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An apprisal of arsenic in Indian coal, propensity of arsenic pollution from coal fired power plants and suggested remedies

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A potential source of arsenic mobilization in water was chosen to be examined and it is none other than solid residue of coal generated from thermal power generating installations. Sheer magnitude of coal being put into use for meeting growing energy demand and the presence of arsenic in the coal matrix and its subsequent enrichment in the solid residue following combustion merits serious attention. This paper examines an overall view of the arsenic level (0.1-23 ppm) in Indian coal and lignites across its geographical range which is significantly less compared to what as encountered in western variety (0.5 – 80 ppm). But this offers little comfort, simply because, steam coal fed into the thermal power generation units is significantly high in ash to generate colossal quantity of fly ash with enriched arsenic to offset that advantage of lower arsenic concentration in Indian coal. Washability study reveal that Arsenic is mainly concentrated in inorganic phase in coal and therefore is vulnerable to mobilization from the ash-dumping zone to the ground water beneath soil and other nearby water bodies. Fly ash leachate study also indicate that mobilization of arsenic from the fly ash pond is favoured at the neutral media close to *p*H 7. This establishes further that with the onset of monsoon the probability of ash pond being flushed with rainwater may contaminate the adjoining areas more extensively. To obviate such possibilities, deshaling of coal prior to combustion, and/or simple chemical treatment protocol of contaminated water as substantiated by removal kinetics have been suggested.

Industrial coal may be identified as one of the concerning source for arsenic mobilization in water and soil. It is relevant to mention here that the damaging effects of priority trace elements in general and arsenic in particular through coal residues have long been identified. Lignite deposits in Czechoslovakia having arsenic concentration as high as 900-1500 ppm when put into use for electric power generation have had its damaging impact. Bencko *et al.*[1] reported an increased arsenic level in hair, urine and blood associated with progressive audibility loss to complete deafness for a group of children living within 5 km radius around the power plant. Further, pastureland around the power plant get loaded with arsenic to such an alarming level that contaminate even the milk of cows.

Historically, it was Simmerbach[2] who reported the presence of arsenic in coal as early as in 1917. Later many other investigators studied the arsenic content of coal and coal ash which had been compiled by Abernethy and Gibson[3]. A rather comprehensive report on trace elements in coal given by Swaine[4] indicates that arsenic occurs in coal as arsenical pyrite and arseno pyrite (FeAsS). This view of occurrence of arsenic in coal stood the scrutiny of Higgins *et al.*[5] and Helble *et al.*[6] who extended their work even in the cases of coal having arsenic level as low as 10 ppm by the application of XAFS spectroscopy and SEM respectively. They further observed that regardless of the original forms of arsenic as occur in coal, all are oxidized to arsenate (AsO_4^{3-}) during combustion[6] and the lethal potency of this oxidized product is quite substantial. Arsenic of original coal on combustion gets partitioned mostly in fly ash and rest in bottom ash. The mobility and fate of arsenate in the ash basin sediments is very concerning as it may contaminate the surrounding water bodies as well as underground water by long term leaching over the years. The Indian coal has very high ash content (30-50%); the annual production of fly ash was estimated at more than 40 million metric tons and this is expected to increase to about 120 million metric tons by 1999-2000[7]. This enormous production scale of fly ash merits attention as the problem of contamination of water bodies adjacent to ash dumping zones needs be addressed properly. Workers[8-12] undertook coal ash leaching studies observed that leachates from waste disposal sites are the potential source of ground water

Table 1—Statistical distribution of arsenic in Gondwana and Tartiary coal and lignite

Coal fields	Ash range (%)	Conc.Range (ppm)	Arithmetic mean	Geometric mean	Standard deviation	No. of samples
1.Gondwana Coals						
Damodar –Koel Valley	12.7-47.6	0.32-22.2	9.26	3.05	5.01	50
Son –Rihand Mahanadi Valley	12.5-45.9	0.10-23.0	3.79	1.59	5.25	26
Pench Kanhan Tawa Valley	29.9-36.9	0.60-6.4	3.34	2.64	2.03	11
Wardha Godavari Valley	16.4-42.3	0.22-6.5	2.18	1.63	1.75	12
2.Tertiary Coals	4.1-21.2	2.0-11.0	5.83	5.02	3.07	12
3.Tertiary Lignites	3.2-53.6	2.0-22.0	8.37	6.04	6.76	12

Table 2—General characteristics of power coal

	Range	Average
1. Proximate Analysis		
Ash %	30-45	38
Moisture %	1-5	1.5
V. M. %	22-28	24
F. C. %	35-40	37
C. V. Kcal/Kg	3500-4500	4000
2. Ash Composition		
Elemental oxide %		
SiO_2	55-65	58
Al_2O_3	25-30	28
Fe_2O_3	3-10	7
CaO	2-4	2.5
MgO	1-3	2
TiO_2	1-2	1.5
Na_2O	0.8-2.5	1.6
K_2O	0.8-2.5	1.6
P_2O_5	0.1-0.8	0.4
SO_3	0.15-1.0	0.3

contamination. This study attempts to systematically characterize the arsenic content and their mode of occurrence in Indian coal which are mainly fed into power plants covering geographical range of four main coal basins. This investigation further suggests that substantial reduction of arsenic level in the impounded ash may be effected by deshaling of coal prior to combustion. The remedy suggested to prevent or reduce arsenic contamination from the ash impounding zones is cost-effective as well.

Experimental Procedure

Analytical method used was atomic absorption spectrophotometry. In atomic absorption spectrophotometric analysis, the sample solutions were prepared by dissolving 0.25 g of low temperature (450°C) ash in pressure dissolution vessel maintained at 160°C for an hour. Low temperature ashing as chosen at 450°C just ensures to retain arsenic as present in coal, thereby, volatilization loss is avoided. The principal solvent used was a mixture of hydrofluoric, hydrochloric and nitric acid. Boric acid was added to neutralize the excess of hydrofluoric acid and to ensure the dissolution of the precipitated fluorides[13-15]. A second heating step was adopted in each case of dissolution to convert fluorides to fluoroborates completely in order to improve the efficiency of dissolution. A Philips PU 9360 continuous hydride vapor generation system linked to a Pye Unicam SP 2900 atomic absorption spectrophotometer was used for arsenic estimation. Sodium borohydride was used as a reducing agent in all cases as it was found more effective in terms of speed and efficiency of reduction of the metal in sample solution. Concentration of arsenic was determined from the calibration curve drawn for the metal in the appropriate wavelength (193.7 nm) with simulated synthetic standard containing interfering trace metals for hydride generation[15,16].

Results and Discussion

Coal continues to and shall remain the major source of energy in India. The total coal reserve in the country is over 202 billion tonnes of which more than 97 percent is located in the Gondwana Region[17,18]. The major coal reserves are situated in the South Eastern quadrant of the country, which covers the state West Bengal, Bihar, Orissa and Eastern Madhya Pradesh. Besides, some tertiary coal and lignite deposit are located in north eastern region (Assam) and Jammu & Kashmir respectively. Table 1 depicts the statistical data on arsenic content comprising range, arithmetic mean, geometric mean and standard deviation value for coal samples drawn from almost all the major working coalfields and lignite deposits in India. It is apparent from the table that the concentration range varies from 0.1-23.0 ppm in case of coals drawn from Son Rihand Mahanadi Valley and 0.32-22.2 ppm in case of Damodar Koel Valley whereas a comparatively lower range of values 0.22-6.5 ppm is observed for Pench Kanhan Tawa and Wardha Valley coal deposits. The arsenic concentration varies be-

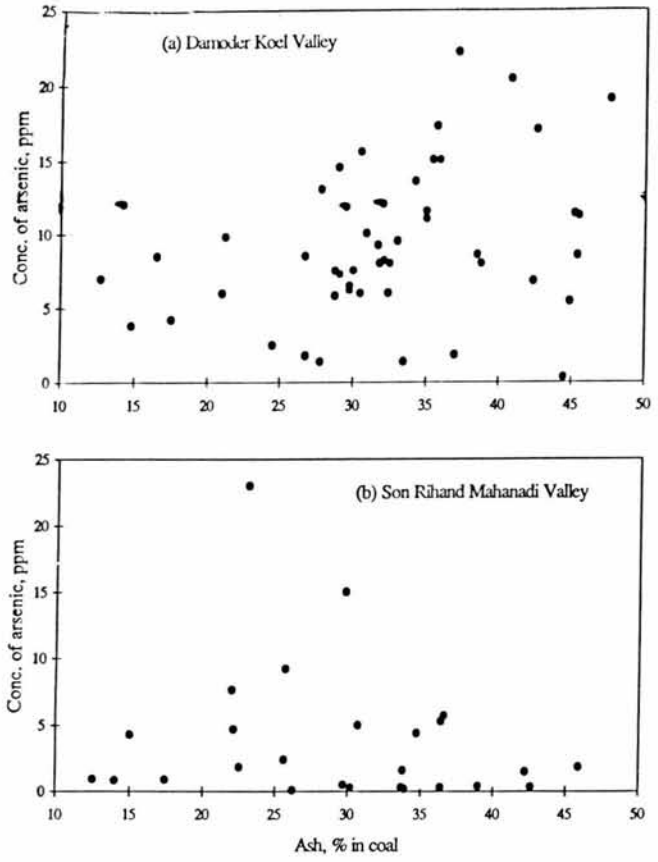

Fig. 1—Variation of arsenic concentration with ash content in—(a) Damoder Koel Valley and (b) Son Rihand Mahanadi Valley.

tween 2.0 to 22.0 ppm in case of tertiary coals and tertiary lignites. An attempt to correlate the ash percentage of coal with arsenic (ppm) in Damador Keol and Rihand Mahanadi Valley distribution is destined to be elusive is well established from Fig. 1.

The lower arsenic content in the Indian coal in comparison to Western coals[19,20] (0.5 to 80.0 ppm) cannot be attributed specifically but considering arsenic association with arsenopyrite, it may be argued that sulphur as well as phosphorous content in Indian coal[16] being significantly lower than most other foreign coals[4,18], a lower arsenic concentration in Indian coal may find logical explanation.

It is accepted that trace elements in coal could be associated with either the mineral matter or the organic parts of the coal. Therefore, cleaning of coal[21] could be an important pollution abatement measure prior to combustion. Washability curves and histogram of washability data are effective means of depicting the mode of combination of trace elements including arsenic in coal; they indicate, whether the elements are associated with the organic or inorganic

Table 3—Arsenic distribution in coal fields of Damodar Koel Valley

Coal fields	Ash range (%)	Conc. range (ppm)	Arithmetic mean
Raniganj	15-20	2.5-6.9	5.0
Jharia	18-35	7.5-20.4	12.7
East Bokaro	15-28	6.0-24.0	12.9
West Bokaro	15-22	1.4-8.5	8.0
North Karanpura	20-35	12.0-14.0	13.0
South Karanpura	15-30	4.2-7.5	6.2
Rajmahal	20-45	10.0-20.0	16.3
Ramgarh	18-30	1.4-19.0	16.5
Auranga	13-21	5.4-15.5	10.8

fractions of coal. In this study, arsenic removal efficiency by physical cleaning method was examined. Washability curve and histogram for arsenic along with ash percentage as determined for Kalakot, Talcher as well as for Nichom lignite are shown in Fig. 2, the positive slope of the washability curve indicates that arsenic is concentrated in the inorganic fraction (mineral matter) while distribution patterns of arsenic are well discernible from the corresponding histogram. The results of the reduction of arsenic along with ash content of coal from different coalfields on deshaling at specific gravity 1.8 is shown in Table 5. In general a specific gravity cut at 1.5 separates mostly inorganic forms of sulphur and since arsenic is normally associated with pyritic sulphur, a specific gravity cut at 1.8 (deshaling) was chosen because at this cut most of the pyritic sulphur as well as shaly matter get separated. The findings also suggest that arsenic is mainly in inorganic association and therefore by simple deshaling its concentrations in coal prior to its utilization can be reduced to some significant extent.

It is mainly power coal drawn from Damodar Valley basin which is linked to various power plants located in the eastern part of the country used for combustion were selected for further study. The quality of these coals in general is decidedly inferior because of its high ash content varying between 30-45% with dirt band eliminated. The general characteristics of power coal is presented in Table 2. The emphasis on power coal seeks to justify the path ways[20,22] of arsenic which in essence contaminate air, water and soil simultaneously. Arsenic load in coal sample from different coalfields in Damodar-Koel Valley basin is given in Table 3. Distribution of Arsenic from feed coal in solid waste as discharged from power plant

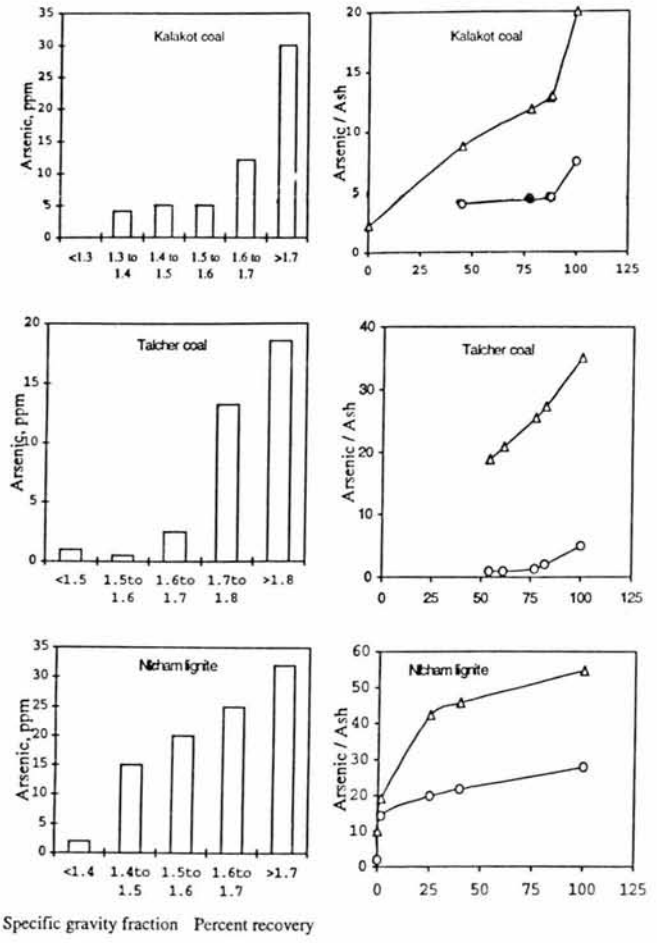

Fig. 2—Histogram and washability curve of arsenic.
Left—Histogram of arsenic for specific gravity fractions.
Right—Washability curve, -O- arsenic, ppm; -Δ- ash, % against percent recovery

situated in the eastern region of India has been shown in Table 4. It is apparent from the table that the redistribution of arsenic occurs following combustion and it is shared by both bottom ash and fly ash, the larger portion of arsenic is redistributed in the fly ash. As a matter of fact, feed coal to power plants normally represents a composite of power coals drawn from various mines contributing complexity in the above coals. Regardless of the distribution pattern of arsenic, bottom ash and fly ash together are disposed in the same ash pond or disposal area and the contamination from this source is a distinct possibility[23]. Arsenic discharge in tonnes per annum as depicted in Table 4 brings into focus the magnitude of this problem. The absolute amount of arsenic has been computed assuming installed capacity of power generation in respective plants.

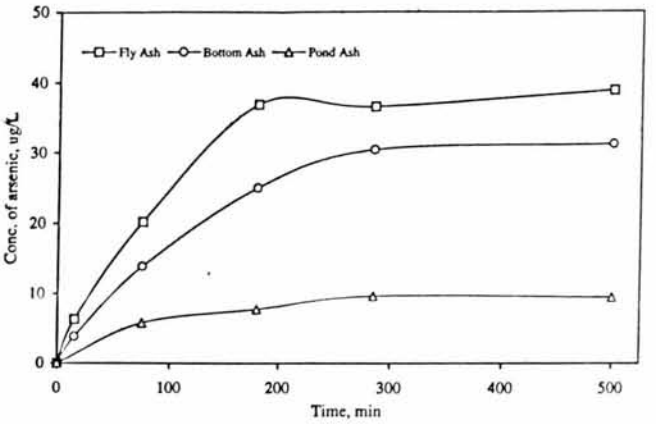

Fig. 3—Kinetics of leachability of arsenic from fly ash, bottom ash and pond ash

Kinetics of arsenic leachability from fly ash, bottom ash and pond ash

The leachability behaviours of coal ash residue as studied by Dressen *et al.*[8], Theis and Wirth[9], and Kuryk *et al.*[12], indicate that *p*H of the medium and solid/liquid ratio are the prime controlling factors for releasing metal ion from the waste solid. But the metalloid arsenic solubility in aqueous medium is quite different. Thermodynamic calculations suggest that As^{5+}(aq) ($HAsO_4^{2-}$ > $H_2AsO_4^-$ at *p*H 7) are more abundant in aqueous oxic condition and As^{3+}(aq) ($HAsO_2^0$ = $H_3AsO_3^0$ > AsO_2^- = $H_2AsO_3^-$ at *p*H 7) in anoxic condition. The chemistry of arsenic is further complicated as it undergoes with solid phase interaction, coprecipitation, adsorption and desorption as well as acid base reaction. Such complicated behaviours of arsenic at solid/liquid interface still remain ambiguous. Field observation suggest that release of arsenic from discrete coal ash particles occurs very slowly (Fig. 3) which may be due to different chemical composition of the waste solids (Table 7).

Assessment of leaching behaviour by Shake test

A definite quantity of solid residue ranging from 5–30 g of sample drawn from Chandrapura TPP (Thermal Power Plant) were mixed with measured volume of leaching medium at three different *p*H and were subjected to shake test. The experiments were conducted under constant shaking condition at room temperature (27°C) using mechanical shaker/vibrator for a period of 24 h with varying solid/liquid ratio. The ratio of the solid residue and leaching media was so adjusted that the possible settling effect could be avoided. The *p*H of the leaching media in this study

Table 4—Arsenic distribution and discharge from power plants situated in Eastern part of India

Name of the power Station with capacity	Ash %	Ash discharged (t/day)	Arsenic Concentration (ppm)			Arsenic discharged (t/annum)
			Feed coal	Bottom ash	Fly ash	
Chandrapura (780)	42.4	3307	10	13	17	12.07
Patratu (840)	38.5	3234	8	11	12.5	9.44
Bokaro (240)	36.7	880	11	12	25	3.53
Durgapur DVC(475)	41.4	1962	12	30	40	8.59
Farakka (2100)	37.0	7770	7	5	8	19.85

Table 5—Reduction of arsenic vis-a-vis ash on deshaling

Coal	Raw coal		Deshaled Raw coal		Percent removed	
	Ash %	As (ppm)	Ash %	As (ppm)	Ash %	As (ppm)
Piparwar OCP Central C.F.	44.5	0.32	37.1	0.18	16.6	43.8
Durgapur OCP Chandrapura Area WCL	24.2	0.22	23.3	0.11	3.70	50.0
Dipka OCP Korba C.F.	42.6	0.34	30.0	0.26	29.6	23.5
Jagannath Coal Talcher C.F.	36.4	0.15	30.9	0.08	15.1	46.7

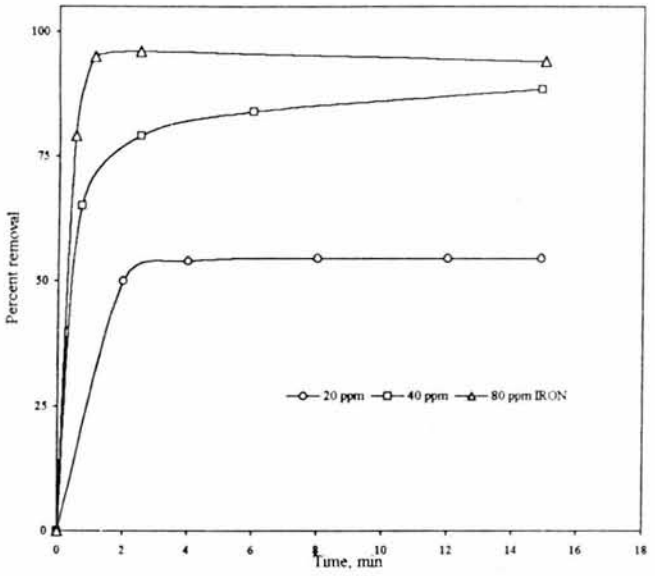

Fig. 4—Removal kinetics of arsenic from fly-ash leachate (arsenic conc. 20 µg/L)

was maintained at 3.0, 6.5 and 10.5 so as to examine the effect of *p*H on leaching pattern.

The results of shake test as shown in Table 6 indicate that the order of arsenic release increase with increasing solvent flux. It may be noted that the percent of arsenic release is maximum when the ash/solvent ratio is 1:150 at *p*H 6.5 whereas such release of arsenic is significantly low when ratio is 1:10 at *p*H 10. The reason may be attributed to the fact that at the higher solid/solvent ratio generating higher ionic strength hinders further release of soluble arsenic from the mass of the solid. This observation may lead to the conclusion that the seasonal variation of ash/water ratio in ash impoundment zone is likely to influence the leaching rate.

Table 6—Leachability assessment of fly ash, bottom ash and pond ash from chandrapura T.P.S. by Shake test

Sample	Conc. (ppm)	Solid water ratio	Percent of metal released		
			*p*H		
			3.0	6.5	10.6
Fly ash (As)	17.0	1:150		9.0	
		1:75		6.5	
		1:35		5.6	
		1:25		5.0	
		1:10	2.5	4.2	1.0
Bottom ash (As)	12.0	1:10	1.9	4.5	1.2
Pond ash (As)	8.4	1:10	0.5	2.4	1.5

The effect of *p*H on the leachability of arsenic, indicates that the most favorable *p*H for maximum release of arsenic ion is at the neutral region of the *p*H scale.

Kinetics of leachabilty

A set of five stopper conical flasks each containing 5 g of pretreated ash sample in 200 ml of water as leaching media (*p*H 6.5) was stirred by magnetic stirrer (300 rpm) and the sample so obtained at various time intervals were determined for arsenic content of the solution by AAS technique. The concentration of arsenic in leaching media verses time curve represents the kinetics of leachability as has been shown in

Table 7—Chemical composition of fly ash, bottom ash and pond ash sample from Chandrapura Thermal Power Station

% Constituents	Fly ash	Bottom ash	Pond ash
SiO_2	62.85	61.2	63.32
Al_2O_3	22.29	17.66	18.54
Fe_2O_3	5.37	9.88	10.12
TiO_2	1.63	1.10	1.09
P_2O_5	0.21	0.21	0.40
SO_3	0.39	0.16	0.64
CaO	3.26	2.90	3.28
MgO	1.11	0.60	0.66
Na_2O	1.23	1.15	0.92
K_2O	0.46	0.47	0.38

Fig. 3. The figure shows that the rate of release of arsenic, increases steadily and subsequently equilibriate after certain time; in the case of fly ash and bottom ash this time lag is 180 and 285 min respectively where as the pond ash follows the same pattern with pronounced sluggishness. The observed differential rate factor for the attainment of equilibrium may be due to different chemical and physical form of arsenic in association with discrete particulate phases formed at high temperature in the combustion zone[22,24,25]. The pond ash, it may be noted, may be looked upon as an composite of both i.e. fly ash and bottom ash and may have already suffered depletion of arsenic through leaching prior to sampling. In general, the trend indicates that slow release of leachable arsenic may continue over decades to contaminate the water bodies beneath and surface alike.

Removal kinetics of arsenic

A variety of treatment processes have been tried for arsenic removal from wastewater. The most commonly used technologies include coprecipitation and adsorption onto coagulated floc, lime softening, sulphide precipitation, adsorption onto activated alumina, carbon and humic acid residue etc[26-28]. The ferric salt treatment was proved to be more effective than other conventional methods[22,25] and was, therefore, adopted in this study.

Removal kinetics of arsenic from leachate were conducted in laboratory scale. To a volume of 200 mL of arsenic laden (20 µg/L) leachate solutions, ferric salt in varying concentration (20, 40, 80 mg/L) were added in a stirring condition using magnetic stirrer maintaining temperature 27°C. The solid coagulant flocs of $Fe(OH)_3$ was formed when the mixture was brought to *p*H 6.5 by adding dilute NaOH solution. The arsenic as present in the forms of dissociated oxy-arsenic acids were coprecipitated. The variations of arsenic concentrations with time were determined by isolation of aliquot portion of the mixture separating after filtration. The equilibrium concentrations of the reaction mixture were determined from the rest of the solution after allowing sufficient time to reach the concentration of arsenic at constant value. Removed percent of arsenic was plotted against time axis as represented in Fig. 4. It is well discernible from the figure that acid - base reaction are responsible for arsenic removal as reflected in the sharp rise of the curve and obviously this reaction is almost instantaneous to be completed within two minutes to reach terminal concentration.

Among the three iron dosage applied, the kinetic profile suggest that 80 ppm dose is quite effective, and simultaneously ensures almost complete removal of arsenic. Whereas the 20 ppm one is unable to remove beyond 50% of the arsenic load, therefore, inadequate, while the intermediate dosage, i.e., 40 ppm iron concentration is fairly effective to remove arsenic to render the waste acceptable to the prescribed norms and perhaps economically viable. The stage of addition of iron salt needs to be worked out which largely depends on the provision for interpond treatment plant, alternatively iron salt may be added at fly ash sluicing zone itself.

Conclusions

(i) The study indicate that concentration range of arsenic content of Indian coal varies with geographical depositions and no correlation can be drawn with coal type and the ash content.

(ii) The arsenic in Indian coals is mostly associated with inorganic fraction (mineral matter) of coal. It has been suggested that simple physical treatment by deshaling of raw coal arsenic concentration can be minimized substantially in the solid waste generated from power plants.

(iii) The effect of *p*H on the leachability of arsenic from solid waste of power plants reveals that most favourable *p*H for maximum release of metal is in at the neutral region and at higher solvent flux. This study leads to conclude that maximum release of arsenic from ash dumping zone might occur during rainy season.

(iv) The slow release of leachable arsenic as evidenced from kinatics of leachability indicates that

leaching of this toxic metal from the ash impounding area may continue for decades.

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