 4 and oleic acid which are ionizing collectors were used in search of some better system than combination of Kerosene oil and MIBC for floating coals in the light of their higher HLB numbers and hence more activity (Becher, 1965; Myers, 1988).

The reverse flotation of coal with high ash or clays is still a dream of researchers. This is used in two stages (direct and reverse flotation) to remove pyrite from high sulphur coals (Miller and Deurbrock, 1982). In single stage it was attempted with partial success by Stone Street and Franzidis (1988;1989) for floating artificial mixtures of coal and quartz using quartenary amines. In this study single stage reverse flotation tests were carried out on 35.1 % ash coal using amines (Flotigam ENA, Armoflote 18 and Armoflote 21) while dextrin was used as the coal depressant (Miller and Deurbrock, 1982).

Finally a combined two stage flotation (direct and reverse) was attempted on 35.1 % ash coal. In first stage, the direct flotation using Pamak 4 was carried out and the concentrate so obtained was subjected to single stage reverse flotation using Flotigam ENA and dextrin.

7.4.1 Direct Flotation

7.4.1.1. Direct Flotation of Clean Coals

Kerosene oil as collector and MIBC as frother were used as reagents in these tests. The results are given in Tables 7.14 to 7.16.

Table 7.14. Determination of Collector (Kerosene oil) Amount in Direct Flotation of Clean Coals

K.oil (g/t)	K.oil (drops)	Ash in Coal, (%)	Concentrate Yield, %	Concentrate Ash, %
340	1*	4.5	86.7	2.0
680	2	4.5	91.2	2.5
1020	3	4.5	95.0	3.0
340	1	9.8	85.1	7.0
680	2	9.8	90.0	7.5
1020	3	9.8	94.3	8.0

* Each drop of Kerosene oil = 0.017 grams.
(MIBC=85 g/t : Flotation Time = 1 minute: pH=6.5)

Table 7.15. Determination of Frother (MIBC) Amount in Direct Flotation of Clean Coals

MIBC (g/t)	Ash in Coal, (%)	Concentrate Yield, %	Concentrate Ash, %
42.5	4.5	88.1	3.0
85.0	4.5	86.7	2.5
170.0	4.5	80.2	2.5
42.5	9.8	86.5	7.5
85.0	9.8	85.1	7.0
170.0	9.8	79.0	6.0

(Kerosene oil= 340 g/t : pH = 6.5)

Table 7.16. Determination of Flotation Time in Direct Flotation of Clean Coals

Flotation Time (Minutes)	Ash in Coal, (%)	Concentrate Yield, %	Concentrate Ash, %
1	4.5	86.7	2.5
2	4.5	88.0	2.5
3	4.5	90.5	3.0
1	9.8	85.1	7.0
2	9.8	87.1	7.5
3	9.8	89.0	8.0

(Kerosene oil=340 g/t : MIBC=85 g/t :pH=6.5)

7.4.1.2 Direct Flotation of High Ash Coals With Kerosene Oil

The direct flotation of high ash coals (35.1, 39.9 and 67.1 % ash contents) were carried out by using Kerosene oil as collector and MIBC as frother. The results of these tests are given in Table 7.17.

Table 7.17. Direct Flotation of High Ash Coals With Kerosene oil.

K. Oil (g/t)	K. Oil (drops)	Ash in Coal (%)	Concentrate Yield, %	Concentrate Ash, %
340	1	35.1	50.5	15.0
680	2	35.1	68.5	17.0
1020	3	35.1	75.	19.5
340	1	39.9	42.1	17.0
680	2	39.9	60.3	19.5
1020	3	39.9	68.9	22.5
340	1	67.1	9.0	27.5
680	2	67.1	20.1	29.5
1020	3	67.1	30.2	33.0

* (MIBC=85 g/t: Flotation Time= 1 minute : pH=6.5)

7.4.1.3 Direct Flotation of High Ash Coals With Pamak4

The direct flotation of coals with different ash contents by Pamak4 was carried out under conditions used before (Table 7.17). The results of these tests are shown in Table 7.18.

7.4.1.4 Direct Flotation of High Ash Coals With Oleic Acid

The direct flotation of coals with different ash contents by using oleic acid were carried out. The results are given in Table 7.19.

Table 7.18. Direct Flotation of High Ash Coals With Pamak4

Pamak4 (g/t)	Pamak4 drops *	Ash in Coal (%)	Concentrate Yield, %	Concentrate Ash, %
500	1	35.1	70.5	15.0
1000	2	35.1	·78.6	19.0
1500	3	35.1	89.5	23.5
500	1	39.9	62.0	18.0
1000	2	39.9	68.5	21.5
1500	3	39.9	78.0	25.5
500	1	67.1	24.4	23.5
1000	2	67.1	30.0	27.5
1500	3	67.1	40.0	32.0

* Each drop of Pamak4 = 0.025 grams.

7.4.1.5 Effect of CMC on Direct Flotation of Coal

The effect of CMC (Tylose C30) was investigated as depressant on flotation of 35.1 % ash coal. The results of these tests are given in Table 7.20.

Table 7.19. Direct Flotation of High Ash Coals With Oleic Acid

Oleic Acid (g/t)	Oleic Acid (drops *)	Ash in Coal (%)	Concentrate Yield, %	Concentrate Ash, %
560	1	35.1	34.1	12.0
1120	2	35.1	42.0	15.0
1680	3	35.1	49.1	19.0
560	1	39.9	40.5	17.0
1120	2	39.9	51.0	19.0
1680	3	39.9	70.1	23.5
560	1	67.1	6.0	27.0
1120	2	67.1	18.1	32.0
1680	3	67.1	32.2	38.0

* Each drop of Oleic acid = 0.028 grams.

Table 7.20. Effect of CMC on Flotation of Coal

CMC (g/t)	Concentrate Yield, %	Concentrate Ash, %
Zero	50.5	15.0
50	49.1	15.0
100	45.5	14.0
150	39.1	14.0
200	32.1	13.5

(K.oil 340 g/t: MIBC 85 g/t: Flotation Time 1 minute : pH 6.5)

7.4.1.6 Effect of Sodium Silicate on Direct Flotation of Coal

The flotation of coal with 35.1 % ash was carried out to see the effects of sodium silicate as depressant and dispersant. The flotation results are given in Table 7.21.

Table 7.21. Effect of Sodium Silicate on Flotation of Coal

Sod. Silicate (g/t)	Concentrate Yield, %	Concentrate Ash, %
Zero	50.5	15.0
150	48.1	15.0
250	45.5	14.5
350	43.9	15.0
450	42.5	15.5

(K.oil 340 g/t: MIBC 85 g/t : Flotation time 1 minute : pH 6.5)

7.4.2 Single Stage Reverse Flotation

The single stage reverse flotation was done with Flotigam ENA (alkyl ether amine) as collector for ash bearing minerals and dextrin as the depressant for coal. The coal used in this study contained 35.1 % ash. The results are given in Tables 7.22 to 7.25. Tables 7.22 and 7.23 give results for determining the amount of Flotigam ENA and dextrin used in the tests whereas Tables 7.24 and 7.25 show effects of varying flotation time, and pH respectively.

Table 7.22. Determination of Collector (Flotigam ENA) Amount in Single Stage Reverse Flotation of Coal

Flotation Time,(min.)	Flotigam ENA		pH	Coal, Yield, %	Coal Ash, %
	(g/t)	drops			
3	2880	8	7.0	67.1	19.0
3	3240	9	7.0	65.5	18.0
3	3600	10	7.0	62.2	16.5
3	3960	11	7.0	56.3	16.5
3	4320	12	7.0	51.5	16.0

* Each drops of Flotigam ENA = 0.018 grams. (Dextrin 100 g/t : pH 6.5)

Table 7.23. Determination of Depressant (dextrin) Amount in Single Stage Reverse Flotation of Coal

Dextrin (g/t)	Coal Yield, %	Coal Ash, %
800	59.1	17.0
1000	62.2	16.5
1200	63.5	17.0
1400	64.5	18.0
1600	65.8	19.0

Table 7.24. Determination of Flotation Time in Single Stage Reverse Flotation of Coal

Flotation Time, Minutes	Coal Yield,%	Coal Ash, %
1	72.6	21.0
2	68.0	18.0
3	62.2	16.5
4	52.7	16.5

(Dextrin 1000 g/t: Flotigam ENA 3600 g/t: pH 6.5)

Table 7.25. Determination of pH in Single Stage Reverse Flotation of Coal

pH	Coal Yield, %	Coal Ash, %
4.5	57.6	18.0
6.0	63.0	19.0
6.5	60.7	18.0
7.0	62.2	16.5
8.0	68.9	18.0
9.0	71.8	19.5

(Dextrin 1000 g/t: Flotigam ENA 3600 g/t: Flotation Time 3 minutes)

7.4.2.1 The Use of Other Amines in Reverse Flotation

After reverse flotation tests of 35.1 % ash coal conducted with collector as Flotigam ENA (10 drops), two other amines namely Armoflote 18 (quartenary amine) and Armoflote 21 (alkyl amine acetate) were also tested. The results of these tests are given in Table 7.26.

Table 7.26. Single Stage Reverse Flotation of Coal Using Different Amines

Reagent	Amount		Coal Yield, %	Coal Ash, %
	g/t	Drops		
Flotigam ENA	3600	10	62.2	16.5
Armoflote 18	4200	10*	68.5	25.0
Armoflote 21	4600	10**	48.7	23.0

* Each drop of Armoflote 18 = 0.021 grams.

** Each drop of Armoflote 21 = 0.023 grams.

(Dextrin 1000 g/t: pH 7)

7.4.3 Two Stage Flotation of Coal

The direct flotation of coal containing 35.1 % ash with Pamak4 was combined with reverse flotation using Flotigam ENA. The concentrate obtained in direct flotation was subjected to reverse flotation. The results of these tests are given in Table 7.27.

Table 7.27. Two Stage Flotation of Coal

Reagents and Amounts in Reverse Flotation		Coal Yield, %	Ash in coal, %
Flotigam ENA (g/t)	Dextrin (g/t)		
720	600	62.3	14.0
720	1000	59.2	13.0
720	1600	55.1	12.0
1440	600	0.9	14.0
1440	1600	1.5	16.0

Stage 1 (Direct Flot.) : Pamak4 (500 g/t)

pH= 0 6.5

Flot. time = 1 min.

Stage 2 (Reverse Flot.) : pH = 7

Flot. time = 1 min.

CHAPTER VIII

DISCUSSION OF RESULTS

The results given in Chapter VII, have been discussed here in two parts namely Part I and Part II. Part 1 includes discussions about three topics:

(i) Characterization of coals and clays.
(ii) Electrokinetics of clays and coal.
(iii) Flotation of clean coals and flotation behaviour of coal-clay mixtures.

Part II covers flotation of high ash coals and therefore, will be discussed as direct, indirect (reverse) and two stage flotation.

PART I

8.1 Characterization of Coals and Clays

8.1.1 Chemical Properties of Coal Samples

Five coals having different ash contents were used in this study. Clean coal containing 4.5 % ash consisted only of vitrain bands where as hand picked coal contained 9.8 % ash. Flotation feed which was minus 0.5 mm contained 35.1 % ash (usually it may vary upto 40 % ash). The high ash coal containing 39.9 and 67.1 were fine coals (mostly below 0.5 mm) being processed as flocculation feed after the washery decided to switch over to flocculation instead of flotation during the course of these investigations.

The sulphur content of the flotation feed which was determined to calculate the mineral matter content of coal by Parr Formula was found as 0.48 %.

The mineral matter content of flotation feed found from Parr Formula was 38.2 % where as from acid digestion and low temperature ashing (LTA) it was 39.8 % and 42.2 % respectively. As Gluskoter (1965) stated the mineral matter content of flotation feed determined by LTA was found exactly 1.1 % of that calculated by Parr Formula.

8.1.2 Petrographic Analysis of Coarse Wastes

The waste materials associated with coal were overbreak material from roof and floor of coal seam and were unavoidably mined. They contained on the average 58 % of clay minerals which obviously are the major source of ultrafine particles (less than 2 micron in size) that affect adversely the coal washing processes due to their swelling in water. Besides clay minerals, they contained silicates, carbonates, sulfides and some coal particles. The loss of coal particles in samples D and E reached to 15 and 22 % respectively.

8.1.3 X-Ray Diffraction Analysis

Initial investigations of samples A, F and H in unoriented mounts (Figures 7.1. to 7.3.) and oriented mounts (Figures 7.4. to 7.8.) showed the presence of three clay minerals namely illite, chlorite and kaolinite. The unoriented samples did not show the presence of kaolinite but indicated the presence of quartz, feldspar, calcite and serpentine. The oriented samples on glycolation (Figure 7.7.) revealed the presence of combined chlorite and kaolinite (Ch+K) peak and on heating to 550 ^{O}C, showed the presence of kaolinite on collapse of its structure (Brindley and Brown, 1984); giving reduced intensity of chlorite peak (Figure 7.8.).

The detailed investigations were then carried out to confirm the presence of these clay minerals in coarse wastes, thickener overflow and coal.

8.1.3.1 Detailed XRD Analysis of Coarse Wastes

The samples A,B and E were analyzed in unoriented mounts by XRD shown in Figures 7.9. to 7.11.

All of these samples (Figures 7.9. to 7.11.) showed the presence of kaolinite, illite and chlorite clays in addition to quartz, feldspars and calcite. But in order to confirm the presence of kaolinite, sample A was also subjected to XRD after loss on ignition at 900 °C (Figure 7.11b). The collapse of kaolinite main peak completely in Figure 7.11b as compared to Figure 7.11a clearly indicated its presence as found during the preliminary analysis.

After identification to the presence of three clay minerals qualitatively in preliminary investigation and the above mentioned tests, further XRD investigations in to coarse wastes samples A to E (Group 1) were conducted as given in Figures 7.12. to 7.16, in oriented mounts each as air dried (a), glycolated (b), heated to 350 °C (c) and heated to 550 °C (d) samples. All the samples showed almost similar XRD patterns and indicated the presence of kaolinite in addition to chlorite and illite in the air dried, glycolated and heated to 350 °C. But heating to 550 °C showed no change in illite and chlorite clays where as kaolinite showed the collapse of its structure in all the samples (See. Figures 7.12. to 7.16. in heated to 550 °C traces as "d" in each Figure). Thermal treatment on heating between 450 - 500 °C transforms Kaolinite to the very poorly ordered metakaolin showing little or no XRD pattern (Brindley and Brown, 1984); and is explained further in Appendix A.2.

8.1.3.2 XRD Analysis of Thickener Overflow (Sample H)

Sample H representing black water was analyzed in oriented mounts with XRD as shown in Fig. 7.17. The figure shows collapse of Kaolinite main peak in heated specimen (Fig.7.17c). The clays and other minerals present are the same (i.e. Illite, Kaolinite, Chlorite, Quartz, Calcite and Serpentine) as found in preliminary analysis (Figs. 7.3., 7.6, to 7.8). It was found that no feldspar is present in the black water samples.

8.1.3.3 XRD Analysis of Pretreated and Combined Treated Samples

Sample B containing low organic content but high carbonates (about 6 percent each as given in Table 7.3) together with Samples F and G containing high organic matter (about 33 and 63 % respectively) were subjected to XRD analysis after pretreatment for removal of cementing agents as mentioned in Section 6.2.3. The aim was to compare the effects of pretreatments, on clay peaks in XRD patterns. Another aim was to use the XRD patterns of coal (Sample G) and its tailing (Sample F) for semiquantitative analysis. Also combined treatment (pretreatment + acid treatment) of Samples F and G was aimed towards their comparison with the pretreated samples and selection for semiquantitative analysis.

The XRD patterns of pretreated Sample B (Fig.7.18) and with out pretreatment (Fig.7.13) were similar qualitatively except that pretreatment partially disolved some chlorite peaks and intensified illite and chlorite peaks. It was however observed that peak area ratios of main K+Ch peaks to be used for semi-quantitative analysis by Biscaye's (1965) method remained the same in both the figures. This was encouraging result and therefore pretreatment and combined treatment of Samples F and G were carried out and then subjected to XRD analysis as shown in Figs. 7.19 and 7.20. It was found that pretreatments (Figs. 7.19 and 7.20) have no effect on the Kaolinite - chlorite (7.2 A) peaks but dissolve main chlorite peak whereas combined treatments (Figs. 7.21 and 7.22.) intensified illite peak (10.16 A) and have more pronounced dissolving effect on chlorite (14.45 A) peak even to the extent of entirely obscuring this peak (Figs. 7.21 and 7.22). These effects were as indicated by Carroll (1970). It was found that combined treatments also over shadowed partially main illite peak (10.16 A) and reduced in intensity the combined Kaolinite - Chlorite peaks. Although combined Kaolinite + Chlorite (K + Ch) peaks remained almost unaffected in terms of their area ratios. The combined treated XRD patterns were not found suitable and only pretreated XRD patterns were used for semi quantitative analysis of clays.

The qualitative picture as regards clays in coal remained the same showing the presence of three clays (Kaolinite, illite and chlorite) as in coarse wastes and thickener overflow.

8.1.3.4 XRD Analysis of Flotation Feed (Sample G) After Low Temperature Ashing (LTA)

Two samples of flotation feed subjected to cool oxygen plasma oxidation (COPO) treatment once and twice and analyzed by XRD in oriented mounts are given in Figures 7.23 and 7.24. They show the presence of three clays; Kaolinite, illite and chlorite in both samples in addition to other minerals such as quartz, muscovite, serpentine, calcite, sepiolite, and feldspar. It was found that double COPO treated sample (Fig. 7.24) gave better resolved XRD peaks.

It may be mentioned here that LTA is considered as a standard method for XRD analysis of coal and coal refuse (Gluskoter, 1967: O'Gorman and Walker, 1971: Jenkin and Walker, 1978). However due to non availability of COPO equipment and extremely slow rate of oxidation, it was necessary to look for some alternative method for XRD analysis of these samples. Another consideration was that semi quantitative analysis requires certain quantity of material for the preparation of oriented mounts which is not available by low temperature ashing. Therefore low temperature ashed samples received from Kemerovo (Russia) were analyzed in unoriented mounts to verify the qualitative picture of clays obtained by pretreated samples in the previous section. It was noted that same three clays, Kaolinite, illite and chlorite were present.

8.1.3.5 Semi Quantitative XRD Analysis of Clay Minerals in Zonguldak Washery Coal, Wastes and Thickener Over Flow

Based on the Biscaye's (1965) method already mentioned (Section 6.2.3 and Appendix A.3), calculations were carried out by measuring peak areas of different clays for all the samples.

They were analyzed in oriented mounts by XRD but Samples F and G were pretreated before XRD analysis. The results of these calculations are given in Table 8.1.

Table 8.1. Percentage of Clay Minerals in Zonguldak Washery Coal, Wastes and Thickener Overflow

Sample	Group	Peak Areas, mm^2		Factor K/Ch	Clays, %			Group Average, %
		4xI	2(K+Ch)		I	K	Ch	
A	1	128	209	2.15	38	43	19	I = 47
B	1	628	476	1.09	57	24	19	K = 29
C	1	540	690	1.60	44	35	21	Ch = 24
D	1	580	552	0.60	51	18	31	
E	1	360	401	0.75	47	23	30	
F	2	112	390	4.59	22	64	14	I = 27
G	2	120	272	3.0	31	52	17	K = 58
								Ch = 16
H	3	304	166	2.24	65	25	10	I = 65
								K = 25
								Ch = 10

All coarse waste (Group 1) were dominant in illite varying from 44 to 57 % except Sample A which was abundant in Kaolinite indicating a change in composition due to its weathering (Potter et al., 1980). Next dominant clay mineral was Kaolinite and then chlorite. On average 47 % illite, 29 % kaolinite and 24 % Chlorite were present.

The coal samples (Group 2) were dominant in Kaolinite ranging 52 to 64 %. The next abundant clay is illite and the least is chlorite. An average of 58 % Kaolinite, 27 % illite and 16 % chlorite are present.

The thickener overflow (Group 3) was dominant in illite (65 %), next being Kaolinite (25 %) and chlorite (10 %).

As the Biscaye's method was applied to coal and coal refuse as a pioneering attempt, the qualitative and quantitative picture of clay minerals may be compared to other countries. In U.S. coals O'Gorman and Walker (1971; 1972) found Kaolinite as the principal clay mineral similar to the findings in this study. The other clays present were illite, montmorillonite and very little chlorite (Yancey and Geer, 1962; Gluskoter, 1967; O'Gorman and Walker, 1972). Bradley et al., (1980a) determined mineralogy of U.S. black waters and found it different from coal minerology as it was dominant in illite and montmorillonite. Therefore, Aplan (1988) mentioned that as the coarse waste mineralogy in U.S is not determined, so this difference can not be explained.

Now in this study it is clear that dominance of illite in black water (thickener overflow) is not due to coal but due to coarse wastes coming to the washery as overbreak roof and floor materials and dominant in illite. This may fill the gap in understanding the reason of differences in U.S. Coal and black water mineralogy.

8.1.4 Loss on Ignition Analysis

The loss on ignition analysis (Dean, 1974) showed the presence of organic carbon and carbonates. The organic carbon content of coarse wastes (Sample A to E) was about 5-21 % and carbonates about 4-6 %. Samples F and G (representing coal) contain very high amount of organic carbon, about 33 and 63 %

respectively. Carbonate content of Sample G is also high (6.5 %). sample H also contains high amount of organic carbon to about 27 % (Table 7.3).

These results proved that x-ray diffraction peaks may be diluted or overshadowed by the high percentages of organic carbon and carbonates and showed the need of pretreatment and acid treatment (Brindley and Brown, 1984; Brown, 1972; Carroll, 1970). Therefore Samples A, F and G were pretreated for removing these cementing agents before their XRD examination.

Another observation may be added to the high amount of organic matter in certain wastes (Samples E, F and H) which could be processed by a suitable waste processing flow sheet to recover their coal contents.

YÖK watermark

8.2 Electrokinetics of Clays and Coal

8.2.1 Zeta Potentials of Turkish Clays

The results of zeta potential measurements of three Turkish clays as given in Table 7.10 were plotted in Figure 8.1.

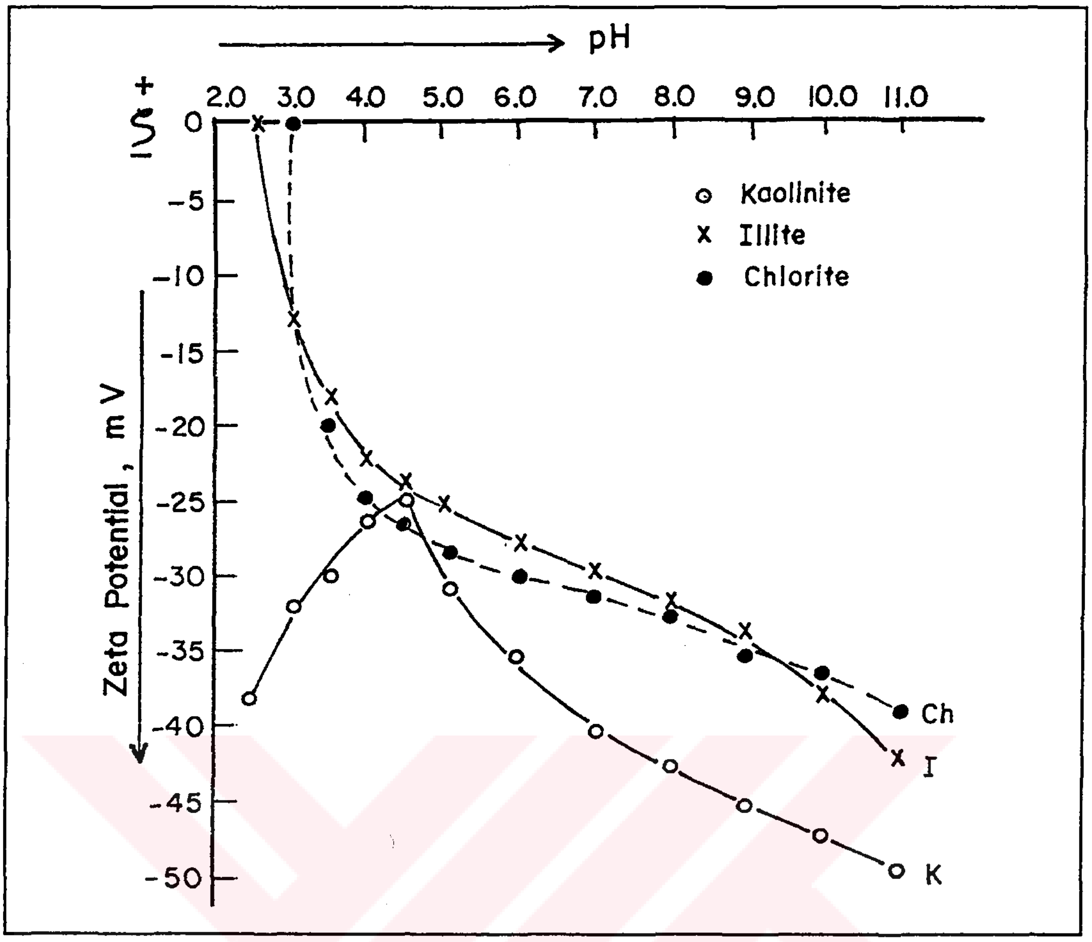

Figure 8.1. Zeta Potentials of Turkish Clays

As shown in Figure 8.1. the kaolinite has more negative charge than two other clays. It has some permanent negative charge due to ion exchange which is independent of pH in acidic range (Wierer et al., 1988). Therefore no pzc (point of zero charge) was obtained for the kaolinite where as Arnold and Aplan (1986b) found a pzc value at pH 2.5 for one of the kaolinite used in their investigations, but for another no pzc was obtained. The illite is least negative and chlorite is intermediate in zeta potential values. The pzc values for illite and chlorite were obtained at pH 2.5 and 3.0 respectively.

These findings fit what has been found to the other properties of clays. The surface area and cation exchange capacity (CEC) of clays follow the sequence kaolinite < illite < montmorillonite (Bolt et al., 1976). Therefore, the clay with greatest surface area and exchange capacity should have less negative charges (zeta potentials). In this study sequence appears to be kaolinite < chlorite < illite, in the light of zeta potential measurements. Grim (1968) gave the following cation exchange capacities in milli equivalent of clay minerals per 100 grams:

Kaolinite......................	3-15
Chlorite........................	10-40
Illite..............................	80-40
Smectites.....................	80-150

As chlorites have great variations in CEC, it is possible that Turkish chlorite have lower CEC value than illite and the sequence proposed here in the light of zeta potential measuremens seems logical. However determination of CEC values of Turkish chlorite and illite used in this study may confirm the findings.

As regards the effect of these clays on flotation (Figure 8.13), illite was having the worst effect, kaolinite the least, which seem to be explained in terms of CEC of these clays, following the sequence proposed. It means that less negative clays were taking greater part in depressing the coals as found by Arnold and Aplan (1986a;b). van Olphen (1963) stated that kaolinite is believed to have negative charges on faces and positive charges on edges (compared to negatively charged coal particles) could lead to slime coatings and hence depression. However Arnold and Aplan (1986b) found that some kaolinities (like Turkish kaolinite) were only negatively charged with no pzc value, and in an alkaline circuit, clay edges and faces of all kaolinities and coal surfaces were negatively charged; hence no slime coatings and coal depression should occur. But in our findings kaolinite is depressing the coal to some extent and illite to a large extent. This is only due to the different CEC values, which depict the type of clay. The chlorite has low CEC value and is non swelling type. However its positively charged brucite layer partially balances its negative charge, affording a chance to attach to negatively charged coal particles during flotation (See Fig. 2.1; Stumm and Morgan, 1981).

The above explanations are only attempts to explain the effect of clays on flotation of coal through zeta potential. But "null hypothesis" regarding the fine clay particles being carried in to the froth in proportion to the amount of water transferred to the froth is another sound explanation, for increase in clay content and ash in the froth product. The greater the concentration of clay in the flotation feed water, the greater is the concentration of ash in the froth.

8.2.2 Zeta Potential of Zonguldak Clean Coal

The results of the zeta potential measurement of clean coal (4.5 % ash) given in Table 7.11 were plotted in Figure 8.2.

It was found that H^+ and OH^- ions are potential determing ions (PDI). The IEP value of clean coal was found from the Figure 8.2. at pH 4.1. This value is the same as already found for vitrain by Özbayoğlu (1977).However Sarıkaya (1988) found IEP at pH 4.2 for unoxidized Zonguldak coal. The more negative zeta potential values may be due to method of agitation (ultrasonic treatment) done prior to electrokinetic measurements in this study. Aplan (1976) stated that of all pH values to above 5, coal is usually negatively charged and this surface negativity of coal is due to its anisotropic nature (Chander et al, 1975).

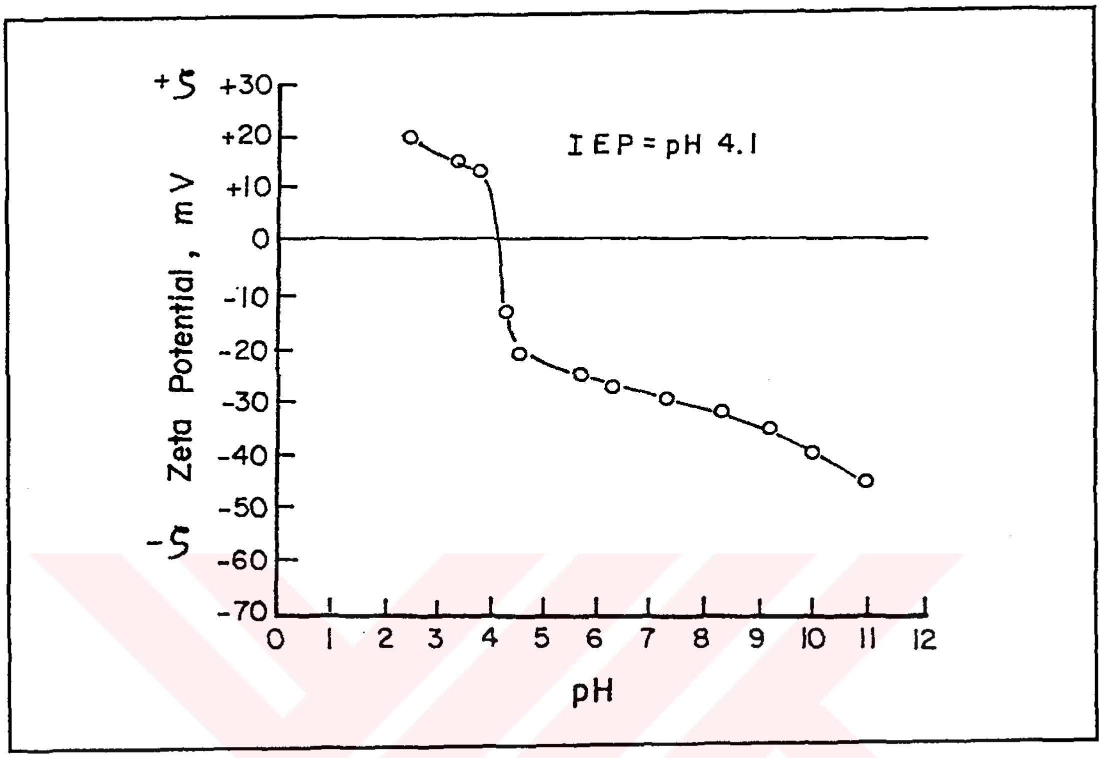

Figure 8.2 Variation of Zeta Potential of Zonguldak Coal

8.2.2.1 Effects of Inorganic Electrolytes on Zeta Potential of Clean Coal

Electrokinetic measurements were carried out with different divalent and trivalent electrolytes and their results presented in Table 7.12 were plotted in Figure 8.3.

The divalent magnesium ($MgCl_2$) and calcium ($CaCl_2$) cations both show negative zeta potentials. The calcium cations are less negative than magnesium cations due to their larger radius, giving greater surface area for adsorption and hence

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DOKÜMANTASYON MERKEZİ

lower potentials. The decrease in zeta potential was stated to be proportional to the specific volume of cations by Klassen and Mokrousov (1963) who proposed that generally the increasing order is given as follows:

$$K^+ = Na^+ < Ca^{2+} < Mg^{2+} < Fe^{2+} < Al^{3+}$$

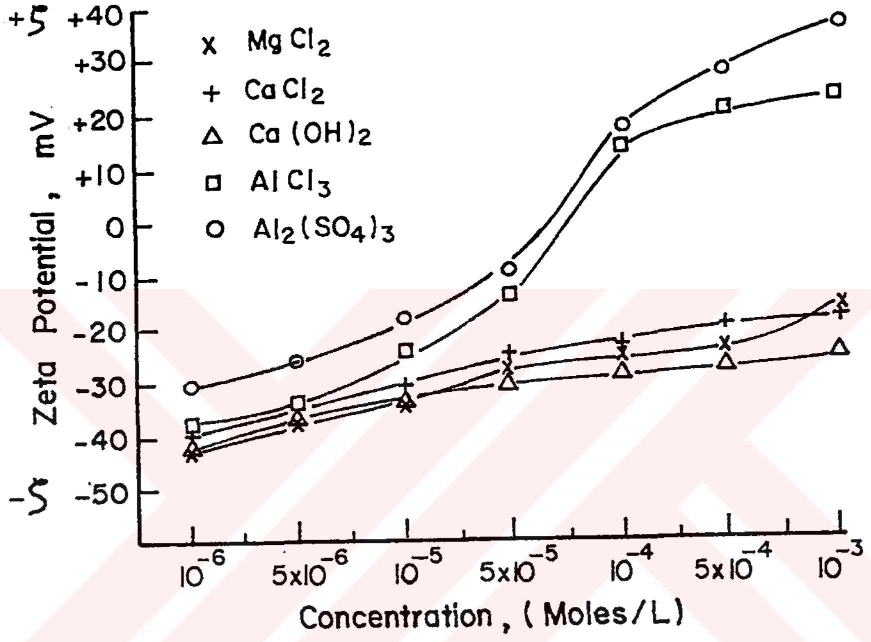


Figure 8.3 Effect of Various Concentrations of Inorganic Electrolytes on Zeta Potential of Zonguldak Coal (ash = 4.5 %)

The decrease in zeta potential shows higher adsorption with increasing radius of cations as van der Walls forces seem to contribute more than Coulombic forces (Jirgenson and Straumanis, 1962).

In $Ca(OH)_2$ more negative zeta potentials were obtained than $CaCl_2$ due to OH^- being potential determining ions (PDI) and therefore adsorbed more selectively than chloride. The adsorption of anions and cations were studied experimentally and it was found that the H^+ and OH^- (PDI) adsorb most strongly: in cationic series than follow the multivalent ions and finally the univalent ones with gradually reducing radius, but in anionic series, it is the reverse; the univalent with largest ionic radius are adsorbed more strongly, then follow the ions with a smaller radius and finally the multivalent ions (Jirgenson and Straumanis, 1962).

On the other hand both aluminum chloride and aluminum sulphate reverse the charge from negative to positive even at lower concentrations. Charge reversal of coal by Al^{+++} ions is due to its hydrolysis forming hydroxy complexes which adsorb on negatively charged coal surfaces by the electrostatic forces, converting it to alumina like surfaces (Mackenzie, 1971). The effect of charge reversal is more in case of sulphate ions than chloride ions due to greater attraction to the surface as is indicated by an increase in the negative surface charge (Özbayoğlu, 1977). Similar observations on Zonguldak coal have been reported by Özbayoğlu (1977) and Sarıkaya (1988). Wen and Sun (1977) and Arnold and Aplan (1986b) reported similar observations to the effect of Al^{+++} ions on coal.

8.2.2.2. Effects of Dispersants and Depressants on Zeta Potential of Coal

The results of zeta potential measurment of clean coal (with varying concentrations of dispersants sodium silicate, Calgon and depressant CMC as given in Table 7.13a and the results of depressants Marsperse CB and depressants Aero depressant 633 and dextrin as given in Table 7.13b, were plotted in Figures 8.4. to 8.6.

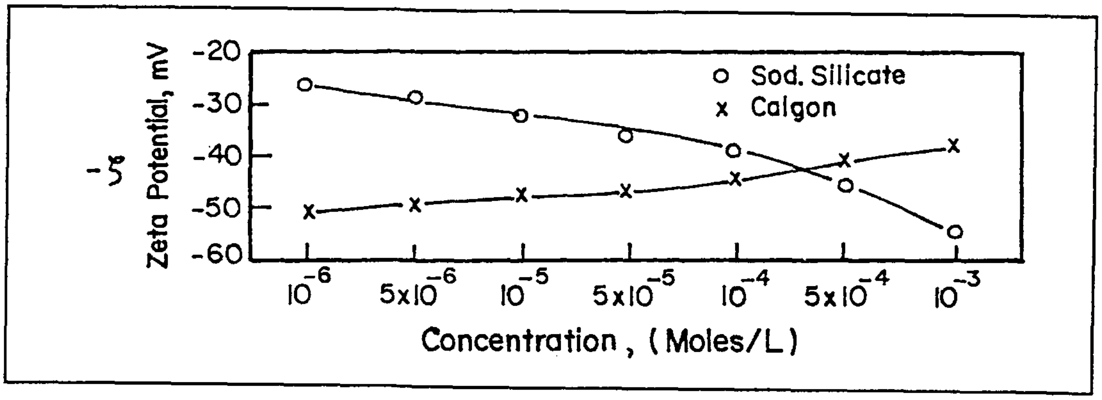


Figure 8.4. Effect of Various Concentrations of Sodium Silicate and Calgon on Zeta Potential of Coal

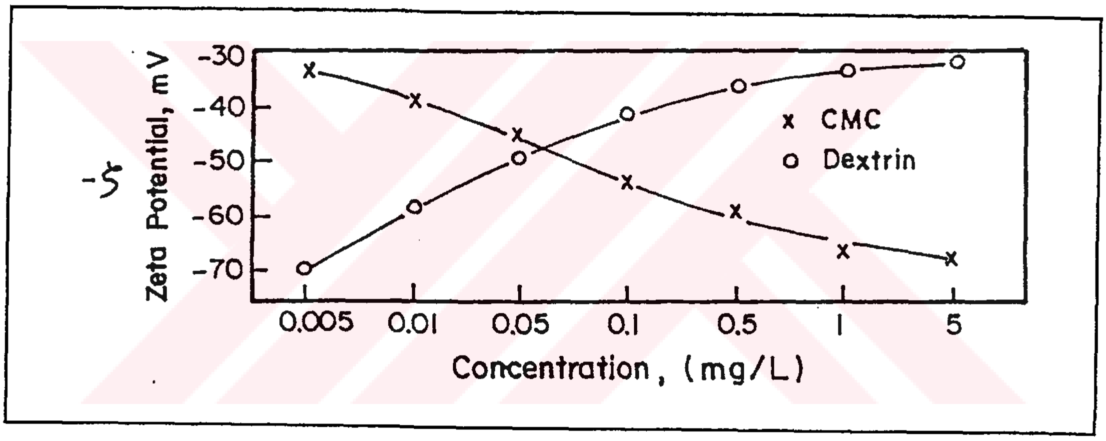


Figure 8.5. Effect of Various Concentrations of CMC and Dextrin on Zeta Potential of Coal

It was observed that gangue dispersants sodium silicate and Calgon (Fig.8.4) both used as gangue dispersants gave negative zeta potentials on coal in 10^{-6} to 10^{-3} molar concentration range. Another dispersant Marsperse CB (Fig. 8.6) behaved like the sodium silicate. As all the dispersants make coal surfaces more negative, their role as dispersing agents is obviously there.

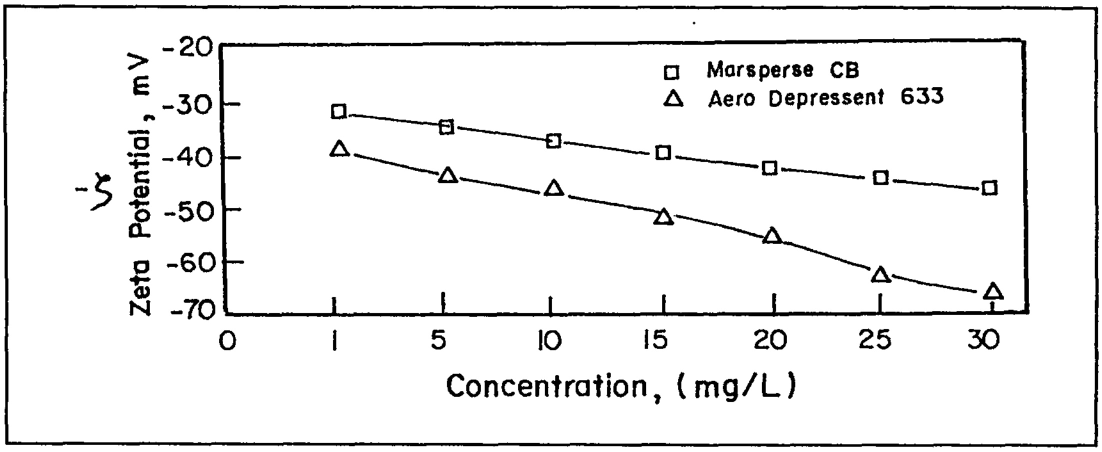


Figure 8.6. Effect of Various Concentrations of Marsperse CB and Aero Depressant 633 on Zeta Potential of Coal

Therefore sodium silicate, phosphates and lignin sulfonates are recommended as dispersants for clays and silicates (Smith, 1988). However, Arnold and Aplan (1986a) found that additions of clay dispersants (Calgon, Marsperse CB and sodium silicate) all tend to depress coal and hence the benefit of their advantageous use is lost. This is supported by the zeta potential measurements on these dispersants in this study due to coal surfaces becoming more electronegative at the natural pH 6.5 (distilled water).

A similar observation was made for the depressants CMC and dextrin (Fig. 8.5) and for Aero depressant 633 (Fig. 8.6). Smith (1988) stated that the mechanism of depression probably involved the masking of coal surface and competition with collector for adsorption sites. However, the advantage of coal depression by these depressants can be beneficial in reverse coal flotation. Laskowski et al., (1985) used advantageously CMC as depressent under alkaline conditions while desulfurizing Canadian coal by single stage direct flotation.

Perry and Aplan (1985; 1988) found that polysaccharides (starches) which were used as pyrite depressant also depressed coal. Miller and Deurbrouck (1982) used dextrin effectively as coal depressant in second stage of their process for desulfurizing the coal.

In the light of these electrokinetic studies and recent literature on dispersants and depressants it was decided to use CMC and sodium silicate for depressing clays and silicates in direct coal flotation experiments while dextrin to be employed as coal depressant during reverse coal flotation.

8.3 Flotation of Clean Coal and Flotation Behaviour of Coal-Clay Mixtures

8.3.1 Preliminary Flotation Tests with Clean Coals

The preliminary flotation tests with clean coals (4.5 and 9.8 % ash) were carried out to determine the flotation conditions in order to apply them in flotation of artificial coal-clay mixtures.

8.3.1.1 Direct Flotation of Clean Coals

The results of Tables 7.14 to 7.16 were plotted in Figures 8.7 to 8.9 which were used to optimize the quantities of reagents for floating coal.

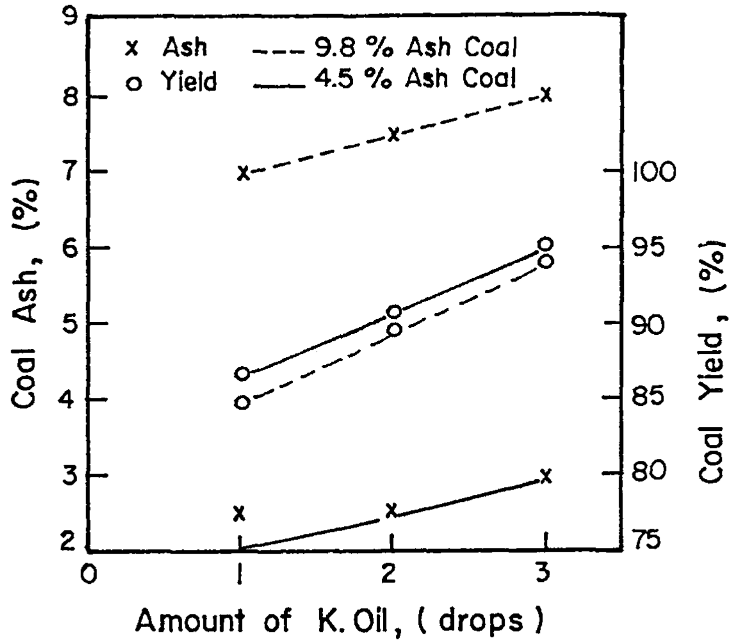


Figure 8.7. Effect of Kerosene oil Addition on Flotation of Clean Coal

Now referring to Figure 8.7, it was found that for both coals (4.5 and 9.8 % ash) increase in Kerosene oil (collector) increased the yield as well as ash. The least ash product with yields greater than 85 % is obtained by using 340 g/t of Kerosene oil. Similarly in Figure 8.8 increased MIBC (frother) reduced the yield and intermediate amount 85 g/t was selected for the tests as it gave lower ash product.

In Figure 8.9, yields increase with increasing flotation time, giving higher ash products and therefore, the lowest flotation time (1 minute) was chosen for obtaining low ash products.

So the optimized parameters for direct flotation of coal were 340 g/t of Kerosene oil, 85 g/t of MIBC and flotation time of one minute.

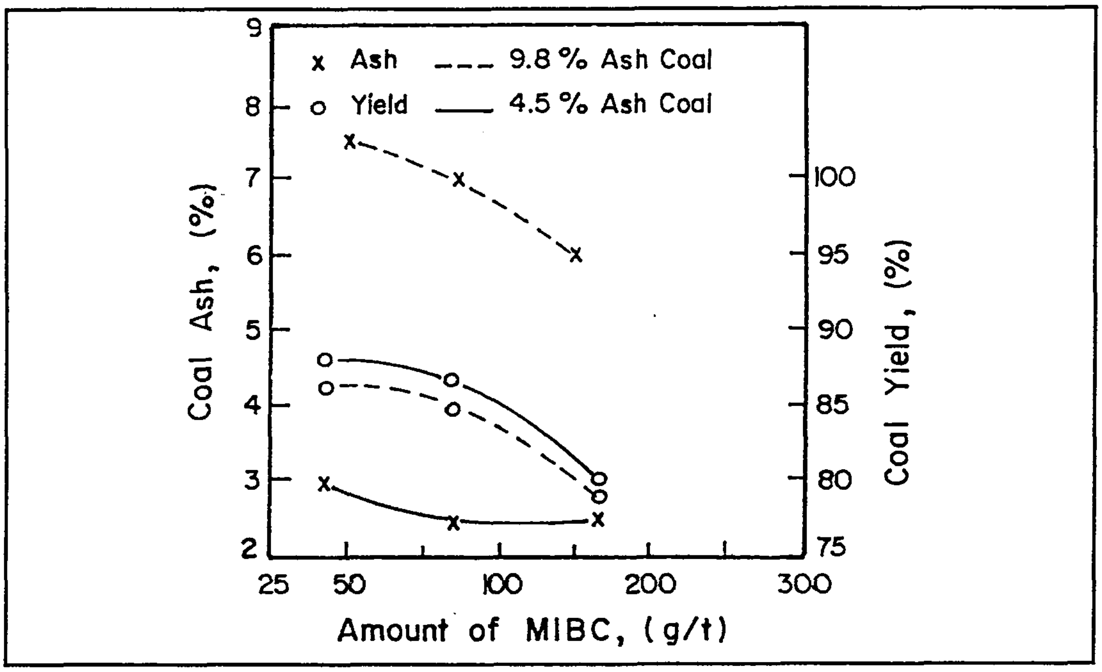


Figure 8.8. Effect of Frother Addition on Flotation of Clean Coal (Kerosene oil=340 g/t; Flotation Time=1 minute)

8.3.2 Effect of Clays on Coal Flotation

8.3.2.1 Effect of Amount of Kaolinite

The effect of various amounts of pure kaolinite on clean coal (4.5 and 9.8 % ash) was given in Table 7.4. The results were obtained at two oil additions and plotted in Figure 8.10.

The maximum range (25 %) for clay addition was chosen on the basis of average clay content of coarse wastes which was found petrographically as 58 % and mineral matter in flotation feed which was determined as 42.2 %.

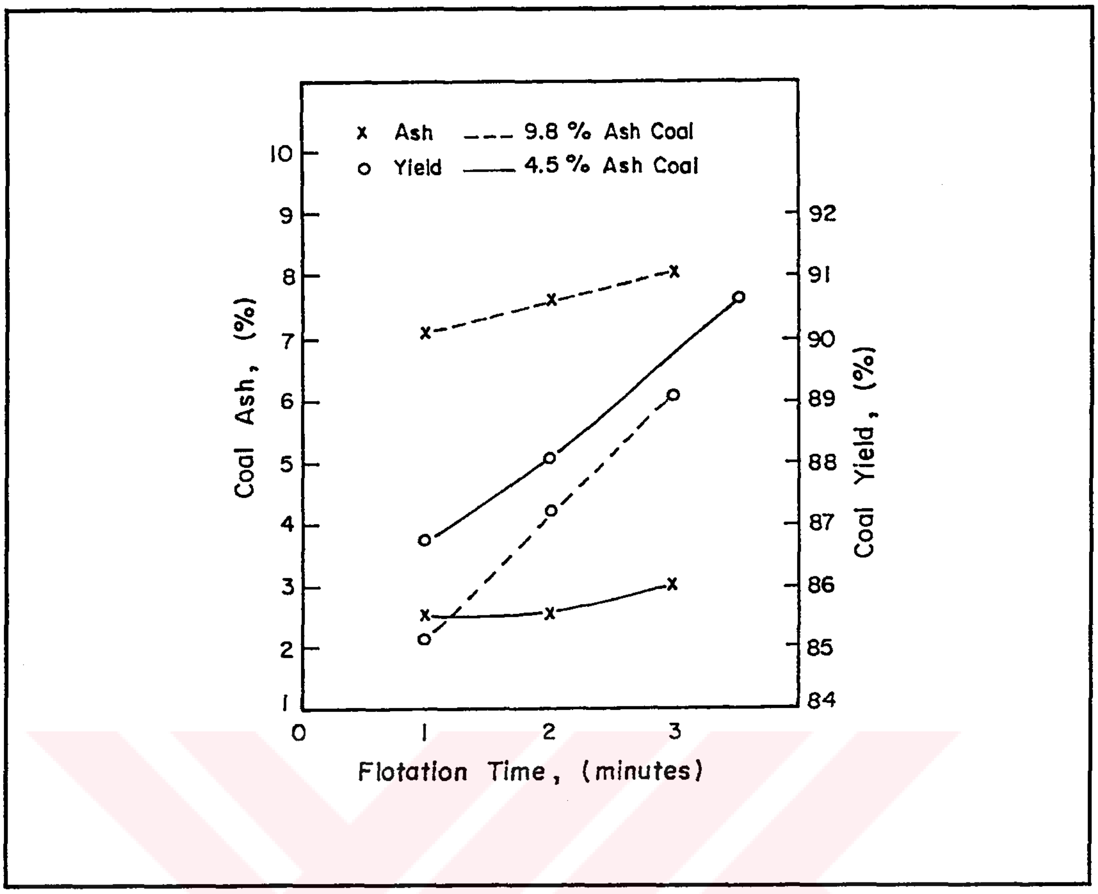


Figure 8.9. Effect of Flotation Time on Flotation of Clean Coal (K.oil=340 g/t; MIBC=85 g/t)

The Figure 8.10 shows that the increase in kaolinite amount contributes the ash content of coal which shows an increasing trend in the ash curve. This effect is the same for both oil additions. On the other hand the increase in kaolinite is adversely affecting the coal floatability as the yield is decreasing continously. The decrease in yield is much more pronounced in high ash coal.

The higher kerosene oil addition (1020 g/t) increased the flotation of clay and this was in agreement with the findings of Arnold and Aplan (1986a). The increase in yield can occur due to bridging over of clay coated particles of coal by the kerosene oil, making them hydrophobic. Szczypa et al., (1973) showed that fuel oil is a collector for slime coated particles and Iwasaki, et al (1962) proposed that depression can occur if the slimes adsorb collector. Therefore lower oil additions (340 g/t) will definitely eliminate the role of excess oil towards floating the clay coated particles (slimes). The effects of kaolinite on coal flotation were in agreement to those of Arnold and Aplan (1968a) who studied them on U.S. coals.

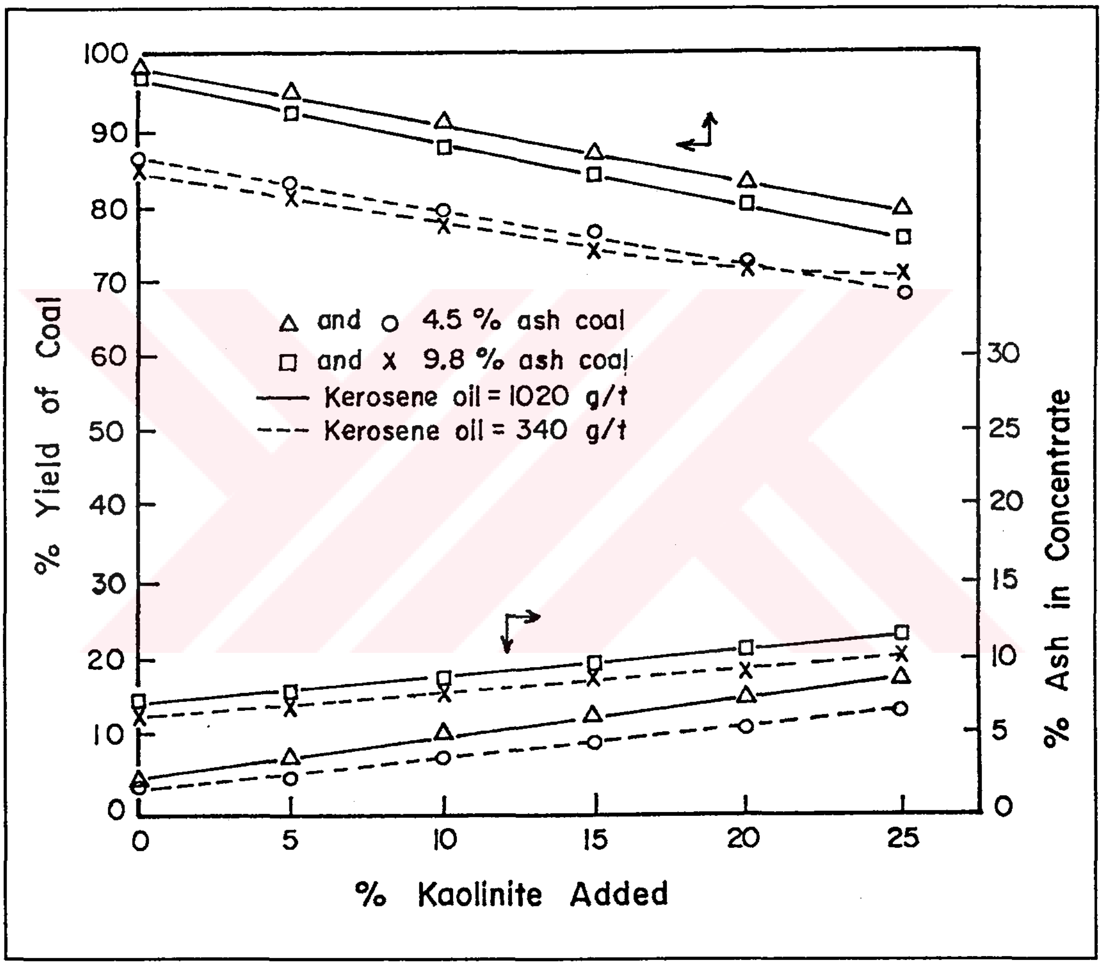
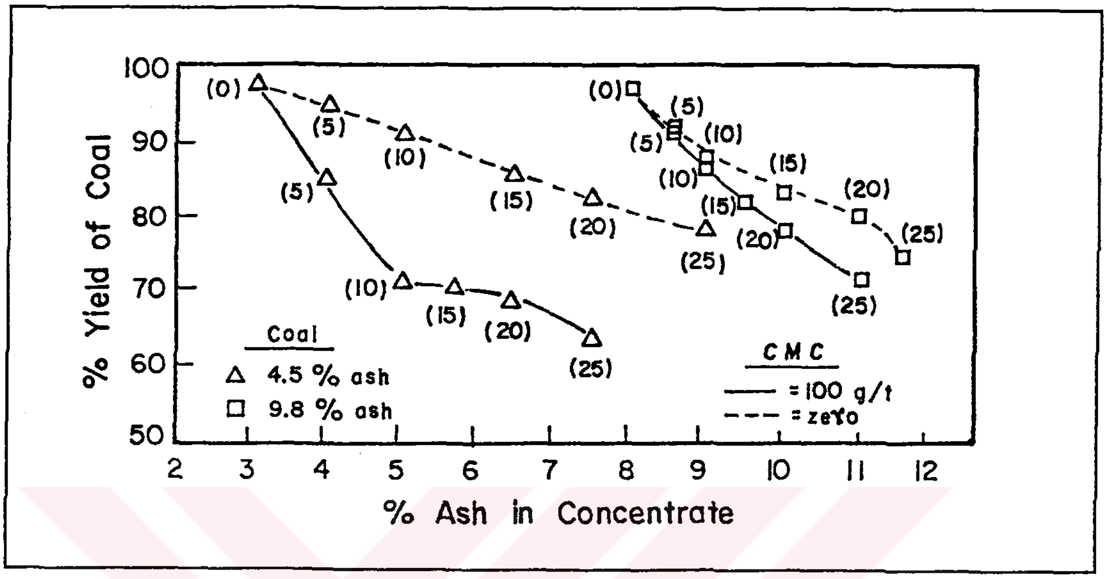


Figure 8.10. Effect of Addition of Kaolinite on Yield andAsh of Coal

In order to see the effect of CMC as a dispersant on kaolinite, a small quantity (100 g/t) was used. The kerosene oil=1020 g/t (not according to the optimized quantity) was used in this test in order to project the effect of CMC prominently. The results of Table 7.5 showing the effect of CMC have been plotted in Figure 8.11.



* (25) The numbers in brackets show the percentage of kaolinite.

Figure 8.11. Effect of CMC (Tylose C-30) on Zonguldak Coal-Kaolinite Flotation

It can be clearly seen in Figure 8.11. that 4.5 % ash coal was considerably depressed due to CMC (15 % less yield with CMC than with out CMC) when 25 % kaolinite was added. But 9.8 % ash coal shows lower depression. CMC is a polymer and adsorbs on coal through the electrostatic altraction and hydrogen bonding (Perry and Aplan, 1985). Therefore, in lower ash coal, adsorption is maximum operating through these two mechanisms. But with higher ash coals, comparatively less number of reactive OH^- groups are available to participate in adsorption; resulting depression with out any control on ash reduction. Hence CMC was depressing coal without considerable reduction in ash. Sezgin (1973) reported that use of CMC on flotation of Zonguldak coal (below 0.5 mm) caused only depression of coal and did not improve the grade.

8.3.2.2 Effect of Amounts of Kaolinite, Illite and Chlorite on Coal Flotation

The flotation results of coal with the addition of kaolinite, illite and chlorite (Tables 7.4., 7.6. to 7.7.) were plotted in Figure 8.12.

As shown in Figure 8.12, illite has the worst effect both on yield and ash when floated with clean coal. The chlorite was found to have an intermediate effect on yield and ash. It can be seen that up to 10 % kaolinite and chlorite no appreciable effect was observed, but up to 25 % they reduce yield to about 18 and 20% respectively. Illite addition up to 25 % gave a loss of yield to 28 % and increase of ash to 6.5 %. A comparatively higher depression of coal by illite than kaolinite was also indicated on U.S. coals by Arnold and Aplan (1986a).

The effects of three clays on clean coal (4.5 % ash) flotation are evaluated as yield-ash curves in Figure 8.13. which are plotted from the results of Tables 7.4 and Tables 7.6. to 7.7

This (Figure 8.13.) shows a comparative assessment of clays on coal flotation but in actual system clays are present according to the mineral matter in coal, in mixed form. So an exact idea about their effects can be arrived by adding them in mixed form and then comparing the flotation results with an actual system.

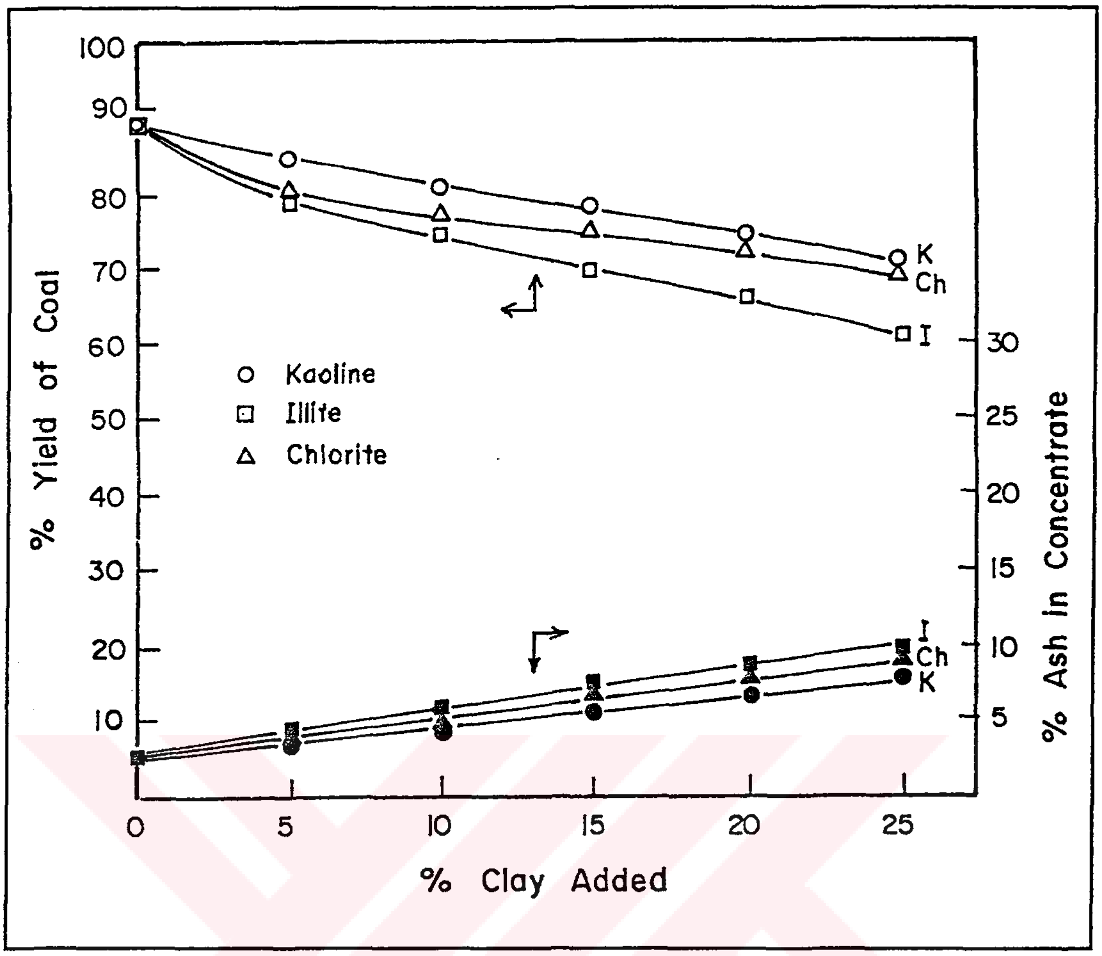


Figure 8.12. Effect of Kind and Amount of Clay on Yield and Ash of Coal (K.oil/340 g/t; MIBC=85 g/t; Flotation Time=1 minute; pH=6.5; Ash in Coal=4.5 %)

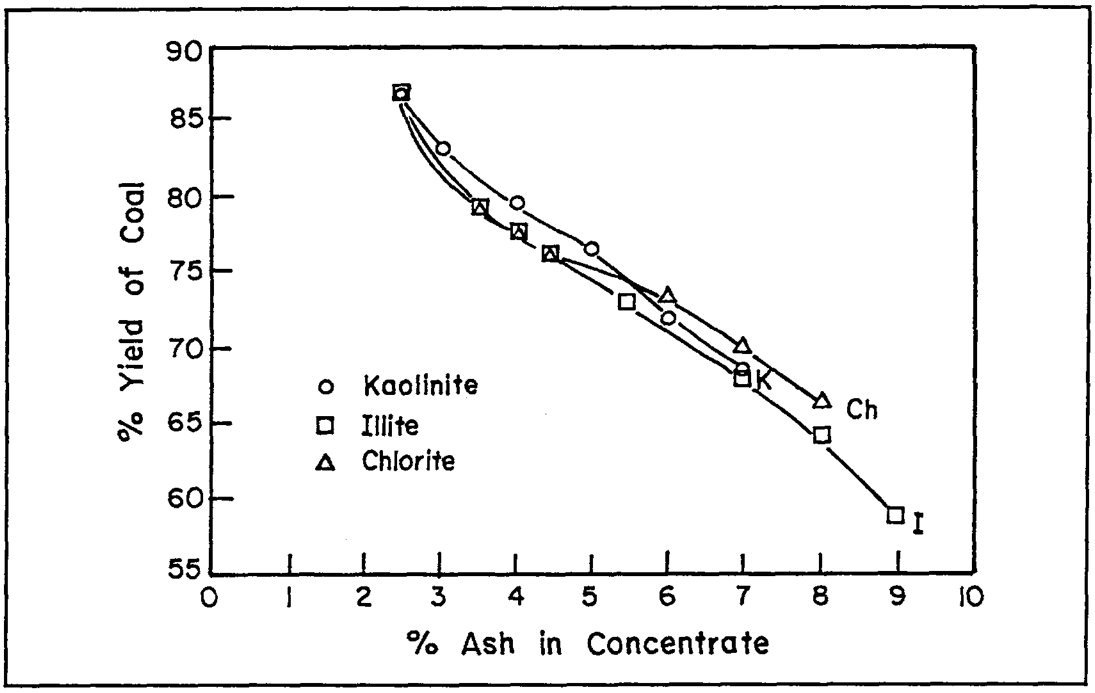


Figure 8.13. Effect of Clay Additions (0-25 %) on Flotation of Coal

8.3.2.3 Comparison of Coal-Clay Flotation With Actual Flotation System

In order to compare the effects of clays in amounts determined by XRD (Kaolinite=52 %; Illite 31 %; Chlorite 17 %); these were converted to their proportions of maximum amount (25 %). This gave the amount of each clay (K=13 %; I= 8%; Ch=4 %) to be included in the artificial mixture of clean coals (4.5 and 9.8 % ash), and their flotation results are given in Table 7.9. Also flotation feed (35.1 % ash coal) designated as actual system was floated under similar conditions (Table 7.8).

The comparison of the results of Table 7.8 with individual clays showed that the flotatin with 25 %. Illite (the worst clay) falls short of actual system in yield to the extent of about 9 % (Yield with 25 % clay=59.5% and with actual system=50.5 %). Similarly ash wise actual system gives 6 % higher ash product (ash in concentrate with 25 % clay is 9 % compared to ash in actual system=15 %).

With kaolinite due to less effect on coal depression, gap is wider to the extent of 18 % yield-wise and 8 % ash-wise and of course with chlorite it is in between these two extremes. This is an evidence that clay type is affecting the results of coal flotation definitely as found by Arnold and Aplan (1986 a). Previously it was established that amount of each clay also matters in flotation.

The clean coal (4.5 % ash) gave higher yield and better ash product (70.1 % and 9.0 % respectively) as compared to coal containg 9.8 % ash (being 64.1 % and 12.0 % respectively). However, the results of floating coal (35.1 % ash), logically should be compared with 9.8 % (to give 25 % clay + 9.8 % ash = 34.8 % ash). A comparison revealed that the actual system (Table 7.9) does not match with the artificial mixture flotation and gave a lower yield of about 14 % and increased ash of 3 %. This can be due to the nature of clays which are well liberated in the artificial mixture than in the coal.

In literature there are two opposite views about effect of clay slimes on coal flotation. Most investigators (Sun, 1943; Jowett, et al., 1956;: Fuerstenau, et al, 1958; Iwasaki, et al., 1962) believe that slime coatings are the real cause of loss in recovery values in mineral flotation and they are heaviest, when the slime is uncharged or oppositely charged to the material being floated. Similarly others (Brown and Smith, 1956; Burden, et al., 1976; Mishra, 1978; Lynch et al., 1981;

Arnold and Aplan 1986a) noted depression of coal due to clay slimes. Contrary to this Firth and Nicol (1981) found no effect due to Kaolin (clay) on coal flotation.

Some other investigators (Trahar and Warren, 1976; Warren, 1984; Subrahmanyam and Forssberg, 1990) explained the flotation of clays due to the water carry over or entrainment mechanism. This controversy is still unresolved.

Now looking back to the comparison of actual system with artificial mixture of coal-clay flotation, it may be said that both the mechanisms are playing part. The type of clays and their amounts have the major role in coal depression and water carry over mechanism has minor effect. It was found that water carry over mechanism in coal was only contributing towards increase in ash content of the product but has no role in the depression of coal. The depression of coal is only related to clay type and their slime coatings on coal particles masking them from reagent adsorption. However both the mechanisms, one reducing the recovery and the other decreasing the grade are operative in coal flotation.

It is fortunate that Zonguldak washery coal did not contain any montmorillonite type clays which are very harmful for U.S. coal flotation (Gluskoter, 1967; O'Gormon and Walker, 1971; O'Gorman and Walker, 1972; Arnold and Aplan, 1986a). So a less gloomy picture as to the effects of clays on coal flotation has emerged. However they definitely affect coal flotation badly and more adverse effects may be expected on other processes such as heavy media separation, dewatering and filtration.

PART II

FLOTATION OF HIGH ASH COALS

This part is devoted to the flotation test results of high ash coals (35.1, 39.9 and 67.1 % ash) given in Section 7.4. It will be discussed in three separate sections, namely direct, single stage reverse and combined two stage flotation.

8.4 Direct Flotation of High Ash Coals

8.4.1 Direct Flotation Of High Ash Coals With Kerosene Oil

The results of direct flotation of high ash coals containing (35.1, 39.9 and 67.1 % ash) as given in Table 7.17 were plotted in Figures 8.14 to 8.16 in order to determine the quantity of Kerosene oil for each coal while Keeping MIBC (85 g/t) and flotation time (1 minute) constant as optimized for clean coals.

On floating 35.1 % ash coal (MIBC 85 g/t and flotation time 1 minute), it was found that one drop of Kerosene oil (340 g/t) gave a yield of 50.5 % with lowest ash=15.5 % while 39.9 % and 67.1 % ash coals on flotation gave yields 42.1 % and 9.0 %, and ash 17 and 27.5 % respectively.

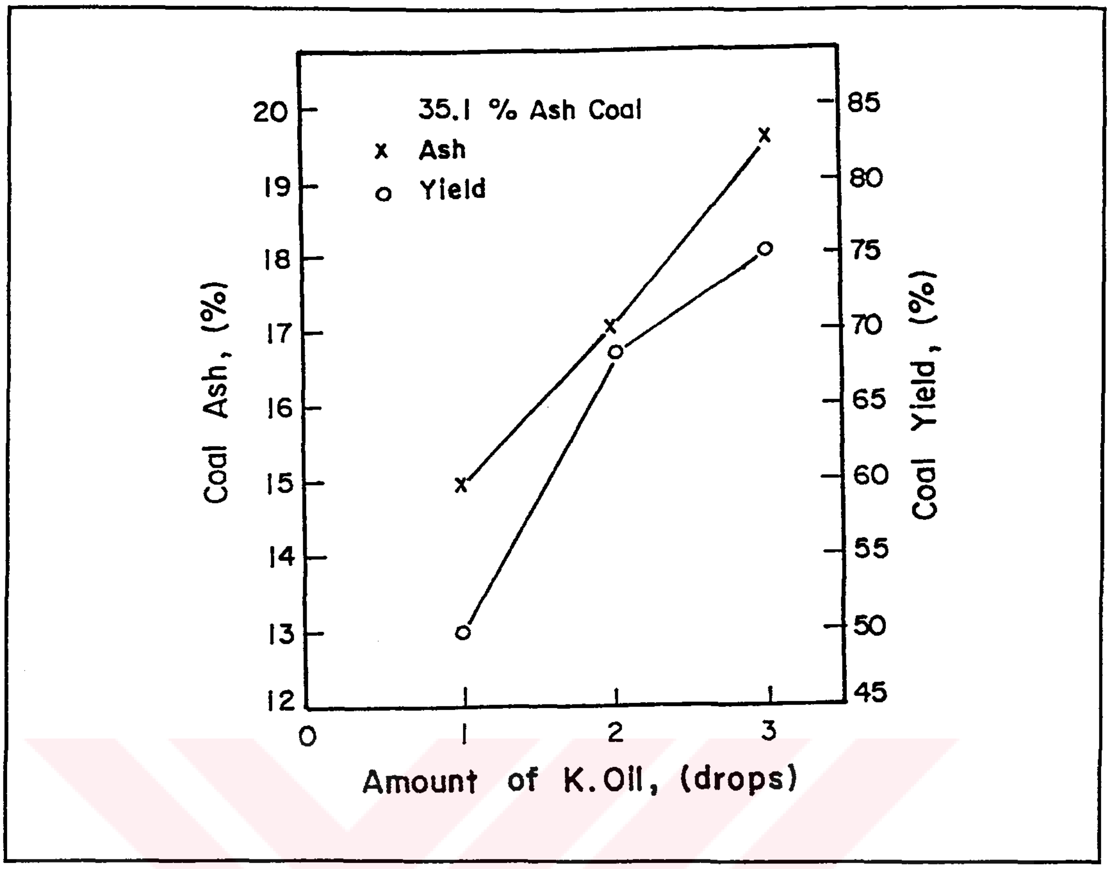
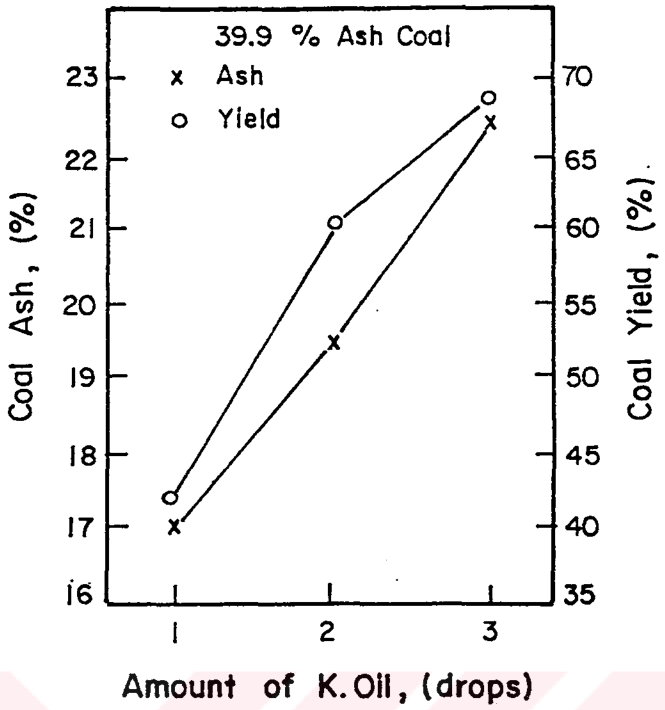


Figure 8.14. Effect of Kerosene oil Addition on Direct Flotation of Coal (35.1 % ash)

In other words, for the same ash level (15.5 %) obtained in 35.1 % ash coal with the yield 50.5 %; the yields around 30 % in, 39.9 % ash coal may be expected and which seems to be impossible in 67 % ash coal. The reason is that 35 % ash coal contains only about 24 % clays (a product of 58 % mineral matter and 42.2 % low temperature ash) where as 39.9 % and 67.1 % ash coals with high amount of LTA ash will definitely have very high amount of clays which not only depressed them considerably but also made the froth contaminated through water carry over mechanism. Therefore, it became impossible to clean these coals to the same extent as coal containing 35.1 % ash.



Figures 8.15. Effect of Kerosene oil Addition on Direct Flotation of Coal (39.9 % ash)

8.4.1.1 Effect of CMC on High Ash (35.1 %) Coal Flotation

Direct flotation results of 35.1 % ash coal with varying CMC quantities, using Kerosene oil and MIBC (Table 7.20) were plotted in Figure 8.17.

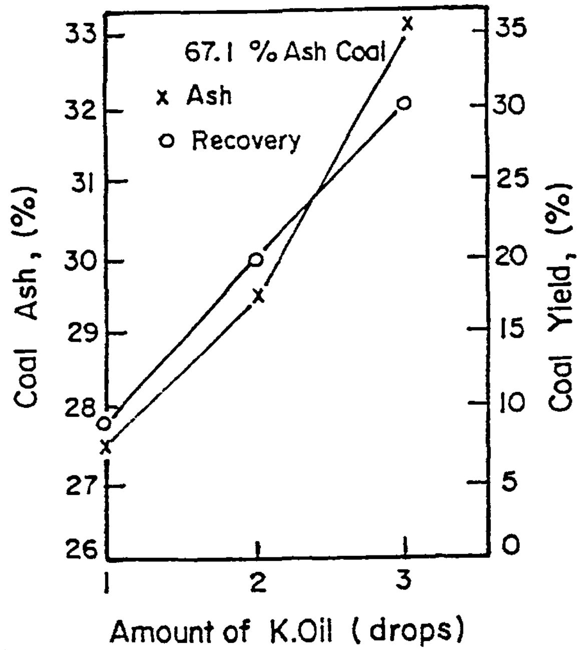


Figure 8.16. Effect of Kerosene Oil Addition on Direct Flotation of Coal (67.1 % ash)

It can be observed (Figure 8.17.) that CMC reduces yields considerably with out little improvement in the ash content of the floated product. Therefore no distinct benefit could be achieved with the use of CMC in coal flotation. Similar observations were noted in Figure 8.11. while floating clean coal and kaolinite mixture where the role of CMC towards coal depression was explained (Section 8.3.2.1). As high ash coals have comparatively less OH^- groups to participate in adsorption, CMC results depression without reduction in ash selectively.

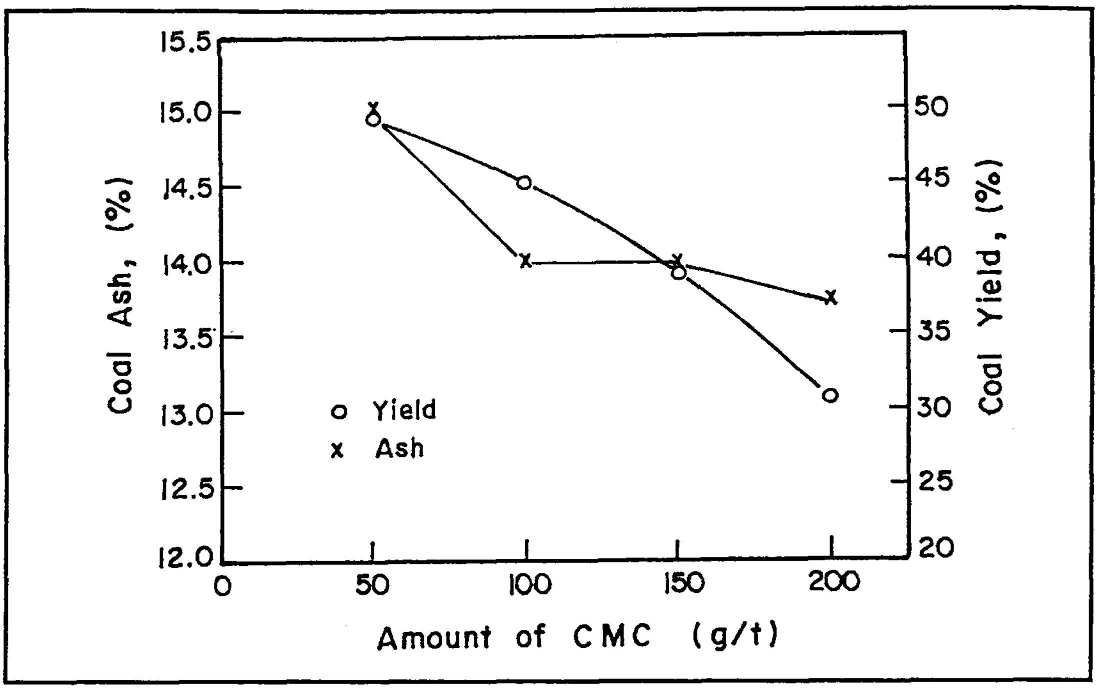


Figure 8.17. Effect of CMC on Direct Flotation of Coal (35.1 % ash)

8.4.1.2 Effect of Sodium Silicate on High Ash (35.1 %) Coal Flotation

Similar to CMC, 35.1 % ash coal was floated with varying amounts of sodium silicate (Table 7.21.) and the results were plotted in Figure 8.18.

It was observed (Figure 8.18.) that higher additions of Sodium Silicate not only lower the yield, but also increase the ash content of the floated coal. Therefore, the use of sodium silicate as gangue depressent in coal flotation is largely negated.

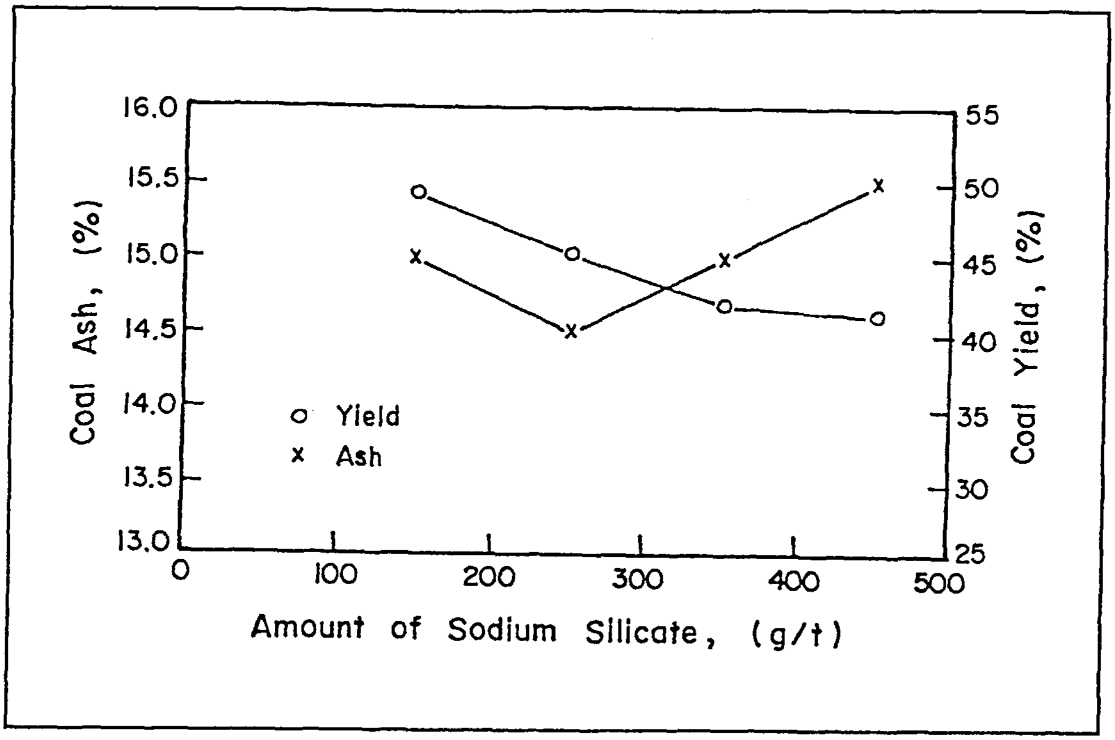


Figure 8.18. Effect of Sodium Silicate on Direct Flotation of Coal (35.1 % ash)

Myers (1988) mentioned that an increase in electrolyte content will cause a decrease in adsorption of surfactants on to oppositely charged surfaces and increase in adsorption of like charged molecules. The presence in the solution of polyvalent cations such as Ca^{2+} and Al^{3+} will generally increase the adsorption of anionic surfactant. However certain inorganic ions such as calcium displace the stabilizing surfactant species by spreading as monolayer or lens on the interface.

However the mechanism of dispersant action in coal flotation is not well understood and sodium silicate is still used in mineral flotation as depressant for calcite and silicate gangues. A study of entrainment factors showed degree of entrainment for coal (Lynch et al, 1981) to be 22 % more than fine gangue (Subrahmanyam and Forssberg, 1988c) and it was considered that this difference in degree of entrainment may reduce the effects of sodium silicate depression in coal flotation.

8.4.2 Direct Flotation of High Ash Coals With Pamak4

The coals containing 35.1, 39.9 and 67.1 % ash were floated with Pamak4 (oleic acid + linoleic acid + rosin oil) and their results (Table 7.18.) were plotted in Figures 8.19. to 8.21.

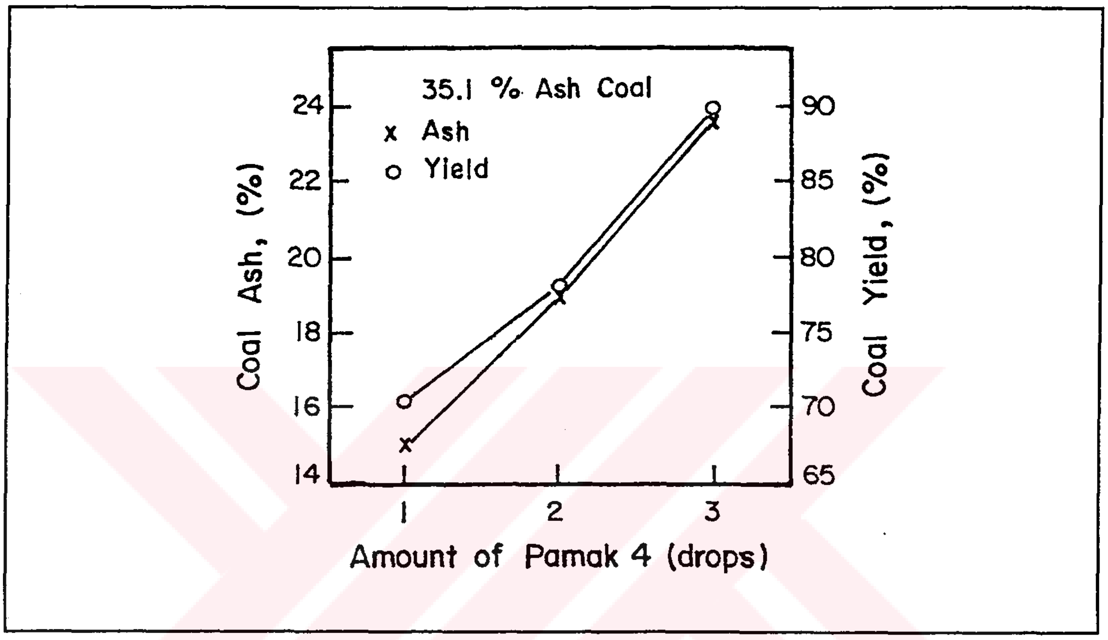


Figure 8.19. Effect of Pamak4 Addition on Direct Flotation of Coal (35.1 % ash)

It was observed that like Kerosene oil flotation, lowest ash product was obtained with Pamak4 = 500 g/t (1 drop). The yield was 70.5 % with product ash equal to 15 % for 35.1 % ash coal (Figure 8.19) showing that Pamak4 gave higher yield than Kerosene oil at the same ash levels. This is due to higher activity of Pamak4 containing 50 % oleic acid in its composition. The oleic acid has higher hydrophile - lipophile balance (HLB) value (=17) compared to Kerosene oil (HLB = 14). Similarly for 39.9 % ash coal (Fig. 8.20) higher yield to about 20 % (as for Kerosene oil for 35.1 % ash coal) and only one percent higher ash product is obtained with Pamak4. A similar higher yield trend for 67 % ash coal (Figure 8.21) is achieved with lower ash product as compared to Kerosene oil.

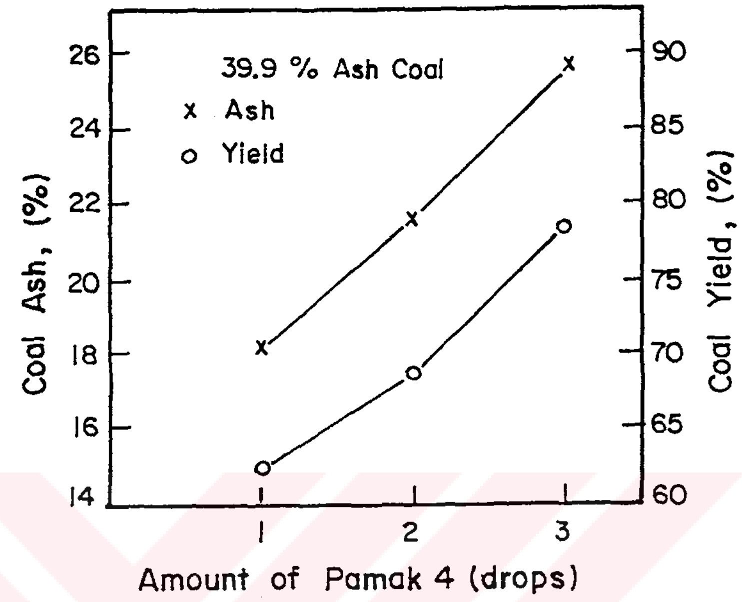


Figure 8.20. Effect of Pamak4 Addition on Direct Flotation of Coal (39.9 % ash)

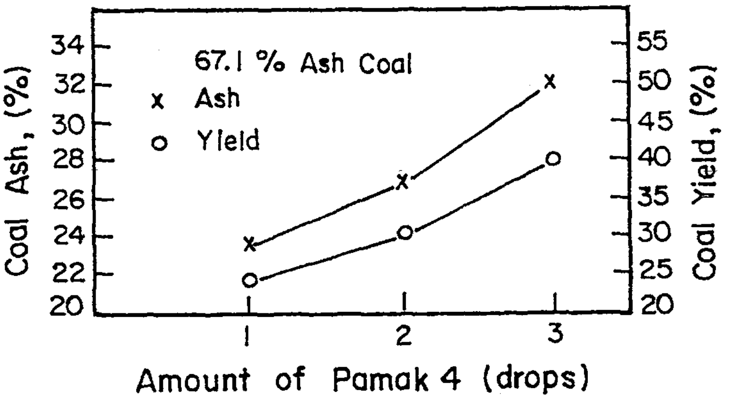


Figure 8.21. Effect of Pamak4 Addition on Direct Flotation of Coal (67.1 % ash)

It is concluded that Pamak4 due to its higher activity is more suitable for floating high ash coals(35.1, 39.9 and 67.1 % ash) as it gives about 20 % higher yields with lower ash products, as compared to conventional Kerosene oil and MIBC combination. As ash reduction is also achieved for coals having more than 39.9 % ash, it is more selective. Therefore Pamak4 or other oleic acid based reagent, although at present is of scientific interest according to these laboratory investigations yet it may be of a great potential for future commercial coal flotation. As Pamak4 does not need the use of any frother,its economics can be worked out keeping in view about 20 % more yield obtained in coal flotation, against the use of Kerosene oil and frother combinations.

8.4.3 Direct Flotation of High Ash Coals With Oleic Acid

The oleic acid was used for the flotation of coals (35.1, 39.9 and 67.1 % ash) as in cases of flotation with Pamak4 and Kerosene oil and the results of Table 7.19. were plotted in Figures 8.22. to 8.24.

On comparing the results of oleic acid in respect to, its yield and ash with Pamak4 for 35 % ash coal, it was revealed that better ash reduction is there (12 % ash compared to 15 %) but the yield was reduced considerably (34 % from 70.5 %). Similar results were obtained for 39.9 % ash coal (Figure 8.23) however, 67.1 % ash coal (Figure 8.24) did not respond well towards ash reduction. As oleic acid has higher HLB(=17) than Kerosene oil, it is more selective towards ash reduction of 35.1 and 39.9 % ash coals. But its lower activity compared to Pamak4 renders it less attractive for commercial use.

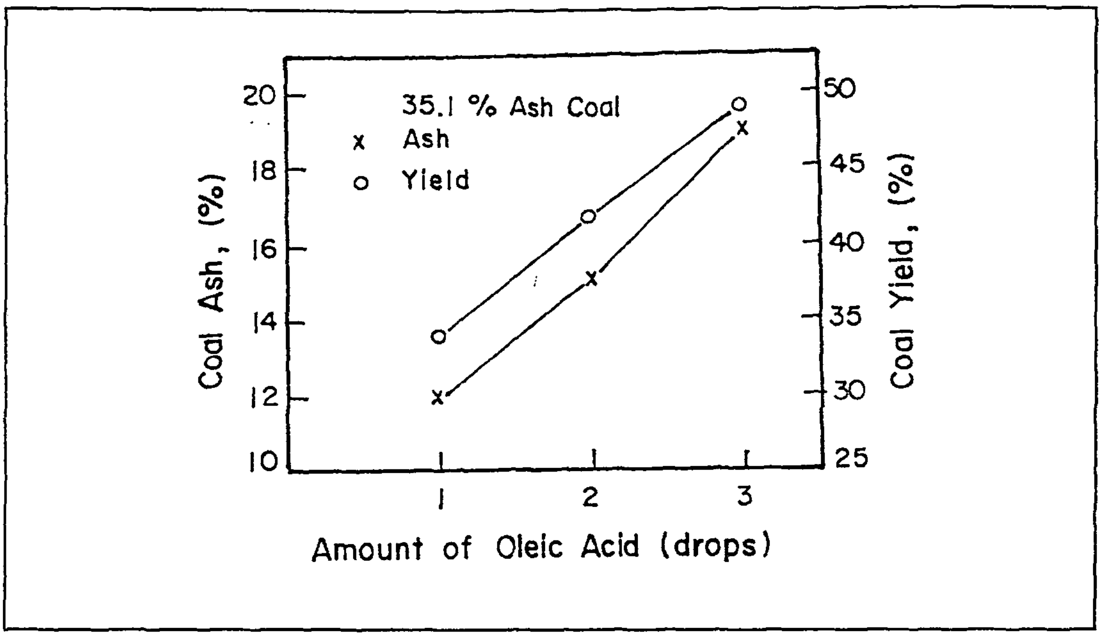


Figure 8.22. Effect of Oleic Acid Addition on Direct Flotation of Coal (35.1 % ash)

8.5 Single Stage Reverse Flotation of Coal

The single stage reverse flotation of coal (35.1 % ash) was carried out by using Flotigam ENA as collector and dextrin as coal deressant to determine the collector amount, depressant quantity; flotation time and pH. In order to determine the amount of Flotigam ENA, results of Table 7.22 were plotted as in Figure 8.25.

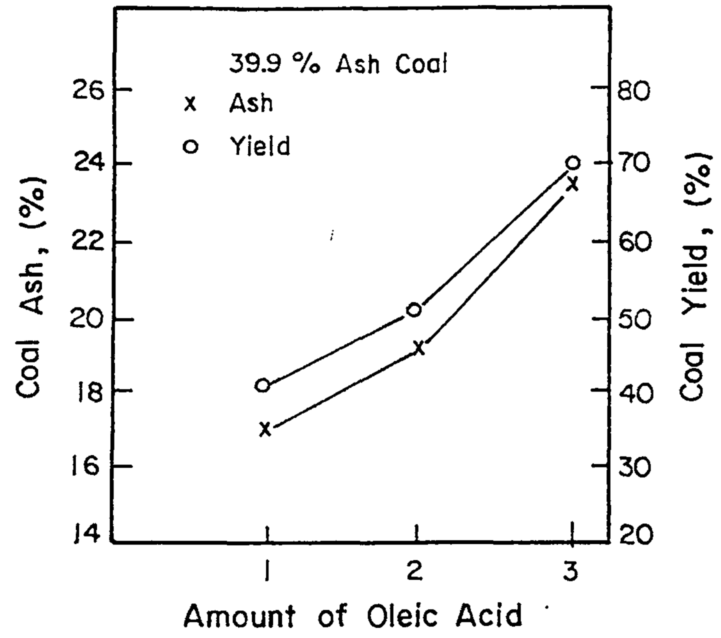


Figure 8.23. Effect of Oleic Acid Addition on Direct Flotation of Coal (39.9 % ash)

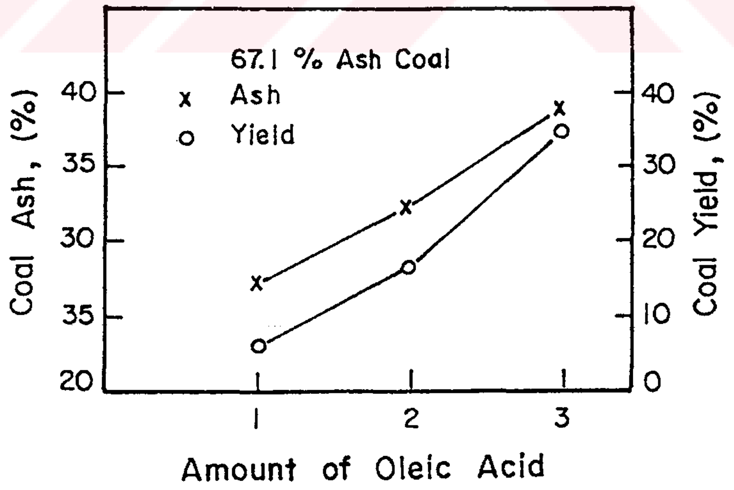


Figure 8.24. Effect of Oleic Acid Addition on Direct Flotation of Coal (67.1) % ash)

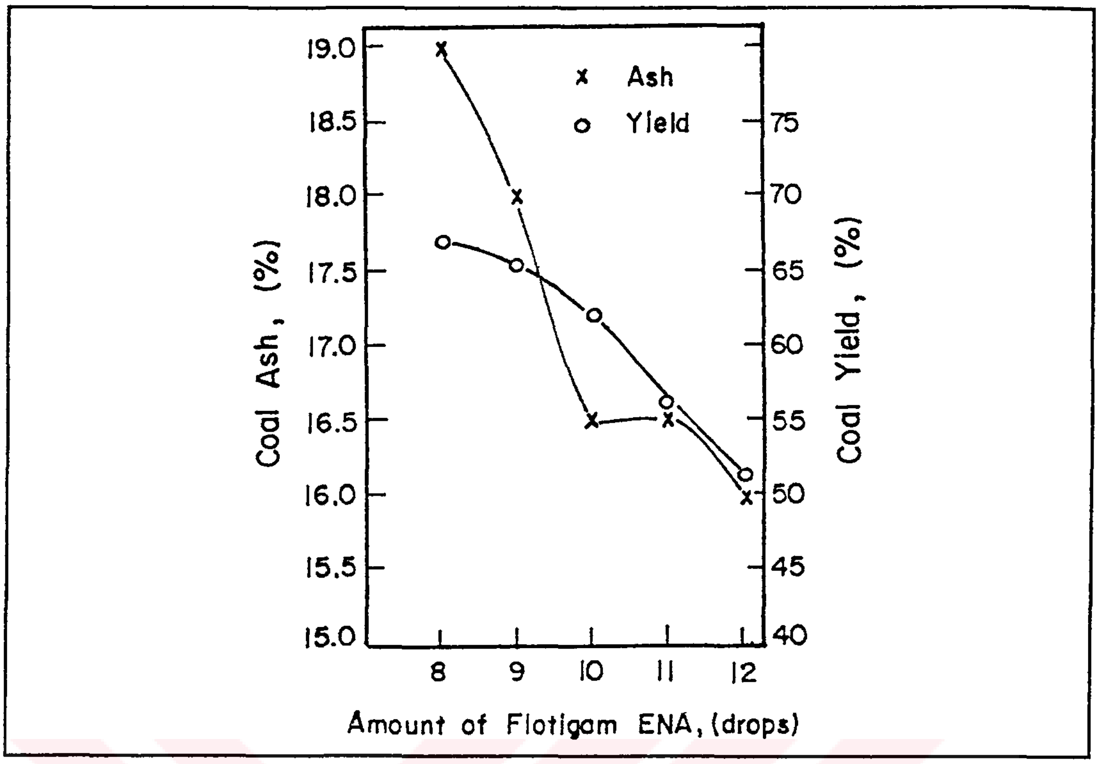


Figure 8.25. Effect of Flotigam ENA Addition on Reverse Flotation

It was found that up to 10 drops (3600 g/t) of Flotigam ENA, gave a sharp decrease in the ash content and then it lost its effect. This appeared to be the optimum quantity of collector, beyond which no greater benefit of ash reduction could be achieved. Amines are good collectors for ash. At higher dosage than 3600 g/t due to hemimicelle formation, collecting action of Flotigam ENA is decreased.

The effects of dextrin addition on coal in Figure 8.26 (results in Table 7.23.) showed that 1000 g/t was the optimum quantity for depressing the coal in reverse flotation. More dextrin increased the yield as well as the ash content of coal.

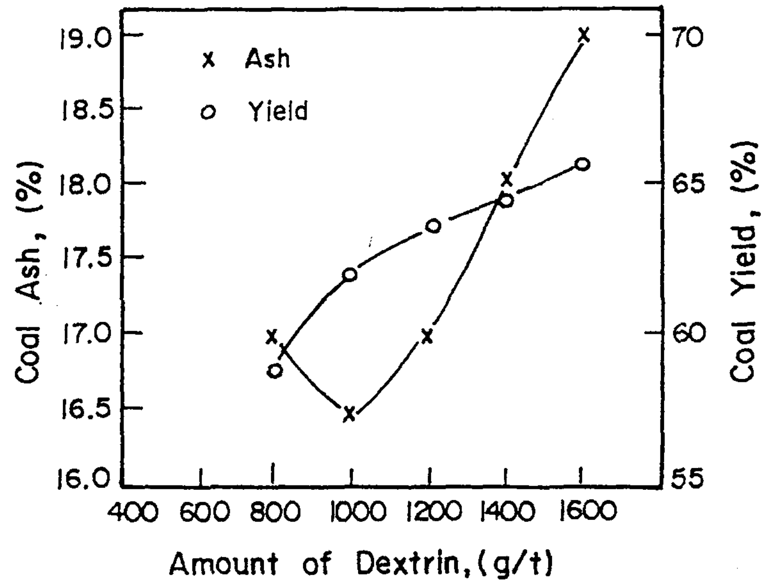


Figure 8.26. Effect of Dextrin Addition on Reverse Flotation

Dextrin is a polysaccharide and attachment of this polymer is through some combination of the two mechanisms i.e. electrostatic attraction and hydrogen bonding as explained before (Section 8.3.2.1). The mechanism of depression probably involves masking of coal surface and competition of collector for adsorption sites (Smith, 1988).

The effect of flotation time which was shown in Table 7.24. and plotted in Figure 8.27. revealed that by the increase of flotation time, both yield and ash percentages of coal have decreased. This statement is opposite to the direct flotation, as here more time causes more gangue to be flotated leaving less coal as lower ash product.

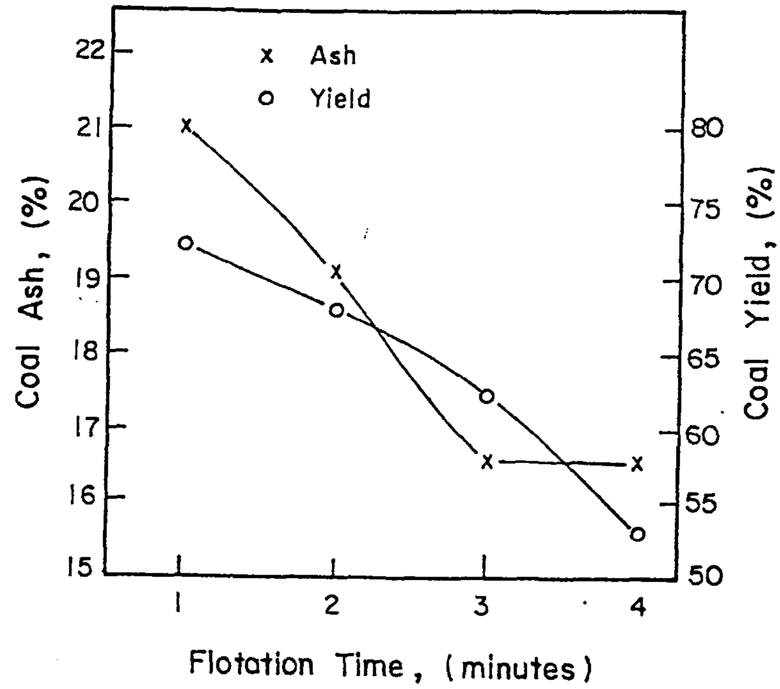


Figure 8.27. Effect of Time on Reverse Flotation

Finally the results of Table 7.25. were plotted in Figure 8.28. to determine the pH for reverse flotation.

An optimum pH=7 was found for reverse flotation tests. This finding is in agreement with literature, where a definite optimum floatability of coal was found at pH near neutral point (Klassen, 1953; Brown, 1962; Sarıkaya, 1988).

The yield and ash obtained as optimized results for single stage reverse flotation of 35.1 % ash coal were 62.2 % and 16.5 respectively. As mentioned previously, the reverse flotation to float clays from high ash coals is still an area unexplored and without much success.

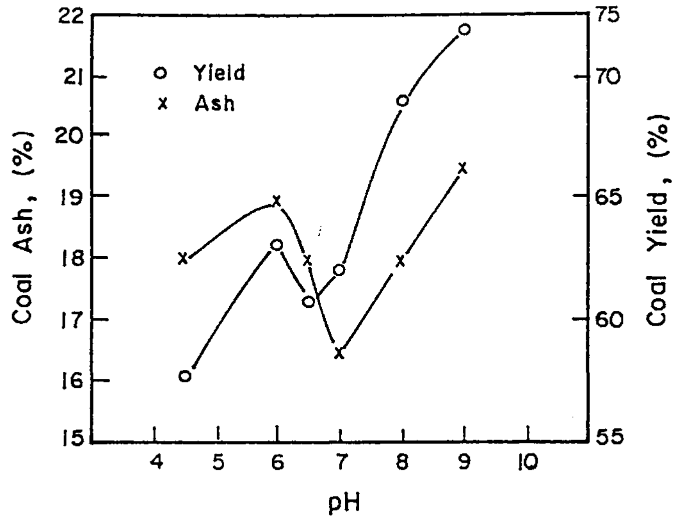


Figure 8.28. Effect of pH on Reverse Flotation

Reverse flotation is generally applied in two stages to desulfurize coal by floating pyrite in the second stage (Miller and Deurbrouck, 1982). Recently Stone Street and Franzidis (1988; 1989) used various quartenary amines to clean high ash South African coal. They used coal and quartz artificial mixtures in their single stage reverse flotation and claimed partial success and called it a novel way of reverse flotation. No study yet exists in literature for actual system. In this study single stage reverse flotation was used to float Zonguldak flotation feed (below 0.5 mm and containing 35.1 % ash) with Flotigam ENA (alkyl ether amine). These results can be compared with 50.5 % yield and 15 % ash obtained with Kerosene oil and MIBC system.

Having achieved the success in reverse single stage flotation of coal, other commercial amines Armoflote 18 (quaternary amine) and Armoflote 21 (alkyl amine acetate) were also tried. These results are shown in Table 7.26 and summarized in Table 8.2 to compare with Flotigam ENA.

A comparison of three amines shows that although Flotigam ENA on reverse flotation gave slightly lower yield than Armoflote 18, yet the ash contents were quite low and comparable to direct flotation of coal with Kerosene oil due to its selective nature. Armoflote 21 was found to be inferior to both of them.

Table 8.2. Comparison of Three Different Amines in Reverse Flotation

Type of Amine	Coal Yield, %	Coal Ash, %
Flotigam ENA	62.2	16.5
Armoflote 18	68.5	25.0
Armoflote 21	48.7	23.0

8.6 Two Stage Coal Flotation

After having achieved greater success with Pamak4 in direct flotation and with Flotigam ENA in single stage reverse flotation, a combined flotation with Pamak4 and Flotigam ENA was attempted by subjecting the coal obtained in direct flotation (first stage) to reverse flotation (second stage). The aim of this study was to see the possibility of further cleaning of coal from ash.

The results obtained in Table 7.27 were plotted in Figure 8.29 to determine the dextrin amount while using Flotigam ENA = 720 g/t. The higher amounts of this reagent floated even coal and lower amounts were not giving proper frothing to float gangue.

Finally a comment may be added that although reverse flotation of coal may not be attractive economically, yet it can be used to clean high ash clay coals or difficult to float coals under special circumstances where normal oil flotation can not be applied.

As shown in Figure 8.29, the dextrin amount is controlling the ash in reverse flotation (second stage). A low ash product with 12 % ash and 55 % yield is obtained at much higher amount of dextrin (1600 g/t). In case the dextrin amount (Table 7.27) is reduced very much (600 g/t), and the collector amount is increased to 1440 g/t almost all the material is floating.

It may be pointed out that all the factors namely collector, depressant, time and pH control the reverse flotation and therefore, an optim ization for each coal is necessary in some detailed investigations.

As the direct flotation with Pamak 4 in this two stage process yields 70 % coal containing 15 % ash, and employing reverse flotation to its concentrate, yields 55 % coal with 12 % ash, therefore the application of reverse flotation is desirable, only if a very clean product is desired. This two stage flotation may also be useful for floating other high ash/clay coals and coal refuse, where Kerosene oil and MIBC can not be applied efficiently and economically due to its limitations.

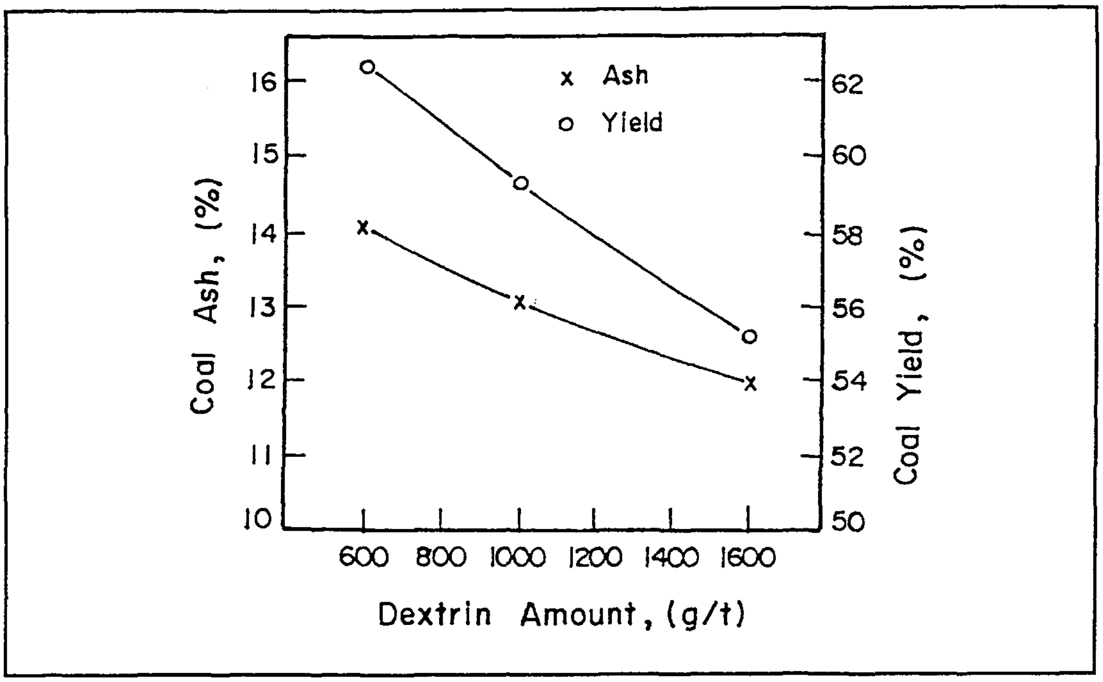


Figure 8.29. Effect of Dextrin Amount in Two Stage Flotation

CHAPTER IX

CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions

1. Under the light of petrographical analysis of coarse wastes (Samples B to E) of Zonguldak washery, it was found that they are composed of 48-68 % clay minerals, 15-22 % silicates, 3-22 % organic matter and the rest carbonates, sulphides and oxides. The clay minerals in these wastes amount to an average of 58 %.

2. Preliminary and detailed XRD investigations for the identifications of clay minerals in coarse wastes, coal and black water showed that three clay minerals, namely illite, kaolinite and chlorite are present. Washery wastes are dominant in illite where as kaolinite and illite are dominant in coal and black water respectively. Low temperature ashing (LTA) and semi quantitative analysis verified the qualitative results.

   In the absence of LTA facilities for XRD analysis of clay minerals in coal and coal refuse, chemical pretreatment was successfully applied to remove organic carbon in order to obtain qualitative as well as meaning full semiquantitative results using Biscaye's method.

3. The loss on ignition analysis showed the presence of high amount of organic matter in waste samples E, F and H (21, 33 and 27 % respectively) indicating the loss of coal.

4. Zeta potential measurements of Turkish clays showed that kaolinite had more negative charge than two other clays and no pzc. The illite was least negative and chlorite was intermediate in zeta potential values with pzc's at pH 2.5 and 3.0 respectively.

5. Zeta potential measurements of clean coal from Zonguldak has an IEP value at pH = 4.1. Inorganic electrolytes $MgCl_2$, $CaCl_2$ and $Ca(OH)_2$ on coal behaved as indifferent electrolytes however, $AlCl_3$ and $Al_2(SO_4)_3$ reversed the sign of charge on coal surfaces converting them in to alumina like surfaces. Similarly the dispersants (sodium silicate, calgon and Marsperse CB) and depressants (CMC, dextrin and Aero-depressant 633) used on coal, made the coal surface more negative.

6. The flotation tests on artificial mixtures of clean coal-individual clay, revealed that each clay influences coal flotation differently according to its type and amount. Illite was having the worst effect on coal flotation, followed by chlorite and kaolinite;

    (a) In the light of zeta potential measurements it was concluded that most negative clays like kaolinite have least depressing effect on coal flotation than least negative ones like illite where as chlorite occupies an intermediate role. This was in agreement with the CEC values mentioned by Grim (1968) and sequence proposed by Bolt et al., (1976) with regard to kaolinite and illite. However chlorite may occupy an intermediate position.

(b) The slime coating on coal and water carry over mechanism of fine clay were effective towards deteriorating the yield and ash of coal respectively. A comparison to the effect of clays with the actual system (flotation feed) did not match with the results of artificial coal/clay mixture taken in exact proportions, determined semi-quantitatively for the presence of three clays found in coal. This can be related to ease in flotation of freely liberated clay from coal, giving cleaner product than the actual system.

Increased oil addition to float clean coal from coal/ clay mixture, raised the ash content of the concentrate and use of CMC as dispersant could not improve it but depressed largely the coal.

7. The optimized parameters for direct flotation of clean coal were: Kerosene oil = 340 g/t, MIBC = 85 g/t, flotation time = 1 minute and pH = 6.5 (distilled water).

8. In the flotation of high ash coals containing 35.1 % ash, it was found that Pamak 4 (ionizing collector) gave 20 % higher yield than Kerosene oil + MIBC combination at the same ash level (15 %) in concentrate, and the oleic acid reduced the yield to 34 % with an ash content of 12 %. This concluded that Pamak 4 was more active and selective towards floating high ash coal where as oleic acid was only selective. Similar trends were observed for coals containing 39.9 and 67.1 % ash. All results showed that the use of Pamak 4 opened a door for investigations leading to its commercial application.

9. The reverse flotation of high ash coal (35.1 % ash) in single stage was successful by using Flotigam ENA as collector and dextrin as coal depressant; obtaining 62.2 % yield and 16.5 % ash in coal. These results were comparable to direct flotation of this high ash coal. On floating this coal with other two amines, it was found that only the alkyl ether amine was more selective for floating such coal, at a higher dosage (3600 g/t).

10. A combination of direct flotation using Pamak 4 followed by reverse flotation using Flotigam ENA and dextrin showed that dextrin is controlling the ash in reverse flotation if used in greater amounts (1600 g/t) and a product containing 12 % ash was produced. The reverse flotation was also affected by collector amount, flotation time and pH to obtain the desired results.

    It can be concluded that the application of reverse flotation may be helpful in special circumstances where ash reduction to lower levels is required otherwise direct flotation using Pamak 4 is advisable.

9.2. Recommendations

1. There is a need to characterize wastes, coal and black water from other washeries in Turkey for identifying the clay minerals and solve their problems in various coal washing processes such as flotation, heavy media separation, flocculation, dewatering and filtration.

   Here, the technique developed to pretreat coal and coal refuse samples (in the absence of LTA equipment) for their semi quantitative analysis using Biscaye's method, can be a useful tool for the future researchers.

2. In order to evaluate the possibility of commercial use of Pamak4 and other oleic acid based reagents in coal flotation, more detailed batch and pilot scale testing is essential.

3. A detailed investigation is required to show the possibility of application of reverse flotation, especially for difficult to float coals. Combined two stage flotation also requires detailed research.

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APPENDICES

APPENDIX A

X RAY DIFFRACTION PRINCIPLES AND IDENTIFICATION OF CLAY MINERALS

A.1 X-Ray Diffraction Principles and Equipment

The phenomena of diffraction involves the scattering of x-rays by atoms of crystals and the reinforcement of the scattered rays in definite direction away from the crystals. The reinforcement of scattered rays is quantitatively related to distance of separation of atomic planes (inter planar spacing) as defined by Bragg's Law $n\lambda = 2d \sin\theta$ (Fig. A.1).

This is usually given as $\lambda = 2\,(d/n)\sin\theta$ and dropping the "n" as $\lambda = 2\,d \sin\theta$. Therefore, for a given set of planes with spacing "d", reflection occurs with a phase difference " λ ". Thus for example, second order reflection from (III) planes can be regarded as the first order from (222) planes (which half the "III" spacing). Since no two minerals have exactly the same interatomic distances in three dimensions; the angles at which diffraction occurs will be distinctive for a particular mineral.

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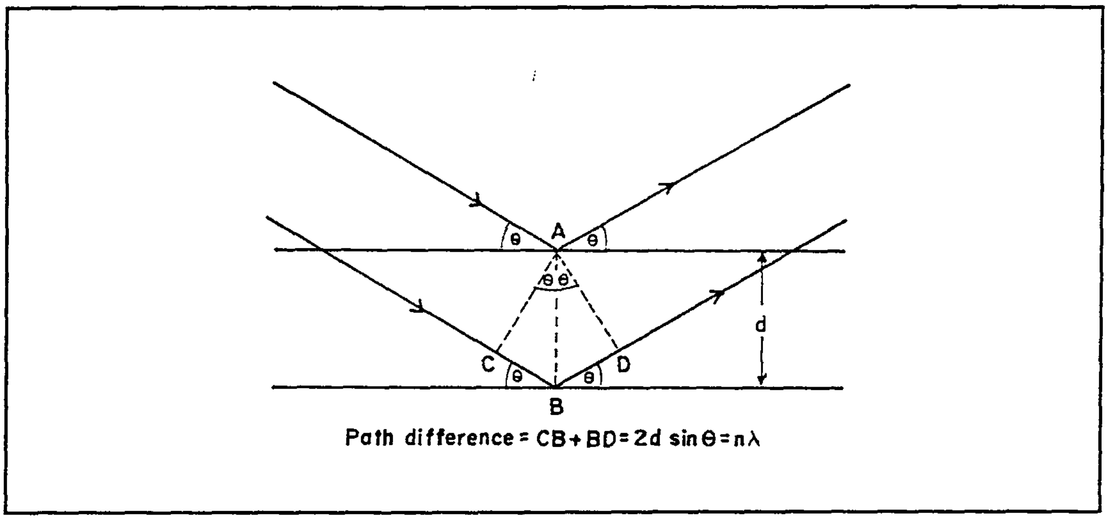

Figure A.1. Diagram Illustrating the Bragg Law (Zussman, 1977) d = interplanar distance; θ = Bragg angle; λ = x-ray wave lengh; n= integar

The interatomic distances within a mineral crystal then result in a unique array of diffraction maxima which serves to identify the mineral. The data in the X-ray Powder Diffraction Files (J.C.P.D.S, 1975) are tabulated in the form of a list of spacing in angstrom (A) units, starting with largest measured spacing together with the intensities relative to "100" for the strongest reflection and the indices hkl when they are known (Zussman, 1977).

A diffractometer should have an appropriate x-ray tube, filters, collimators and detectors to obtain optimum peak intensities and optimum peak to back ground ratios without unnecessary sacrifice of dispersion and resolution (Brindley and Brown, 1984). Zussman (1977) described such equipment details for XRD analysis.

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The choice of most suitable radiation is based on composition of specimen. For the examination of clays with small Fe content (5 % Fe) Cu as anode material gives most intensity whereas CO is preferred for iron rich materials. Therefore, in this study due to lower iron content in samples, Cu radiations were used throughout. The x-ray peak wave length of CuKα radiations is 1.392218 A (1 A=10^{-10} m) as found by Norrish and Taylor (1962). With CuKα radiations, Ni filter is used (Brindley and Brown, 1984).

For most purposes, XRD results are automatically chart recorded at a scanning rate of 1^{o} (2θ) / minute over an angular range of 2^{o} - 65^{o}, with filtered CuKα radiations. For clay minerals CuKα radiations in the range of 2^{o} - 30^{o} A are frequently used (Brindley and Brown, 1984).

A.2 XRD Identification of Clay Minerals: Qualitative Aspects

The qualitative interpretation of diffraction patterns involves the identification of crystalline species from the array of diffraction maxima obtained from a sample either by direct comparison of its maxima with that of known sample or by measurement of diffraction spacings using standard tables or files (Brindley and Brown, 1980). The comprensive guides to the identification of clay minerals are edited by Carroll (1970), Brown (1972) and Brindley and Brown, (1984).

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As already pointed out XRD pattern of clay minerals gives the basal (001) spacing of the minerals in oriented mounts whereas hkl spacings are obtained with unoriented mounts. The basal spacing gives periodicities normal to the plane along c-direction (Carroll, 1970); this dimension may vary with humidity, dehydration, cation interlayer positions and acid treatment etc. The hk spacings are a and b directions of the unit cell except triclinic class. These spacings do not vary with treatments. The most common is the treatment with polar liquids of low volatility such as ethylene glycol to aid the identification of smectites, and various heat treatments that collapse swelling minerals by dehydrating the interlayer material and destroy or transform mineral such as kaolinite and hydroxides (Brindley and Brown, 1984). A diagrammatic representation of general character of clay mineral structures is shown in Figure A.2. (Brindley, 1972). The characteristic 7.2, 10 and 14-15 A spacing are marked in this figure. The diagnostic features for identifying the common clay minerals are given by (Hutchison, 1974). A commonly employed scheme of identification of clay minerals in tabulated form is presented by Carroll (1970). Stoffers and Müller (1972) gave a very simple table for identifying the clay mineral group on the basis of their basal spacings (Table A.1).

As mentioned previously treatments designed to remove common cementing agents (iron oxides, organic matter and carbonates) improved the quality of XRD traces (Whittig, 1965) and also elucidated the nature of components of interstratified minerals. An example of the kind of problem encountered is the recognition of kaolinite in the presence of chlorite (as in this study). The 002 and 004 reflections of chlorites (d= 7.1, 3.55 A) overlap the 001 and 002 reflections of

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Table A.1. Reflections Used for Identification of Clay Mineral Group

Clay Mineral Group	Untreated	Glycolated	Heated to 350^{o}C	Heated to 550^{o}C
Illite	10A	10A	10A	10A
Chlorite	14A	14A	14A	14A
Montmorillonite	12-15A	17A	10A	10A
Kaolinite	7A	7A	7A	-----

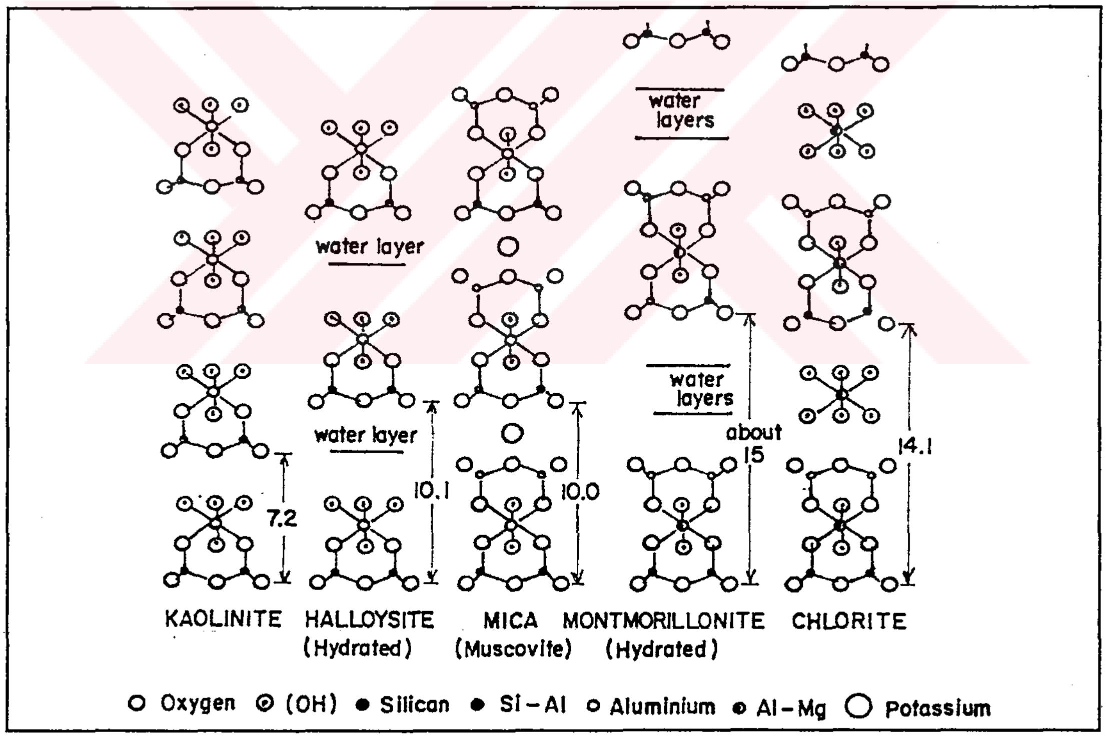

Figure A.2. Diagrammatic Representation of the Succession of Layers in Some Layer Lattice Silicates. (Brindley, 1972) kaolinite (d= 7.15,3.58 A). So a partial resolution of 002 (3.58 A) kaolinite and 004 (3.55A) chlorite is used to solve the problem for recognizing the both. A separation of kaolinite from chlorite is some times done by treating with dilute HCl in which many Fe-chlorites are soluble. Thermal treatment on heating between 450-500 ^{o}C for 2-4 hours transforms the kaolinite to a very poorly ordered metakaolin showing little or no XRD pattern while many dictites, serpentenites and chlorites survive this treatment (Brindley and Brown, 1984).

A.3 Quantitative XRD Clay Mineral Analysis

A quantitative mineral analysis is next step after a qualitative examination has identified the components present. X-ray intensities reflected by the components in mixture are obviously related to the properties of components and are the basis for quantitative analysis. Many text books such as, Klug and Alexandar (1974) and Cullity (1978), describe procedures for accurate measurements of quantitative phase analysis. Some methods use external standards and some internal standards while some eliminate any standards (Brindley and Brown, 1984). Norrish and Taylor (1962) investigated soil clays based on intensity of diffraction and mass absorption coefficients. Schultz (1964) quantitatively estimated shale composition from diffractograms and chemical analysis. Carroll (1970) estimated quantitatively each mineral present by comparing peak areas of principal (001) spacings on diffractograms, measured with a polar planimeter to an accuracy of 5-10 percent. Mackenzie and Mitchell (1966) concluded that most clay mineralogical analysis must be regarded at best as "semi-quantitative". Therefore the recorded intensity (proportional to the actual intensity) should be given allowance for background scattering whether peak height or peak area is measured. The "tails" of diffraction peaks must often be guessed rather than measured. The measurement of peak heights may be less sensitive to errors of background estimation than peak areas. Some times peak height multiplied by angular breadth at half maximum height is used as a measure of intensity. The subject of quantitative analysis is not a closed topic, and mixtures with small number of components, not exceeding three or four, can be fairly analyzed but soil clays with many components are difficult to analyze with precision (Brindley and Brown, 1984).

Biscaye (1965) developed a method for semi-quantitative analysis of clays in Atlantic Ocean sediments by XRD which was used by stoffers and Müller (1972) for Black Sea sediments. Biscaye's method is summarized by Pierce and Siegel (1969) as follows:

The integrated intensity of 17 A glycolated peak is equal to the relative amount of montmorillonite. The area of 10 A peak (glycolated trace) multiplied by four, is equivalent to the relative amount of hydromica (illite). The 7 A peak area is multiplied by two for the relative amount of kaolinite plus chlorite.

The weighting factor for the peak area of kaolinite plus chlorite is obtained from the ratio (Stoffers and Müller, 1972):

3.58 A peak area / (3.58 A + 3.54A) peak areas

This weighting factor divides the 7 A peak area common to both kaolinite and chlorite, between the two in proportion to the fraction of each mineral in the total area under the resolved 3.5 A kaolinite-chlorite doublet (Biscaye, 1965). As already mentioned in qualitative analysis 3.58 A (002) reflection refers to kaolinite and 3.55 A (004) to chlorite (Brindley and Brown, 1984).

Pierce and Siegel (1969) used all the existing five methods for Argentina Sediment cores and suggested to adopt a unified methodology due to different results obtained by each one. This seemed unrealistic to Brindley and Brown (1984) because every mixture due to its particular features needed treatment accordingly, and with good practical procedures and favourable circumstances, each method can afford reasonable results.

A.4 Loss on Ignition Analysis

Dean (1974) recommended determination of carbonate and organic matter of sediments by loss on ignition analysis. The method was first developed by Kolthoff and Sandell, (1952) and later used by Galle and Runnels (1960).

In this method heating to 90-100 ^{O}C for one hour in oven gives moisture, and heating to 550 ^{O}C and 1000 ^{O}C for one hour in muffle furnace yields organic carbon and CO_2 respectively as weight loss, in each determination. The $CaCO_3$(%) is calculated from the amount of CO_2 lost between 550-1000 $^{\circ}$C divided by 0.44 (the fraction of CO_2 in $CaCO_3$). The ignition loss method is rapid and precise and hence chosen in this study for analyzing all the samples from washery.

APPENDIX B

PROCEDURE FOR DETERMINATION OF SULPHUR AND MINERAL MATTER

B.1 Sulphur Determination

One gram of coal sample (-325 mesh Tyler) was combusted in the container of the oxygen bomb calorimeter. The combusted material was washed with distilled water, then boiled after putting 1 mol of ammonium hydroxide in it and filtered through a rapid qualitative paper. The residue was washed with distilled water and volume of solution made to 250 ml. This was neutralized with concentrated HCl and 10 ml bromine water and then evaperated to 200 ml on a hot plate. The 10 ml of 10 % barium chloride solution was added and volume reduced to 75 ml by heating on steam bath. The precipitate was allowed to settle for one hour, filtered through ashless filter and washed with warm water to be freed from chlorides. The paper and filtrate was transferred to a weighed crucible and heated to constant weight at 925 ^{o}C for about half an hour. The crucible was then cooled in a dessicator and weighed for determining the exact weight of barium sulphate precipitate. The sulphur percentage was calculated as follows (Parr Instrument Manual): Sulphur (%)= (Weight of $BaSO_4$ x 13.734) / Weight of Sample. Here 13.734 is a factor obtained from:

$(S/BaSO_4) \times 100 = (32 / 233) \times 100 = 13.734$

B.2 Mineral Matter Determination

Ten grams of sample in a teflon crucible was first treated with 5N HCl for 45 minutes at 55-60 °C (7 ml HCl/gram coal), then it was filtered and washed to eliminate chlorides. The filter cake was dried in oven at 60 °C, and the dried filter cake was treated with 7 ml HF (density = 1.15 gram/cm^3) per gram coal for 45 minutes at 55-60 °C. It was now again filtered and cake was treated with concentrated HCl as before for another 45 minutes at 55-60 °C. Now this was filtered and dried in oven at 60 °C to a constant weight. The weight of filter cake was substracted from the weight of sample and converted to percentage by multiplying with 100 to give mineral matter content (Bishop and Ward 1958; Miranda, et al., 1991).

CURRICULUM VITAE

Syed Abid Hussain was born at Multan (Pakistan) on Jan. 1, 1944. He received his B.Sc. Mining Engineering from the University of Engineering and Technology, Lahore (Pakistan) in 1966 and M.S. Mining Engineering in 1975 from Middle East Technical University, Ankara (Turkey). In 1984, he completed his Master of Philosophy Degree from the University of Nottingham (U.K).

He served the mining industry of Pakistan (1966-75) and obtained training in Mine Safety and Mine Management. In 1975, he joined the Mining Engineering Department of the Engineering University, Lahore as Assistant Professor, became Associate Professor in 1984 and Professor in 1986.

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