

## Effect of Leaching Time on the Removal of Lithophile Elements of Operational Concern from Coal Samples

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**Summary:** Results of a study to minimize the ash content in some Pakistani coals have been presented. Leaching of some coal samples with distilled water, hydrochloric acid, nitric acid and acid mixture has been performed for time duration of 0.5 hour and 2.0 hours. Effect of contact time was evaluated and extended time has been found to be effective for maximum leaching of Fe, Ca, Mg, Na, and K. Amongst the leachants employed, acid mixture proved more effective in removing significant amount of ash forming inorganic elements. Amongst the coals studied, inorganic elements were effectively leached from Shahriq and Makarwal samples.

### Introduction

The role of fossil fuels is well established in the energy market. The sources of energy are diversifying; oil and coal have been joined in succession by natural gas, nuclear power, and other types of fuel. However, fossil fuels still account for about 90 percent of the supply, and the share occupied by coal comes to about 27 percent. In the Asian region, just over 45 percent of the energy supply depends on coal.

The dependence of modern civilization on energy resources has created a shortage of petroleum-based oils; as a result the world energy sector has tilted towards the use of coal. Most of the world's electricity power plants are coal based. Due to low carbon hydrogen ratio and heteroatom contamination, as well as the presence of inorganic crystallites, coal does not burn smoothly and cleanly. The combustion of coal is therefore associated with noxious, odiferous, and sulfurous emissions. These emissions may be aerial, liquid effluents and solid wastes. The environmental problems may be worth if other means of utilization will not be available in the near future.

Emission of trace elements and noxious gases from coal-fired power plants has been reported [1,2] and their impact on terrestrial environment has been underlined by many workers [3-5]. Liquid effluents are mainly the processing water laden with condensates and some dissolved inorganics. If carelessly disposed, these may cause land and water pollution [6]. Ash content of coal has also been reported to cause many mechanical and operational problems of reactor clogging, scaling, fouling, and catalyst Passivation [7]. Their careless disposal may

cause land pollution. To achieve "noble use" of coal, researchers must strive for optimal utilization of coal in environment-friendly modes. Extensive research is underway world wide for minimizing ash content of the coal prior to its utilization [8-11]

In order to minimize the extent of these problems, it is imperative to clean coal prior to its utilization. The present work deals with the removal of some inorganic elements from coals by leaching with water, some acids, and their mixture. Focus has been made to study the effect of leaching time on the mineral depletion with either of these leachants

### Results and Discussion

Leaching time was varied in order to study the effect of contact time on effective removal of the metals under study. Leaching has been performed with H<sub>2</sub>O, HCl, HNO<sub>3</sub>, and their mixture for time duration of 0.5 and 2.0 hrs respectively. The very positive results obtained for some elements are presented here. Other elements like Cu, Mn and Zn were also studied, however some fluctuation in data, which might correspond to the sampling error as well as failure of the analytical method to give usable numbers, these metals are not included in the current discussion. The results are compiled in Tables 1-2. It can be seen that there is a marked effect of extension in time upon leaching particularly on coarse inorganic elements i.e. those that usually occur in fissures and cavities in the coal and are coarsely intergrown with it. For those metals that are often so finely intergrown with the coal, leaching is not effective in removing most of them. It can be

Table-1: Amount of Inorganic Elements ( $\mu\text{g/g}$ ) Leached with Different Leachants

Leachant	Coal sample	Cu	Mn	Zn	Fe	Ca+Mg	Na	K
Distilled Water	Makarwal	11	10	25	2220	3000	664	39
	Degari	10	13	13	2120	6000	935	49
	Shahrigh	14	106	24	7434	15000	1181	175
	Sor-Range	11	2	14	1950	16000	1556	39
Hydro chloric Acid	Makarwal	6.8	9	29	2720	4800	955	51
	Degari	3	20	52	2193	8000	1667	60
	Shahrigh	3.1	207	21	13820	13440	730	1461
	Sor-Range	2.6	6.4	324	1432	7680	2015	65
Nitric Acid	Makarwal	10	12	42	5510	4480	275	51
	Degari	8	46	10	5386	9920	1138	93
	Shahrigh	17	184	23	14730	8000	1679	129
	Sor-Range	8	20	8	1530	7360	1871	56
Acid Mixture	Makarwal	10	13	104	2170	3840	360	56
	Degari	8	53	16	5580	14400	1871	140
	Shahrigh	18	204	29	6479	ND	324	170
	Sor-Range	8	22	20	1750	10240	198	64
Leaching Time	=	0.5 Hrs						
ND	=	Not Detectable						

Table-2: Amount of Inorganic Elements ( $\mu\text{g/g}$ ) Leached with Different Leachants

Leachant	Coal sample	Cu	Mn	Zn	Fe	Ca+Mg	Na	K
Distilled Water	Makarwal	23	32	185	3530	12000	2194	191
	Degari	22	91	27	5885	19200	5587	1946
	Shahrigh	20	168	126	10220	15200	3714	2184
	Sor-Range	28	39	45	2990	ND	3680	518
Hydro chloric Acid	Makarwal	10	11.6	31.6	3340	6400	122	1154
	Degari	5.6	26	7.2	3658	7680	1891	56
	Shahrigh	12.8	212	20.4	12730	16640	1513	256
	Sor-Range	5.6	17.6	6.4	1638	ND	2122	93.6
Nitric Acid	Makarwal	11.2	12.8	39.2	4330	6080	275	154
	Degari	7.6	41.6	8.8	2770	10560	1564	65
	Shahrigh	14.8	180	19.6	10300	7040	45	143
	Sor-Range	3.6	14.8	6.8	973	5740	1895	46
Acid Mixture	Makarwal	13.2	10.4	31.2	2896	ND	386	90
	Degari	9.6	45.6	15.6	4090	1600	1697	624
	Shahrigh	3.6	186	108	13190	ND	1656	102
	Sor-Range	8.8	18.8	12.8	12.8	2881	1881	312
Leaching Time	=	2 Hrs						
ND	=	Not Detectable						

underlined that time factor is of prime importance for effective leaching. Amount of Fe, Ca, Mg, Na, and K determined in leachates with HCl for time duration of 0.5 hr is quite low compared to their amount leached with the same leachant for time duration of 2.0 hrs. Similar trend can be observed in case of leaching with  $\text{H}_2\text{O}$ ,  $\text{HNO}_3$ , and acid mixture. There are numerous arguments one can marshal for the trend, porosity of the coal is one of these. Coal is believed to be an inhomogeneous porous material [12] and maximum of its surface is enclosed in pores i.e. macro, meso, and micro pores. Coal porosity plays a key role in practically all aspects of its utilization [13-14]. In case of leaching performed for small duration of time, those sites that are enclosed in these pores have not been accessed effectively. Upon extension in time, the accessibility was believed to

have enhanced. The other reason can be imagined, is the dissolution of some metal salts housed in pore mouths upon extension in time, which lead to opening of the blind pores.

It would be unsound not to include the reason of sorption-desorption of the metals under study. As we have reported in our previous paper [9] that equilibrium is established between desorption and reabsorption of metals under study at sites i.e. ion exchange. The rate of desorption from the sites, which provide accommodation to these metals is slow in the beginning, however upon extension in time, this rate is increased. One of the reasons that is also attributed to the maximum leaching upon extension in time is the digestion. Another reason that springs readily into mind is the natural

ferromagnetism associated with some of the metals under study [15], which interfere with their extraction. Due to magnetism, the affinity of the metals with the chelating sites is firm due to which these do not get leached effectively. Upon extension in time these metals get fouled; coated by clay or other inert materials. Their magnetism is effected and also their affinity to readsorption is minimized, thus they get effectively dissolved in the extractant and leached away or remain intact in the leachant as precipitate.

### Experimental

#### Extraction procedure

Four coal samples from Makarwal, Degari, Shahrigh, and Sor- Range coalmines were used in current investigation. Five grams portion of each coal sample was extracted separately with H<sub>2</sub>O, HCl, HNO<sub>3</sub> and their mixture (molar ratio of 10:5:1). Specified amount of coal was slurried in 50 cm<sup>3</sup> of extracting solution in Pyrex made beaker. A Teflon coated magnetic stirring bar was also immersed. The beaker was placed on a water bath and the whole assembly was installed on a magnetic stirrer. The contents were stirred for the specified duration of time at 50°C. The temperature was maintained throughout the extraction process by addition of hot water into the water bath. After being contacted for the specified duration of time, the slurry was filtered using whatman filter paper. The residual coal was washed exhaustively with copious amount of hot distilled water. The filtrates and washings were combined and evaporated to a constant volume of 200 cm<sup>3</sup> and used for the determination of inorganic elements.

#### Determination of inorganic elements

Cu, Mn and Zn were analyzed by Atomic absorption spectrophotometer (SP-100 Pye uncam Ltd, Cambridge England) using oxyacetylene flame. Instrument was calibrated by preparing standard solutions over the concentration range of interest and measuring their absorption under the same conditions as for sample measurements. Absorbance measurements were made at 324.8, 279.6, and 213 nm for Cu, Mn, and Zn respectively.

#### UV spectrophotometry

Fe was determined spectrophotometrically by potassium thiocyanate method using double beam, shimadzu UV visible, 160-A spectrophotometer.

#### EDTA titrimetry

Ca and Mg were determined combinedly by EDTA titration method.

#### Flame photometry

Na and K were determined by flame photometer (Gallen Kamp, England).

### Conclusions

Coal beneficiation can be accomplished effectively with leachants like H<sub>2</sub>O, HCl, HNO<sub>3</sub> and their mixture particularly with acid mixture.

Extended time leaching proved to be helpful in nearly complete demineralization of the coal samples under study.

The method will be helpful in removing ash forming inorganic elements not only will mitigate ash problems but also will alleviate environmental problems associated with combustion of such coals.

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