Demineralization of Sor-Range Coal with HNO_3 and The Determination of Trace Elements in the Acid Extracts

M.ARSALA KHAN* AND M. ISHAQUE. MOHMAND
Department of Fuel Technology and Material Science, University of Peshawar, Peshawar, Pakistan.

(Received 8th August, 1989, revised 19th June, 1990)

Summary: Sor-Range coal was demineralized with HNO_3 and trace elements were determined in the acid extracts by atomic absorption spectrophotometer. Effect of time and concentration of acid on the extraction of trace elements were studied.

Introduction

Demineralization of Sor-Range coal with water [1] and HCl [2] revealed a significant difference in the amount of extraction of various trace elements. Time and concentration of HCl were found to have noticeable effects on the extraction of trace elements. However amounts of trace elements extracted with even the concentrated HCl, were not comparable to their respective amounts in the coal ash, and significant amounts of trace elements remain in the coal after extraction with HCl.

Demineralization with HNO_3 of Makarwal [3] and Shahrigh [4] coals showed that considerable increase occured in the extraction of Fe compared to its respective extraction with HCl [5,6]. High extraction of Fe with HNO_3 was thought to be due to the extraction of pyritic iron. Pyritic iron is extractable with HNO_3 but not with HCl [7]. It was also apparent from these studies that whereas extraction of other trace elements with HNO_3 were comparable to their respective values with HCl, extrac-

tion of Ca was quite low with HNO_3 compared to that with HCl especially in case of Shahrigh coal sample.

The present work has been undertaken to study the extraction of trace elements from Sor-Range coal with HNO_3 and to compare its affectiveness with that of water [1] and HCl [2] extraction from the same coal.

Experimental

Coal sample obtained from Sor-Range coal fields was ground in a clean pistle and mortar and passed through a 120 mesh screen as described earlier [1]. Demineralization of coal with HNO_3 was performed by taking one gram portions of 120 mesh coal samples dried at 105°C, in quickfit conical flasks. In one set of of experiments 50 cm^3 of 1M HNO_3 solution was added to each flask and the flasks were allowed to stand for different duration of time with occasional hand shaking. In an other set of experiments 50 cm^3 of HNO_3 solutions of varying concentrations were added to each flasks containing one gram portions of dried coal and the flasks were allowed to stand for one day with occasional shaking. The slurries of coal in both set of experiments were filtered through Whatman No 540 filter paper. The coal residues were washed repeatedly with hot distilled water, dried at 105°C and weighed, from which the loss in weight and thus the total mineral matter extracted was determined. The filtrates from both set of experiments were used for trace metal analysis using atomic absorption spectrophotometer [5].

Results and Discussion

The effect of time on the extraction of total mineral matter with 1M HNO_3 is given in Fig. 1. No noticeable increase in the amounts of extract can be observed, when the time of extraction was extended from 1 to 5 days. Similar effect of time on the extraction of total mineral matter was also observed with HCl from the same coal [2].

The effect of time on the extraction of trace elements with 1M HNO_3 is shown in Figs. 2,3 and Table-1. A slight increase in the values of most of the elements can be noticed with increase in the duration of time, which is quite pronounced in case of Fe and Ca. The extractions of most of the elements with 1M HNO_3 are comparable to their respective values with 1M HCl from the same coal with exception to Fe and Ca [2]. The amounts of various trace elements for example with 1M HNO_3

Table-1: Amount of Ca and Mg Extracted by 1M HNO_3 from Sor-Range Coal within 3 and 5 Days ($\mu g/g$).

Time (Days) Element	3 Days	5 Days
Calcium	6210	11850
Magnesium	21.6	24.6

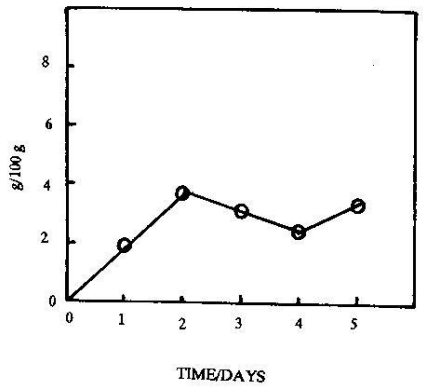

Fig.1: Total Mineral Matter Extracted by 1M HNO_3 from Sor-Range Coal within Different Duration of Time.

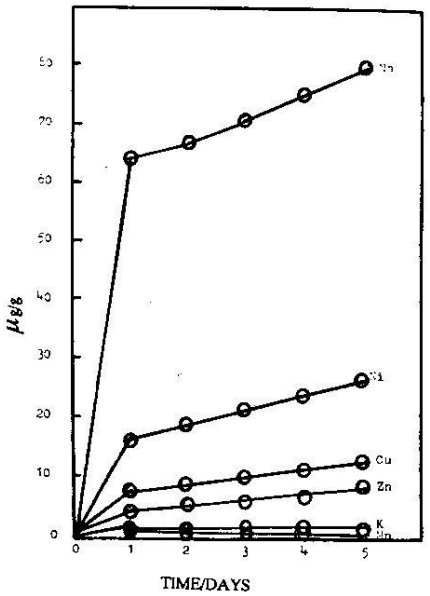

Fig.2: Trace Elements Extracted by 1M HNO_3 from Sor-Range Coal within Different Duration of time.

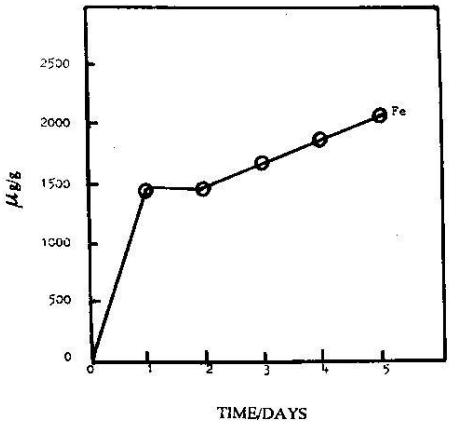

Fig.3: Fe Extracted by 1M HNO_3 from Sor-Range Coal within Different Duration of Time.

within 5 days are Ca (11850 µg/g), Fe (2076 µg/g), Na (80 µg/g), Ni (27 µg/g), Mg (24µg/g), Cu (13 µg/g), Zn (9 µg/g), K(2 µg/g) and Mn(0.2 µg/g) where as their respective values with 1M HCl within the same duration of time are Ca (12720 µg/g), Fe(1773 µg/g), Na(171 µg/g), Ni(21 µg/g), Mg (21 µg/g), Cu(16 µg/g), Zn(16 µg/g), K(4 µg/g) and Mn(0.2 µg/g). This shows that Ca and Mn are present respectively in highest and lowest amounts in both the 1M HNO_3 and 1M HCl extracts. Moreover, it can also be noticed that the amount of Ca in 1M HNO_3 extract is lower compared to its amount in the IM HCl extract, whereas the amount of Fe is higher in the 1M HNO_3 extract compared to its value in the 1M HCl extract. The amounts of these elements extracted with water within 5 days from the same coal are Ca (620 µg/g), Fe(17 µg/g), Na(43 µg/g), Ni(14 µg/g), Mg(10 µg/g), Cu(8 µg/g), Zn (4 µg/g), K(1 µg/g), and Mn (not detected) [2] which shows that the amounts of these elements in the IM HNO_3 extracts are high compared to their respective amounts in the water extracts, which is quite pronounced in case of Fe and Ca and less significant in case of other elements. The amounts of the various trace elements in the coal ash are Ca (18100 µg/g), Fe(5100 µg/g), Na(200 µg/g), Ni(35 µg/g), Mg (22 µg/g), Cu (20 µg/g), Zn(1458 µg/g), K (295 µg/g), and Mn(0.5 µg/g), which shows that the values of elements like Ca, Fe, Zn, Na and K are quite low in the 1M HNO_3 extract compared to their respective values in the coal ash, whereas the amounts, of Ni, Mg, Cu and Mn are comparable to their respective amounts in the coal ash.

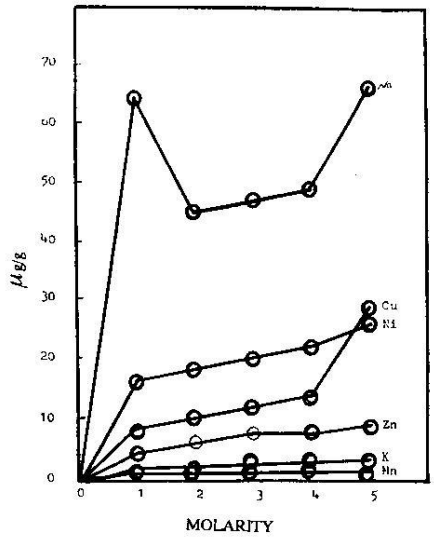

Fig.4: Trace Elements Extracted by Different Molar HNO_3 from Sor- Range Coal within 1 Day.

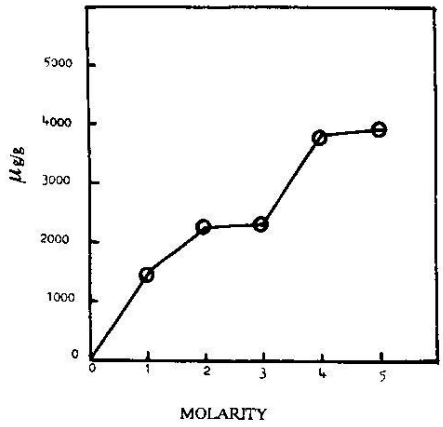

Fig.5: Fe Extracted by Different Molar HNO_3 from Sor-Range Coal within 1 Day.

The values of most of the elements in the 1M HNO_3 extracts of Sor-Range coal are comparable to their respective amounts in the 1M HNO_3 extracts from Makarwal [3] and Shahrigh [4] coal samples. The values of various trace elements extracted for example with 1M HNO_3 within 5 days from Makarwal coal sample are Ca(8702 µg/g), Fe(1855 µg/g), Na(15 µg/g), Mg(17 µg/g), Cu(54 µg/g), Zn (29 µg/g), K(2 µg/g), and Mn(0.1 µg/g), whereas that from Shahrigh coal sample are Ca(8400 µg/g), Fe(26743 µg/g), Na(39 µg/g), Ni(71 µg/g), Mg (13µg/g), Cu(34 µg/g), Zn(22 µg/g), K(4

μg/g), and Mn (2 μg/g). This shows that the amount of Ca is quite high in the 1M HNO_3 extract of Sor-Range coal compared to its respective values in Makarwal and Shahrigh coal samples. The amount of Fe in the 1M HNO_3 extract of Sor-Range coal is comparable to its respective value in case of Makarwal coal, however it is significantly lower compared to that in Shahrigh coal. Shahrigh coal has been found to contain the highest amount of Fe compared to Makarwal and Sor-Range coals as is evident from ash analysis of these coals [1].

The effect of concentration of HNO_3 on the amounts of extraction or various trace elements within a duration of one day is shown in rings. 4,5 and Table-2. A slight increase can be see n in the values of most of the trace elements, which is significant only in case of Fe and Ca. The amount of Fe extracted with 5M HNO_3 within one day is quite higher compared to that extracted with 1M HNO_3 within five days. The value of Ca, however in the one day 5M HNO_3 extract is lower compared to that in the five days, IM HNO_3 extract.

Table-2: Amount of Ca and Mg Extracted by 3M and 5M HNO_3 from Sor- Range Coal within 1 Day (μg/g).

Molarity / Element	3M HNO_3	5M HNO_3
Calcium	6250	9300
Magnesium	24.2	27.4

The effect of time and concentration of HNO_3 on the percentextractabilities of various trace elments are shown in Table-3 and 4 respectively. It can be seen that time and concentration have positive effects on percent extractabilities of most of the trace elements. Zinc and K have quite low percent extractabilities. Calcium which is present in highest amount in Sor-Range coal, has quite high percent extractabilities with IM HNO_3 within five days, than with 5M HNO_3 within on day. Iron which is the seond most abundant element present in coal shows quite high percent extractability with 5M HNO_3 within one day, than with IM HNO_3 within five days. The percent extractability of Fe with HNO_3 especially with can.acid is quite high compared to that with HCl(2), whereas that of Ca is relatively low with HNO_3 compared to that with HCl. Zinc which is the third most abundant element with Sor-range coal has quite low percent extractability with HNO_3, lower ever than with HCl (2). Sodium has low extractability with HNO_3 compared to that with HCl the amount of most of the other elements with HNO_3 are comparable to their respective values with HCl.

Table-3: Percentage Extraction of Trace Elements with 1M HNO_3 from Sor-Range Coal within Different Duration of Time

Element / Time (Days)	Cu	Ni	Zn	Fe	Mn	Na	K	Ca	Mg
1	38.3	45.7	0.3	28.5	25.5	32.2	0.4		
2	45.0	54..3	0.4	28.8	27.3	33.7	0.4		
3	50.0	62.9	0.4	32.7	27.3	35.5	0.4	51.8	80.0
4	56.7	69.6	0.4	37.5	27.8	37.7	0.6		
5	65	77.1	0.6	40.7	30.9	40.0	0.6	98.8	91.1

Table-4: Percentage Extraction of Trace Elements with HNO_3 of Different Concentrations from Sor-Range Coal within 1 Day.

Element / Molarity	Cu	Ni	Zn	Fe	Mn	Na	K	Ca	Mg
1	38.3	45.7	0.3	28.5	25.5	32.2	0.3		
2	50.0	51.4	0.4	44.9	20.0	22.5	0.6		
3	60.0	57.1	0.5	44.9	25.5	23.6	0.8	52.1	89.6
4	70.0	62.8	0.5	74.3	30.9	24.8	0.8		
5	145	74.3	0.6	76.9	40.0	33.4	0.9	77.5	101.5

The percent extractabilities of K and Zn with HNO3 are comparable to that with water (1). Most of the other elements have quite high percent extractabilities with HNO_3 compared to that with water, which is more pronounced in case of Fe and Ca. Iron is only 0.3 percent extractable with water compared to about 77 percent with Con. HNO_3, whereas the percentage extraction of Ca has increased from 5.2 percent with water to about 99% with HNO_3.

References

1. M.A.Khan and M.I. Mohmand, *J.Chem. Soc. Pak.*, 7(4), 327 (1985).
2. M.I.Khan and M.I. Mohmand (submitted for publication.
3. M.A.Khan and M.I. Mohmand, *J.Chem.Soc. Pak.*, 9(2), 279 (1987).
4. M.A.Khan and M.I. Mohmand, *J.Chem.Soc. Pak.*, 10(2), 165 (1988).
5. M.A.Khan and M.I. Mohmand, *J.Chem.Soc. Pak.*, 9(2), 273 (1987).
6. M.A.Khan and M.I.Mohmand, *J.Chem.Soc. Pak.*, 9(3), 413 (1987).
7. J.N. Chakrabarti, in "Analytical Methods for Coal and Coal Products" Vol. 1 P. 279, Academic Press, New York.