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Short communication

Extent of lead in high sulphur Assam coals

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Abstract

This study has been undertaken to understand the precise nature of association of lead in high sulphur Assam coal. Sequential extraction of lead with ammonium acetate, HCl and RuCl₃ solutions have been carried out. RuCl₃ has been used as a suitable reagent for the extraction of lead. It is found that treatment of sample with CCl₄ increases the extraction of lead by RuCl₃ solution. The amount of lead in the coal studied varies between 43.2 and 50.4ppm. It has been found that lead is predominantly occurring in coals in association with organic matter and needs concerted attention to understand its bio-availability. The chemical principles involved therein are also discussed.

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Environmental awareness has focused studies on the sources of hazardous elements in nature and their source reduction. Combustion of coals in various industrial processes release ash, which contains various metals, especially the toxic metals, and has been a great concern for a long time. Lead is one of such metals, which causes health hazards to a considerable extent. In view of the importance of the metal, some works need to be carried out on the mineral matter of the coal.

The sources of lead have a profound influence on the association of the metal in coal. Seawater contains very low concentration (0.002–0.03 ppb) of lead [1] and, therefore, this

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source cannot supply high amount of lead occurring in coal. The occurrence of 8–20 ppm of lead in peat-forming environments [2] has led us to believe that surface water [3] (and to a certain extent, ground water) is the main source of lead to the early stages of coal formation, i.e., peat-bog. Weathering of rocks, oxidation of lead minerals [1], etc., are the plausible ways by which the metal can be mobilised. Therefore, it is important to know how the metal is associated with the coal mass.

Lead, being an element belonging to the third transition series of the periodic table, may act as good electrophile for reactions with numerous nucleophiles and can even form multinuclear compounds. The organic matters are known to have many unfilled sites and these can interact with lead at the peat-bog stage, resulting in the formation of ion-exchangeable, non-exchangeable and chelate compounds. In some cases, they might undergo redox reactions with the organic matter. On the other hand, the common valence state of lead (divalent lead) is a borderline acid in Pearson's hard–soft acids and bases, and, therefore, it has a tendency to react with either hard or soft bases. In reducing environments, soft bases such as sulphur containing ligands could form covalent bonds with lead forming lead sulphides or the metal could be associated with sulphide minerals. The occurrence of galena (PbS) in most coals [4] and the association of lead in pyrite [5,6] further supports our contention. Moreover, formation of organic bound Pb–S compounds is also not unlikely. As no work seems to have been carried out on the nature of association of lead in high sulphur Assam coals, the following series of experiments have been undertaken.

Three high sulphur coal samples obtained from Tirap, Tikak and Baragolai collieries of the Makum coal field ($27^{\circ}16'–27^{\circ}18'N$ and $95^{\circ}43'–95^{\circ}55'E$), Assam (India) were taken for the study. The samples were ground to size 72 BS. The carbon and sulphur contents of the samples are given in Table 1.

The method used for the extraction of gold from coal [7] is used here for the leaching of lead. Lead was sequentially extracted from 0.5 g coal by 20 ml 1 M ammonium acetate solution at 25 °C for 1 h followed by 20 ml 1 M HCl with constant stirring. The residue was treated with CCl_4 to remove minerals by gravity separation. However, the extent of removal of mineral matter by such treatment from coal is not precisely known, but the sample obtained after such treatment is considered here as the mineral free sample for our study. The residue was further treated with 20 ml 0.01 M $RuCl_3$ solution at 80 °C for 1 h to extract the metal. The residue after $RuCl_3$ treatment was made to ash by heating at 750 °C

Table 1
Elemental composition and chemical fractionation of lead in Assam coals

No.	Coal sample	Carbon ^a (wt.%)	Sulphur ^a (wt.%)	Ammonium acetate extract (ppm)	HCl extract (ppm)	RuCl ₃ extract of	Ash after RuCl ₃ extract of
						Mineral free sample (ppm)	Mineral free sample (ppm)
1	Tirap coal	75.5	7.7	ND	ND	50.4	ND
2	Tikak coal	72.7	5.2	ND	ND	43.4	ND
3	Baragolai coal	73.3	6.4	ND	ND	43.2	ND

ND=not detected (<1 µg/g).

^a As received basis.

for 1 h. The ash was dissolved in a mixture containing HNO_3 , HF and HClO_4 taken in a Teflon bomb and heated at $120\text{ }^\circ\text{C}$ for 1 h. Finally, the mixture was treated with H_3BO_3 solution. Lead in each of the fractions was determined repetitively by using a Perkin-Elmer (Model: 2380) Atomic Absorption Spectrophotometer with detection limit $1\text{ }\mu\text{g/g}$ and the average values of replicate analysis are used for the present study.

The chemical fractionation procedure involves leaching of ion-exchangeable cations by 1 M ammonium acetate solution and the same sample on subsequent extraction with 1 M HCl removes coordinated species (non-exchangeable) [8,9] and acid soluble carbonates and oxides [8]. Table 1 shows the amount of lead extracted by different reagents. On leaching with ammonium acetate solution, the metal was not detected signifying that lead is not present in all the coals in ion-exchangeable form. This may be ascribed to the fact that very high concentration and also preferential uptake of other metals might have occupied the exchangeable positions in the organic matter and as a result lead was unable to form exchangeable species. Moreover, extraction with HCl could not show the presence of metal (Table 1). This reveals that HCl was unable to leach the metal associated with either mineral or organic matter.

In order to get a precise information on the nature of association of the lead, the mineral free sample was treated with RuCl_3 solution where a higher amount of lead was observed to be leached out in all the coals. It is apparent that the lead is predominantly associated with organic matter as non-exchangeable or chelate form. However, at this stage, it is not clear about the extent of extraction of lead by RuCl_3 solution from the residue.

The RuCl_3 treated samples were made to ash; however, presence of lead was not observed in them. Absence of the lead in ash suggests that a certain amount of metal might have volatilised away at the temperature at which ash was made. A question still remains as to which form of the metal, mineral or organic bound, might have removed during ashing. As the mineral bound lead is converted to oxides during ashing, these cannot be volatilised away easily. Therefore, occurrence of organic bound lead is most likely in coals under study.

The formation of polynuclear complex may be significant for the divalent cations of the transition metals in approximately neutral solution [10]. At pHs well below 7, divalent lead simply exists as $\text{Pb}_{\text{aq}}^{2+}$ while in alkaline solution it is precipitated as the sparingly soluble hydroxide, $\text{Pb}(\text{OH})_2$, a number of polynuclear hydroxo lead cations have been formed [10]. In the change of acidic to neutral pH, Pb is transferred sequentially as: $[\text{Pb}(\text{OH})_2]^+$, $[\text{Pb}_2(\text{OH})]^{3+}$, $[\text{Pb}_3(\text{OH})_4]^{2+}$, $[\text{Pb}_4(\text{OH})_4]^{4+}$ and $[\text{Pb}_6(\text{OH})_8]^{4+}$. In alkaline medium precipitation of $\text{Pb}(\text{OH})_2$ occurs and on further increase of pH, plumbites are formed.

As the peat stage has near neutral pH, it seems likely that there will be considerable concentration of polynuclear hydroxo cations of lead. The cations, being very reactive [11], can immediately react with organic matter resulting in the formation of very stable complex compounds. This is due to the fact that the polynuclear hydroxo lead cations exists as hydroxo bridged species (which occurs as gel) and when these species interact with the organic matter (occurs as colloid) a complicated structure of non-exchangeable lead should be formed because of colloid–colloid interaction. This complicated structure had been transformed into still more complex networks during the coalification process controlled by temperature and pressure. On treatment with either ammonium acetate

solution or dilute HCl, leaching of lead is not possible and this could be the reason why we did not get lead in the extracts with these reagents. On the other hand, on treatment with RuCl_3 solution, Ru^{3+} ion, being an oxidant, can oxidise divalent lead to higher oxidation state and as a result, the structure of the polynuclear hydroxo-organic matter network is susceptible to break due to involvement of electron transfer process. Again, the RuCl_3 solution is acidic, therefore, leaching of lead by this reagent is quite possible. This could be the reason for the extraction of lead by RuCl_3 solution.

The Clarke value [12] of distribution of elements in the earth crust for lead is 12.5 ppm. Lead level for Tirap coal is four times higher, whereas its level is three times higher in Tikak and Baragolai coals than the Clarke value. As the occurrence of galena in Assam coals has not been known to us, the presence of lead in minerals is very negligible. We may conclude that (a) lead is predominantly occurring in high sulphur Assam coals, studied here, in association with organic matter, and (b) RuCl_3 is a suitable reagent for the extraction of lead. If the major fraction of lead is associated with organic matter contents as observed from the present study, the bioavailability of metals in an environment under changing pH and Eh conditions need concerted attention. However, Fe–Mn oxide and organic matter fractions sometimes shows scavenging effect and act as sink for retention of toxic heavy metals in natural environment.

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