Settling characteristics of coal washery tailings using synthetic polyelectrolytes with fine magnetite

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Transaction Paper

Synopsis

The study examines the potential reuse of waste water from coal preparation plant tailings, which are often problematic in terms of solid liquid separation and dewatering. The settling rate of fine coal particles by interaction with proper coagulants and flocculants is important in the dewatering process. The tailings water from the Kedla coking coal preparation plant, Central Coalfield Limited (CCL), India is highly turbid with a negative surface charge dominating at pH values between 2 and 10.

A polymeric flocculant in conjunction with fine magnetite was used to achieve a faster settling rate with the lowest level of water turbidity. The conditions affecting the interaction between the reagents and the turbid particles present in the tailings water are investigated. It was possible to reduce the turbidity of the water to 73 NTU from a very high turbid tailing water by using 1.2 mg/ℓ of the polymer with 0.1 g/ℓ of fine magnetite at the natural pH of the tailing slurry. The finely divided positively charged magnetite particles, when combined with the flocculent, coat the negatively charged impurities in the water, which results in a faster settling rate under the influence of a magnetic field.

Keywords: dewatering, flocculant, magnetite, turbidity

Introduction

In the coal preparation plant, the run of mine coal undergoes a series of operations, including washing, wet screening, sedimentation and dewatering. The process requires the circulation of large volumes of water from which large volumes of waste water containing a variety of solid particles are generated. Clarification of the tailing water is often carried out in a thickener by adding suitable polymeric flocculants. The main objective of the clarification is to obtain clear water with a low turbidity value. It is important to produce good quality recirculation water for the smooth operation of the plant, otherwise the presence of suspended and dissolved solids in the wastewater can lead to a reduction in the efficiency of the washing process. Waste waters produced from coal preparation plants contain high percentages of ultrafine particles and inorganic impurities, which are composed of clay minerals such as kaolinite, illite, muscovite, quartz, and coal particles. The natural sedimentation rate of these particles present in colloidal and finely divided suspended form is very slow. Flocculation technology is applied in most coal preparation plants to recover water from the tailings of coal washing operations. The flocculation is accomplished through the use of inorganic salts, polymeric flocculants or both, depending on the chemical and physical characteristics of the pollutants present in suspended and dissolved states[1]. Synthetic or natural polymeric reagents are generally used as flocculating agents in most coal preparation plants. Synthetic polymers are comparable to natural polymers due to their use in small quantities for the separation of solids from liquids. In order to achieve the faster settling rate, the optimization of process parameters such as suspension pH, polymer type and dosage are very important to achieve the desired settling rate and the water clarity values. Various flocculant combinations, viz. cationic, anionic, non-ionic have been used to achieve the highest settling rate with lowest turbidity[2–4].

In this investigation, the clarification of waste water was carried out by the incorporation of a suitable reagent together with fine magnetic material known as magnetic carrier technology. Magnetic carrier technology is an innovative way of selectively manipulating fine particles in suspensions by coating them with a magnetic species. It utilizes the physical, chemical and surface properties of a magnetic carrier to enable selective attachment with the desired particles. The selective increase in floc formation and faster settling rates with magnetic response of the particles are achieved by incorporating a strongly magnetic phase. The negatively charged impurities such as clay, bacteria, viruses and colour present in

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waste water are removed by the magnetic aggregation of particles, which is induced by a low intensity magnetic separator[5]. The technology for the treatment of waste water is also marketed as the Sirfloc process. An acidic pH is maintained in the system to provide a positive magnetite surface to aid the adsorption of the negatively charged impurities.

Several studies such as purification of drinking water and recovery of mineral fines by this technology have been successfully carried out at the Regional Research Laboratory, Bhubaneswar, India. It was possible to lower the turbidity of river water from 236 NTU to less than 5 NTU, which is quite suitable for drinking purposes, by the combination of polyelectrolytes in conjunction with fine magnetite[6]. An extensive study was carried out for the recovery of hematite fines from iron ore slimes. The best separation was observed at pH 7.2, in the presence of colloidal magnetite and a magnetic intensity of around 7.8 KG. The coating of oleate colloidal magnetite with hematite exhibits the presence of a very thin rim around the hematite while the quartz remains unaffected[7].

The application of magnetic materials as a carrier has been successfully applied to biological processing, effluent processing and mineral processing. In mineral processing, a large number of separations based on selective adsorption of magnetite have been reported. Minerals from paramagnetic groups and non-magnetic groups have been successfully tested by this technique. Removal of carbonates, such as calcite and dolomite from apatite, with chemically precipitated magnetite has been demonstrated[8]. The level and the selectivity of the magnetite coating was strongly pH dependent when used in the presence of a surfactant such as sodium oleate. Based on the good results obtained from artificial mixtures, the process was tested in a continuous pilot-scale operation on high dolomite sedimentary phosphate ore. The rejection of rutile and anatase from kaolin has been achieved by seeding the slurry with fine magnetite in the presence of fatty acids[9,10].

The objective of this investigation was to enhance the clarification of waste tailings from the Kedla coking coal washery of Jharkhand State, India. The waste water was characterized by different physico-chemical techniques and the performance criteria such as faster settling rate with minimum turbidity of water were analysed by magnetic carrier technology in which a poly-electrolyte was conjugated in the presence of magnetite particles under the influence of a magnetic field.

Experimental

Waste water sample

The wastewater slurry sample used in the experiments was collected from one of the discharge points of the Kedla coking coal washery plant of Central Coal Field Limited (CCL), Jharkhand, India. A raw water sample from the plant, which is generally used as the make-up water, was also collected and analysed for comparison. The pH, solids concentration of the pulp, hardness, conductivity, concentration of different anion and cations were analysed by wet chemical and atomic absorption spectrophotometer techniques (AAS).

Reagents

The high molecular weight commercial grade flocculants under the trade names Rishi floc, Zetag-32, SN-64, and Spectrum-pw were used in the flocculation studies. The reagents were of very high molecular weight, non-toxic with potable character and supplied by different manufactures. Analytical reagent Al_2 $(SO_4)3$ of crystalline grade was used as a coagulant in some cases. A pure magnetite sample was obtained from the Kudremukh iron ore Company Ltd, India. It was crushed, ground to 20 micron, washed several times, and used for rapid adsorption of impurities present in the coal slurry samples. Homogeneous stock solutions (0.1%) of the reagents were prepared using distilled water.

Methods

A series of waste water samples were tested by conventional flocculation methods. For each test, one litre of wast ewater from the plant (~5% solids) was taken in a two-litre capacity glass beaker having 131 mm diameter and 190 mm height and conditioned by stirring with a digital stirrer at 600 rpm to ensure complete dispersion. A desired amount of polymeric reagent solution was than added to the slurry during stirring while the agitation intensity was reduced to 300 rpm. The conditioning was continued further for another few minutes at low agitation to ensure thorough mixing of the reagent. The entire pulp was then transferred to a glass measuring cylinder of ~500 mm height and 70 mm diameter. The flocs that formed were then allowed to settle and the supernatant liquid was withdrawn from the measuring jar down to a fixed level and subjected to turbidity measurement. The height between the floc and water interface as a function of time was recorded to calculate the settling rate of the flocculated suspension. Several commercial polyelectrolytes were evaluated for the clarification of the coal tailings sample obtained from the washery. Tests were carried out with several reagents to identify a suitable polyelectrolyte, which can enhance the settling behaviour of the suspended particles. The fine magnetite of 20-micron size was applied as the carrier. Magnetite was homogeneously mixed with the required amount of polymeric reagent solution before addition to the raw coal tailings sample. Permanent field strength of 2000 gauss was applied to enhance the settling rate. This was achieved by placing the measuring cylinder on a bar magnet. (see Figure 1.)

The particle size analysis of the fine residual impurities present in the sample was carried out using a Malvern particle size analyser, model 3600. Determination of the mineral composition was carried out by X-ray diffraction (XRD) techniques using Cu Ka radiation after igniting the residue at low temperature. By careful thickening and filtering the fine and colloidal residual impurities present in the tailings water were removed and dried at 105°C, powdered and subjected to low temperature fusion mainly to remove the coal particles present in the sample. It took several days to obtain coal-free residues. Rank Brothers Mark II electrophoresis apparatus with flat cell configuration was used to carry out the measurement of Zeta-potential of the residue sample at different pH values. The turbidity values of the samples were measured using a DRT 100D turbidity meter supplied by H.F. Scientific Inc, Florida USA. This is a continuous reading nephelometric instrument, in which light from particles in suspension and direct light passing through a liquid are compared. The ratio of the above light signals is measured as the turbidity of the samples in nephelometric turbidity unit (NTU).

Measurement of the surface charge of the polymer was carried out by using a particle charge detector (PCD-03-pH) from Muetek, Germany. It is based on the principle that colloidal soluble molecules or particle suspensions in water can carry electric charges when dissociable functional groups are found on their surface. The charge density of the polymer was found to be –632. 94 Coulomb/g. The negative sign clearly indicates the anionic nature of the reagent.

Figure 1—Experimental set-up for settling studies

Results and discussion

The physico-chemical analyses of the coal tailing water sample of Kedla washery are shown in Table I. The quality of the water sample indicates that the turbidity is ~ 10200 NTU and is not suitable for recycling to the plant unless the solid particles are separated from the liquid phase. The pH of the slurry sample was found to be 8.0 indicating the alkaline nature of the sample. Although it contains some trace metal ions such as Fe, Co, Ni, Mn, etc., the concentration of alkali and alkaline earth metals such as Na, K, Ca and Mg are very high. The analysis of the raw water of the plant indicates that all the parameters studied are well within the permissible limit. The presence of Al_2O_3, (12.6%) SiO_2 (56.4%) and ferric oxide (1.3%) in the slurry confirms that clay minerals are present in the tailings. The X-ray diffraction analysis of the residue material is shown in Figure 2, which indicates the presence of minerals such as quartz, kaolinite, illite and muscovite. The results are similar to the mineralogical composition of the ash materials found in most of the Indian coals[11]. The particle size analysis of the Kedla impurities is shown in Figure 3. The sample contains some coarse particles of 500-micron size but the weight fraction of 62.8% is below 30 microns.

According to the particle size data of the coal preparation plant impurities the percentage of particles present in the clay, silt and sand are presented in Table II. It was observed that the percentage of silt is greater than clay or sand. Most of the coarser size particles contain quartz and coal particles.

The measurement of zeta potential of the coal tailings as a function of pH is shown in Figure 4. The tailings exhibit negative charge at all pH values with no point of zero charge. The absolute value of zeta potential increased with an increase in pH up to 6.0 and then showed some ups and downs up to pH 11.5. The behaviour of the zeta potential at alkaline pH showed that the surface of the impurities present in the sample is complex in nature. The surface charge of coal tailing particles is essentially due to the presence of

Table I

Characterization test results of Kedla processed water

Parameters	Tailing water	Raw water	Parameters	Tailing water	Raw water
Natural pH	8.2	8.5	Co	-	-
Density	1.0772	0.995	Ni	0.06	0.05
Cl^- (mg/ℓ)	183.942	111.965	Mg	60.0	34.7
SO_4^{--} (mg/ℓ)	564.44	76.931	Ca	133.2	15.0
NO_2^- (mg/ℓ)	0.37039	0.3258	Fe	0.13	0.17
Turbidity, NTU	10200	7.0	Na	30	31
Total solid content %	5.5	0.0425	K	14.8	11.1
Total hardness (mg/ℓ)	720.65	144.131	Mn	0.069	0.03
Conductivity (mhos/cm)	44.9	41.0	Cd	0.014	0.014
CO_3^{--} (mg/ℓ)	1.0	1.5	-	-	-
HCO_3^{--} (mg/ℓ)	14.6	36.475	-	-	
Mineral present in residue: Quartz, kaolinite, illite and muscovite					

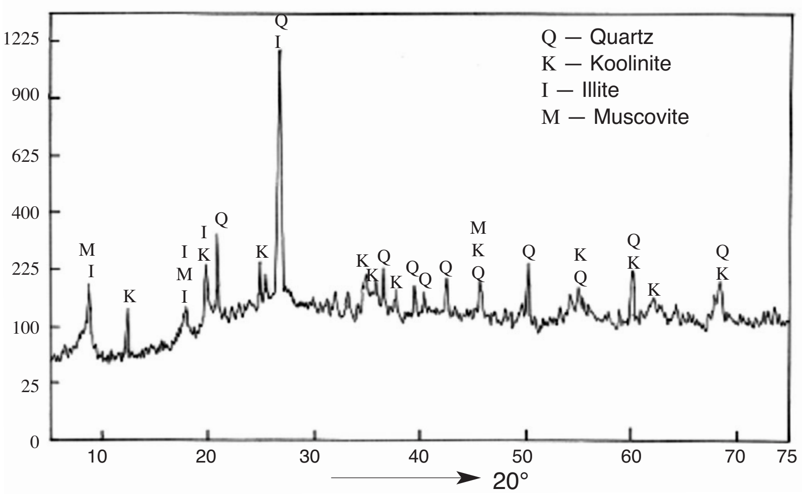

Figure 2—X-ray diffraction studies of Kedla processed water

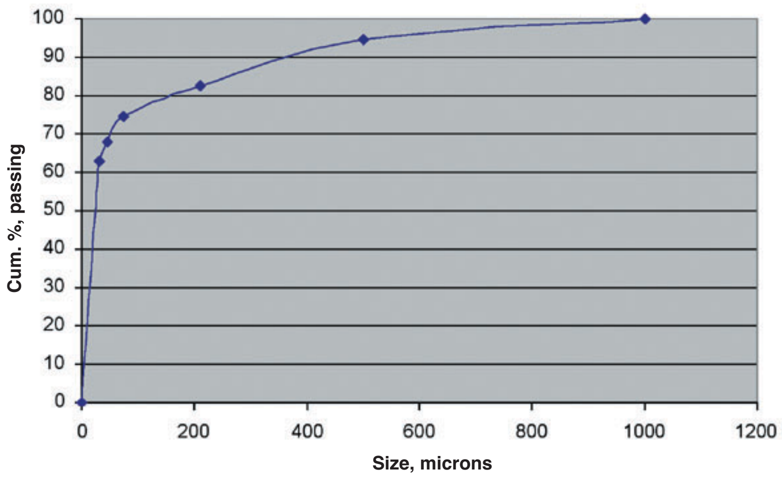

Figure 3—Size analysis of the waste tailing residue

Table II

Texture of impurities of coal preparation plant

Texture	Size, microns	Values (%)
Clay	-4 µm	20.3
Silt	4-63 µm	42.5
Sand	+63 µm	37.2

alumina and silicate particles. The tailing sample exhibits more values of zeta potential in the weak acidic medium. The zeta potential in the acidic medium is attributed to the change in surface pH, while that in the alkaline region is ascribed to the binding of more cations.

It has been observed that Kedla tailings water does not settle on its own and even after 5 hours of natural sedimentation, the settling rate is very low at 0. 08 cm/min. The effect of five different polyelectrolytes on the settling behaviour of the coal preparation plant tailings is shown in Figure 5. The settling behaviour of magnetite is also incorporated in the figure. It can be seen that Spectrum-pw shows a better performance with respect to the floc formation and settling behavior (23 cm/s). The settling rate of magnetite on its own is very poor compared to the flocculents.

The corresponding turbidity value for the same reagents is shown in Figure 6. In all cases the turbidity was reduced from the original value by the flocculating effect of the polyelectrolytes. The lowest turbidity was achieved by adding Spectrum-pw as the flocculant. It can be concluded that of the five different flocculants, Spectrum–pw shows the best performance with regard to floc formation, settling behaviour and turbidity.

To improve the settling rate and reduce the turbidity another series of tests was carried out at 1.2 mg/ℓ of the polymer and varying additions of fine magnetite particles. The effect of the reagent in the presence of magnetite as the carrier was evaluated and the results are shown in Figure 7. In each case the magnetite particles with the adsorbed impurities was allowed to settle for five minutes before withdrawal of the sample for turbidity measurement. Figure 7 shows that only a small amount of magnetite is needed to enhance the settling.

The corresponding turbidity values are shown in Figure 8. It was possible to lower the turbidity to 73 NTU

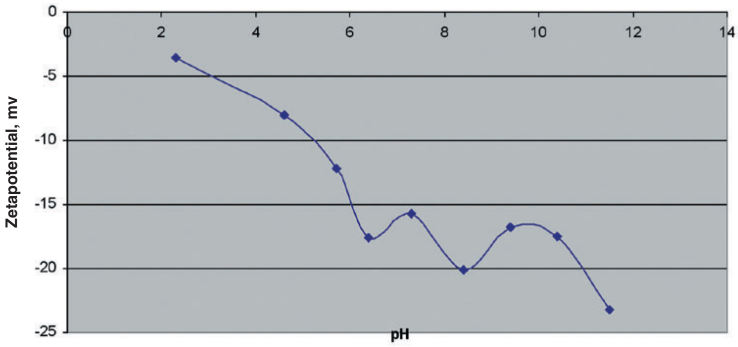

Figure 4—Zeta potential of tailing residue at different ph

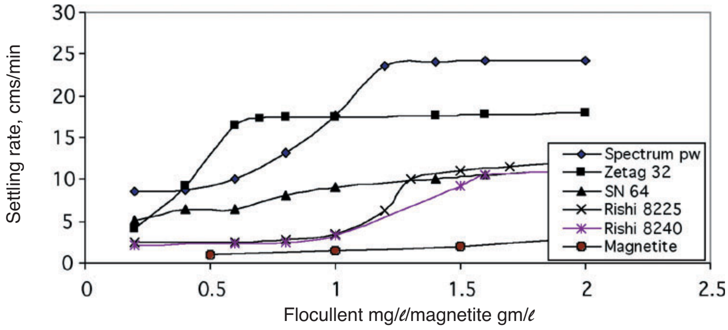

Figure 5—FLocculent and settling rate

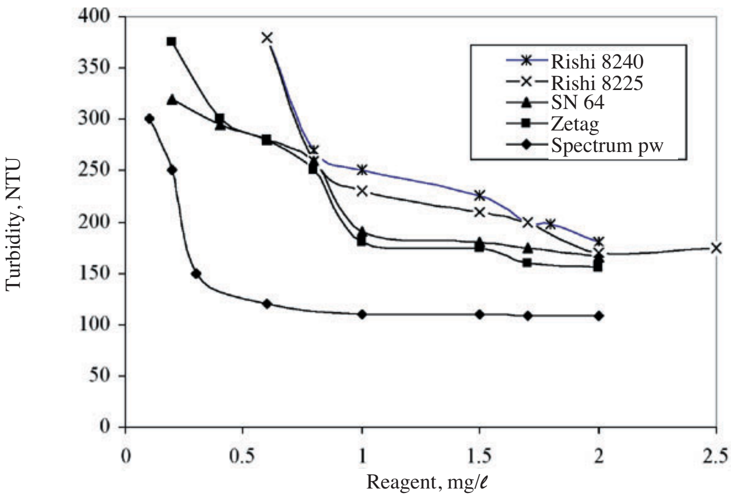

Figure 6—Effect of different flocculant concentration on turbidity at 15 mins settling time

from the initial high turbid water sample (10200 NTU) by using 1.2 mg/ℓ of the polymer and 0.1 g/ℓ of fine magnetite. The explanation is that the finely divided positively charged magnetite particles coat the negatively charged impurities in the water, which subsequently settle very quickly under the influence of a magnetic field. This results in improved clarity of the supernatant liquid and a reduction in settling time.

Conclusions

Characterization studies have shown that the impurities in the Kedla tailings water are heterogeneous in structure and composed of quartz, kaolinite, illite and muscovite types of mineral matter. The proportion of clay and silt is high in the waste water sample.

The best flocculation performance occurs at the natural pH of the tailings sample.

Fine magnetite when added to the system rapidly enhances the settling rate of the particles, which are rapidly sedimented under the influence of a low intensity magnetic field. It is possible to achieve a clarity of 73 NTU from very high turbid water (10200 NTU) in a settling time of five minutes.

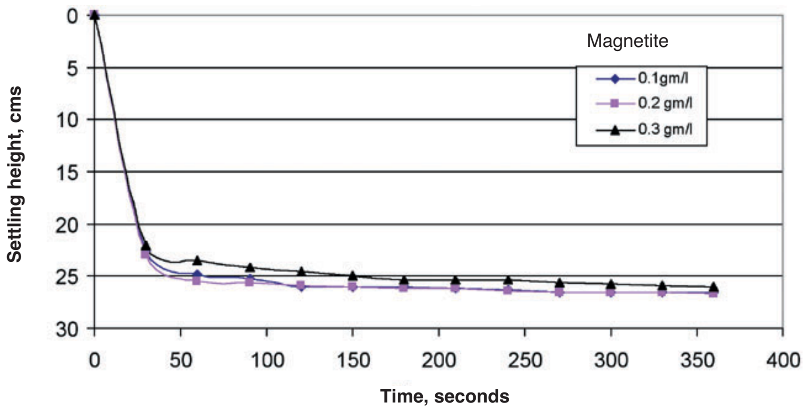

Figure 7—Effect of fine magnetite with spectrum (1.2 mg/ℓ) at natural pH

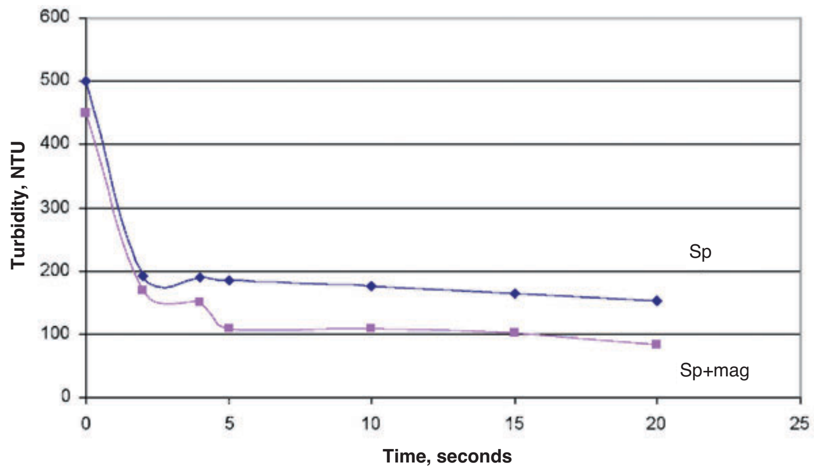

Figure 8—Effect of the addition of flocculant and magnetite on the turbidity of Kedla process water

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References

1. SINGH, G. and GUPTA, R.K. Coal-cleaning, pollution abatement-Water pollution, *Trans. Inst. of Mining & Metallurgy*, vol. 109, no. 3, 2000. pp. C141–144.
2. SABAH, E., YÜZER, H., and ÇELIK, M.S. Characterization and dewatering of fine coal tailings by dual-flocculant systems, *Int. J. Miner. Processing*, vol. 74, 2004. pp. 303–315.
3. SABAH, E. and CENGIZ, I. An evaluation procedure for flocculation of coal preparation plant tailings, *Water Research*, vol. 38, no. 6, 2004. pp. 1542–1549.
4. ANGLE CHANDRA, W, SMITH-PALMER, T., and WENTZELL BYRON, R. The effect of cationic polymers on flocculation of coal thickener feed in washery water as a function of pH, J. *Appl Polym Sci*. vol. 64, no. 4, 1997. pp. 783-789.
5. CLAYTON, R. C., NADEBAUM, P.R., PRIESTLY A.J., and TRUMAN, A.H. Solids Separation Processes, *Ichem. E Symp*, 59, 1980. 8:3/1- 8:3/28.
6. RATH,, B., PRAKASH, S., DAS, B., BISWAL, S.K., REDDY P.S.R., and ROHELLA, R.S. Potable water treatment using synthetic polyelectrolytes with magnetic particles. J. *Surface Sci, Technol*., vol. 13, (2-4), 1997. pp. 220–228.
7. PRAKASH, S., DAS, B., MOHANTY, J. K., and VENUGOPAL, R. The recovery of fine iron minerals from quartz and corundum mixture using selective magnetic coating. *Int. J. Miner. Processing*, vol. 57, 1999,. pp. 87–103.
8. PARSONAGE, P. *et al*. Depressant function in flotation of calcite, apatite and dolomite. In: Jones, M.J., Obalattr (eds.), *Reagents in Mineral Industry*, London, IMM, 1984. pp. 33–40.
9. NOH, A.J. Magnetic beneficiation of clays using magnetic particulates. US patent, 1978. 4125460.
10. NOH, A.J. and PRICE, W.M. Magnetic beneficiation of clays using magnetic particulates. US Patent, 4125460. 1981.
11. DAS, B., BISWAL, S.K., PRAKASH, S., REDDY, P.S.R., and SASTRI, S.R.S. Electrokinetics and X-ray diffraction studies on coal and associated ash from Talcher Coalfield, *International Conference on Challenges in Coal and Mineral Beneficiation*, ISM, Dhanbad, Dec. 7–8th, 2001. ◆