Total Chlorine in Pakistani Coals

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Introduction

Indigenous coal resources would play a more dominant role in the future to supply the energy needs of Pakistan. Coal fired power plants will be established to increase the share of coal in power generation to 280MW capacity upto 1993 [1] from presently negligible share.

Increased coal combustion in the country could cause environmental pollution, therefore, it is necessary to determine various trace elements in Pakistani coals to study the effects of their mobilization on coal combustion. As a part of our continuing programme to determine trace elments in Pakistani coals, total chlorine was determined in coal sample from various Pakistani's mines and the results are reported here. To the best of our knowledge, chlorine contents of Pakistani coals have not been reported earlier.

Results and Discussion

Most of the chlorine appears to have been deposited in the coal from associated ground waters and may be present mainly in the ionic form [4]. There is a stoichiometric imbalance of sodium to chloride ratio, therefore, chlorine in coal can not be totally halite (crystalline sodium chloride). A study of Illinois coals using neutron activation analyses indicated that chloride ions were weakly held on the organic material [5]. Some of the chlorine may be covalently bonded to organic molecules in coal [4]. The present study reports total chlorine content in Pakistani coal and ionic and covalently bonded organic chlorine were not determined separately.

Total chlorine and analyses of Pakistani coals are shown in Table 1. The chlorine contents varied from 155-1936.6 ppm in these samples. The lowest amount of chlorine (155.0 ppm) was found in Makerwal coal while the highest quantity of chlorine (1936.6 ppm) was found in kotli coal. Contents of chlorine in Punjab coals were low while the Sindh coals had comparatively higher chlorine concentrations. Chlorine contents in Sindh coals were close to world wide average (1000 ppm) [6a] while

Table 1: Chlorine contents and analyses of various samples from Pakistani coal mines.

S.No.	Sample Source	Total Chlorine content as Chloride (ppm)	Moisture. %	Ash. %	Volatile Matter. %	Fixed Carbon. %	Total Sulphur. %	Calorific Value BTU/Lb.
1.	Jhampir	1230.2	20.7	6.43	43.64	29.23	2.34	9,525
2.	Khoshab	385.4	6.2	16.8	39.66	37.34	3.21	9,190
3.	Katli	1936.6	8.6	5.91	44.62	38.87	3.34	11,600
4.	Lakhra	1230.0	9.56	9.08	42.48	38.88	4.84	10,205
5.	Makerwal	155.0	3.73	22.32	38.31	35.64	7.04	9,250
6.	Sharigh	790.0	7.66	5.65	42.41	44.28	1.65	10,445
7.	Sonda	1391.6	8.93	6.81	45.64	42.4	3.1	10,270
8.	Sor Range	340.4	9.03	6.74	39.77	44.64	2.37	10,950
9.	U.S. Average*	1000						
10.	Worldwide average*	207						
11.	Western U.S. Coal**	100-1300						
12.	Eastern U.S. Coals**	100-8000						
13.	Illinois basin**	100-5400						

*from [6a], **from [6b]

Punjab coals were close to the U.S. average (207 ppm) [6a]. The Pakistani coals were similar to western U.S. coals (100-1300 ppm) in chlorine contents [6b].

High concentrations of chlorine in coal in excess of 1500 ppm, cause corrosion of power station super heater tubes and chloride may form a glaze on the refractory linings thus damaging the brick work of coke ovens and gas retorts [7]. All the analysed Pakistani coals except kotli coal contain less than 1500 ppm chlorine indicating that combustion of these coals would not cause corrosion of the equipments due to the presence of chlorine in these coals.

A correlation appears to exist between chloride and volatile matter in Pakistani coals as chlorine contents increase, generally, with increase in volatile matter contents indicating association of chlorine with the organic matter in these coals. High chlorine values are known to be associated with high volatile bituminous coals [7]. A significant fraction (20-50%), of the Illinois coal chlorine is soluble in water and lightly bounded to the coal structure and is released quickly to the gas phase during combustion. The remainder of the chlorine is bound to the organic structure and is released at the carbon conversion rate [5].

Fresh water flushing of the coal generally reduces chlorine content [6c] and leaching of chlorine from Illinois coal by boiling water improved from 20% to 50% by reducing the particle size from 50 μm to 25 μm respectively indicating the greater yield of chloride ions from coal by increasing the surface area directly in contact with water [5]. These observations indicate that water washings of coals can improve their quality by reducing their chloride contents. Kotli coal, containing high chlorine, can, therefore, be improved also by washing with water to reduce its chlorine content.

The analysed coal samples did not show, generally, chlorine contents much higher than U.S. and world averages therefore combustion of Pakistani coals, apparantly, would not cause any serious chlorine pollution of the environment.

Experimental

Representative coal samples were obtained from various mines in Pakistan. These included Makerwal, Khoshab and Sor-Range in Punjab, Sharigh in Baluchistan, Kotli in Azad Kashmir and Lakhra and Sonda mines in Sind province. These samples were air dried and ground to 60 mesh for analyses.

Proximate and sulphur analyses were carried out on LECO, MAC-400 proximate analyser and LECO, SC-132 sulphur determinator. Calorific values were determined on Perkin Elmer Paar oxygen adiabatic bomb calorimeter which was also used for digestion of coal samples for chlorine determinations.

All reagents were of analytical grade purity and deionized water was used for preparing solutions for the analyses. Standard solutions of silver

nitrate (0.01M), sodium chloride (0.1M) and 5% W/V potassium chromate were prepared by dissolving 1.7 g/l, 0.6 g/l and 5g/100 ml respectively of these salts in water.

Chlorine was determined by digestion of coal samples in paar oxygen bomb calorimeter and an aliquot of the digested samples solution was titrated with silver nitrate solution as shown by the following representative example.

Procedure, similar to ASTM method D-3261 [2], was followed. A tablet (1 g) was prepared from a powdered mixture of coal (75% W/W) and benzoic acid (25% W/W). The tablet was placed in a platinum crucible, filled with 10 ml water. A 10 cm. long fuse wire was tied across both the ends of the electrodes of the bomb so the wire touched the tablet on ignition. The bomb was covered and screwed air tight and then filled with oxygen gas to 35 atmospheric pressure. The bomb was then placed in a water filled vessel and then into paar oxygen bomb equipment which was switched on to fire the tablet. The melt was then dissolved in water and then diluted by water in a 100 ml volumetric flask upto the mark.

An aliquot (10 ml.) of the above digested sample solution was titrated against the standard 0.01M silver nitrate solution using 5% potassium chromate as indicator till a distinct faint reddish brown colour persisted [3]. The titration was repeated with blank solution. The chlorine contents (as given Table 1) were calculated as following.

1 ml of 0.1 M silver nitrate solution = 0.0003545 g/l Cl^-.

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