Determination of Shahrigh Coal with HNO_3 and the Determination of Trace Elements in the Acid Extracts

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Summary: Shahrigh coal was extracted with HNO_3 for different durations of time and with acid of different concentrations. The extracts were analysed for trace elements by atomic absorption spectrophotometer. Iron was found to be present in highest quantity whereas Mn in lowest quantity in the HNO_3 extracts. Duration of time and concentration of acid have positive effects on the extraction of trace elements, which were however not very significant in most of the cases. Percentage extractions of trace elements within different duration of time and with acid of different concentration have also been calculated.

Introduction

Demineralization of Shahrigh coal has been carried out earlier with H_2O [1] and HCl [2]. In both the H_2O and HCl extracts Ca was found to be present in highest quantities, whereas Mn in lowest quantities. A significant increase occurred in the amounts and percentage extraction of most of the trace elements in HCl extracts compared to that in H_2O extracts. This increase was quite obvious in case of Fe and Ca. Amounts of Fe have increased several hundred times in HCl extracts compared to that in H_2O extracts. Moreover the orders of the amounts of trace elements extract and also of their respective percentage extraction with HCl were quite different from that with H_2O. Time of equilibration and concentration of HCl solution were also found to have positive effects on the amounts and percentage extraction of trace elements.

In our earlier study of demineralization of Makarwal coal with HCl [3] and HNO_3 [4], it was found that the amounts of Ca and Fe were quite high in HNO_3 extracts compared to their respective amounts in HCl extracts. Amounts of most of the other elements in HNO_3 extracts were however quite comparable to their respective amounts in HCl extracts. The amounts of most of the elements in the HNO_3 extracts were low comparative to their amounts in coal ash, however, some elements like Ni and Mg showed increase of their amounts in the HNO_3 extracts compared to their amounts in coal ash. Such types of observation were also made in case of Mn and Mg for the same coal with HCl (3). The percentage extractions of various elements with HNO_3 were different from that with HCl. The order of percent extractabilities of various elements with HNO_3 was also different from that with HCl, showing that some elements had been extracted to a greater extent with HNO_3 whereas other elements to a lesser extent compared to extraction with HCl. Percent-

age extractions of elements like Ni and Mg were above 100, which were though to be either due to experimental error or due to some losses of these elements at the high ashing temperature.

The current work is a continuation of our previous work to know the effect of time and concentration of HNO_3 on the amounts and percentage extraction of trace elements and to compare it with H_2O(1) and HCl(2) extractions of the same coal as well as to extraction of Makarwal coal with HNO_3 (4). Shahrigh Coal which has the highest Fe content of the four coal samples (1) was thought to show greater extraction of this elements with HNO_3 if Fe is present mostly as pyritic Fe(5).

Experimental

Coal sample obtained from Shahrigh Coal fields was prepared and demineralized with HNO_3 of different concentrations and for different duration of time, similar to our earlier work [2-4]. The amounts of trace elements in the acid extracts were determined by atomic absorption spectrophotometer.

Results and Discussion

Figure 1 shows the effect of time of equilibration on the amount of total mineral matter extracted with 1M HNO_3 from Shahrigh Coal. A significant increase in the amount of total mineral matter with time can be noticed. The amounts of total mineral matter extracted with HNO_3 are considerably higher compared to their respective amounts extracted with H_2O (1) and HCl (2) from the same coal. Moreover the amounts of total mineral matter with HNO_3 are considerably higher compared to that extracted with HNO_3 from Makarwal Coal (4).

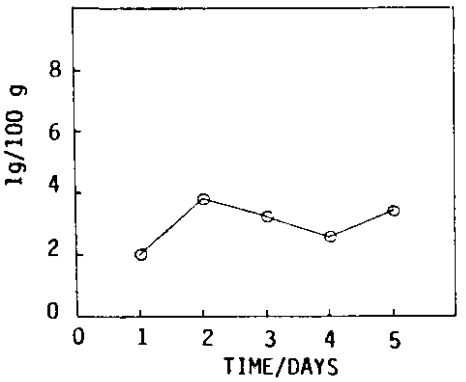

Fig.1: Total Mineral Matter Extracted by 1M HNO_3 from Shahrigh Coal within Different Duration Time.

Table-1 and Figs. 2 and 3 show the effect of time of equilibration on the amounts of trace elements extracted with 1M HNO_3. An increase in the amounts of trace elements extracted with increase in the duration of time can be noticed, which is however not very significant in case of most of the elements.

The amounts of most of the elements in all the 1M HNO_3 extracts are comparable to their respective values in the 1M HCl extracts with exception to Fe and Ca. Iron has quite high values whereas Ca quite low values in the

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

Time (Days) Elements	3 Days	5 Days
Calcium	6150	8400
Magnesium	5.2	13.4

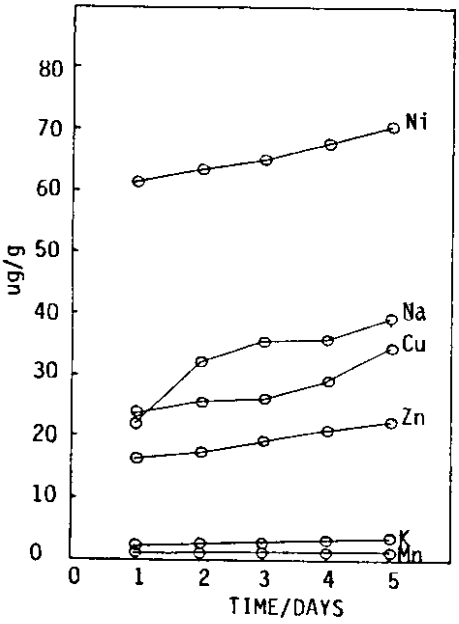

Fig.2: Trace Elements Extracted by 1M HNO_3 from Shahrigh Coal within Different Duration of Time.

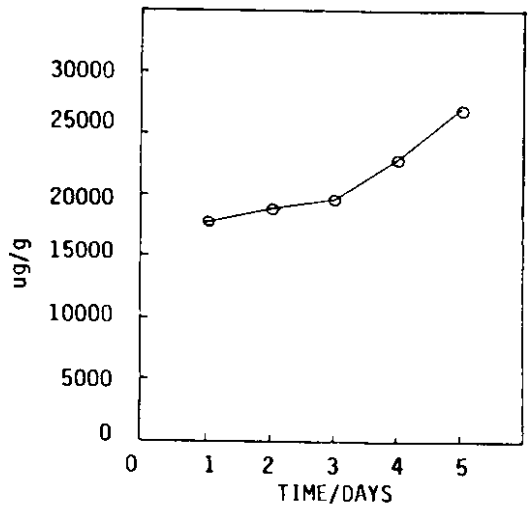

Fig.3: Fe Extracted by 1M HNO_3 from Shahrigh Coal within Different Duration of Time.

HNO_3 extracts compared to HCl extracts. The amounts of various elements extracted for example with 1M HNO_3 within 5 days are Fe(26743 µg/g), Ca (8400 µg/g), Ni (70.7 µg/g), Na (39.3 µg/g), Cu (34.3 µg/g), Zn (22.1 µg/g), Mg (13.4 µg/ g) K (3.6 µg/g)and Mn (1.7 µg/g) where as that with 1M HCl within the same duration of time are Ca (16650 µg/g), Fe (8393 µg/g), Ni (59.0 µg/g) Na (48.8 µg/g), Zn (23.0 µg/g), (21.6 µg/g) Mg (18.2 µg/g), K (2.6 µg/g) and Mn (1.2 µg/g) [2]. This shows that Fe is present in highest quantity and Mn in lowest quantity in the HNO_3 extracts whereas the HCl extracts contained Ca and Mn in highest and lowest amounts respectively. The amounts of Fe in the 1M HNO_3 extracts have increased more than three fold as compared to its respective amounts in the 1M HCl extracts which indicates high pyritic Fe content in Shahrigh Coal. Pyritic iron can be extracted with HNO_3 but not with HCl [5]. Hydrochloric acid extracts only the non Pyritic Fe. However the amounts of Ca in the 1M HNO_3 extracts have decreased significantly compared to its respective values in the 1M HCl extracts. Elements like Ni, Na, Zn, Cu, Mg, K and Mn have values not significantly different from their respective values in the 1M HCl extracts of the same coal. The values of most of the elements however have increased considerably compared to their respective values in the H_2O extracts [1], which is again quite pronounced in case of Fe. The values of K and Na have not changed appreciably compared to their respective values in the H_2O extracts [1].

The amounts of various elements extracted from Shahrigh coal for instance with 1M HNO_3 within 5 days if compared with the amounts extracted from Makarwal Coal, with 1M HNO_3 within the same duration of time, which are Ca (8702 µg/g) Fe (1855 µg/g),

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

Molarity Elements	3M HNO_3	5M HNO_3
Calcium	10890	14850
Magnesium	13.8	23.2

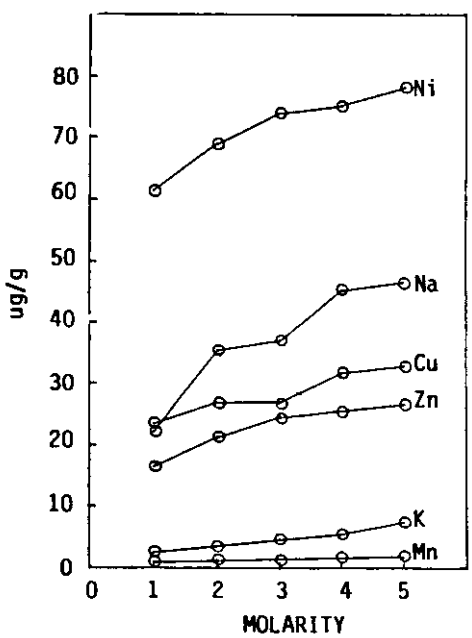

Fig.4: Trace Elements Extracted by Different Molar HNO_3 from Shahrigh Coal within 1 Day.

Cu (53.7 µg/g), Zn (28.9 µg/g), Ni (20.7 µg/g), Mg (16.8 µg/g), Na (15.1 µg/g), K (1.6µg/g) and Mn (0.1 µg/g), reveal that most of the elements extracted from the two coals are quite comparable, with exception to Fe. The amount of Fe in the HNO_3 extracts of Shahrigh Coal are more than ten time higher compared to that in the HNO_3 extracts of Makarwal Coal. Shahrigh Coal has also been found to contain highest amount of Fe in its ash compared to that of Makawarwal Coal [1].

Effect of concentration of HNO_3 on the amounts of various elements extracted are given in Table-2 and Figs 4 & 5. It can be noticed that concentration also has a positive effect on the extraction of all the elements, however the effect is not of much significance in case of most of the elements except Fe and Ca. The amounts of Fe and Ca have increased significantly with increase in concentration of HNO_3. The amounts of various elements in all the HNO_3 extracts of different concentrations, if compared with their respective amounts in the HCl extracts [2], reveal that Fe and Mn are respectively present in highet and lowest amounts in the HNO_3 extracts, whereas in the HCl extracts Ca and Mn are present in highest and lowest amounts respectively. Zn has also low values in the concentrated HNO_3 extracts compared to that in the HCl extracts. However most of the other elements have amounts not significantly different in the HNO_3 and HCl exctracts.

The percentage extraction of various elements with HNO_3 within diferent duration of time and with different concentrations are shown in Tables 3 and 4. Increase in percentage extraction with time and concentration can be noticed. Elements like Cu, Ni, Fe and Mn have comparatively high percentage extractions. The percentage extractions of K and Zn are quite low whereas Ca and Mg have high percentage extraction with concentrated acid. Some of the elements like Ni and Mn have percentage values above 100 in the HNO_3 extracts. Such

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

Elment Time (Days)	Cu	Ni	Zn	Fe	Mn	Na	K	Ca	Mg
1	65.7	88.9	2.2	60.0	91.2	13.1	0.5		
2	70.4	91.8	2.3	64.0	95.2	18.7	0.5		
2	72.2	94.2	2.5	66.1	98.0	20.9	0.6	30.6	18.5
4	80.6	98.6	2.7	75.7	113.6	20.9	0.7		
5	95.4	102.4	2.9	90.3	115.0	23.0	0.8	49.1	47.9

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

Element Molarity	Cu	Ni	Zn	Fe	Mn	Na	K	Ca	Mg
1	65.7	88.9	2.2	60.0	91.2	13.1	0.5		
2	75.0	100.0	2.8	84.8	71.4	20.7	0.7		
3	75.0	107.0	3.2	88.4	91.2	21.6	0.9	63.7	49.2
4	88.9	108.7	3.3	98.9	108.2	26.7	1.1		
5	91.7	113.0	3.5	99.5	111.6	27.3	1.6	86.8	82.9

types of observations were also noticed in case of Cu and Ca in the HCl extracts, which were thought to be either due to some losses of these elements at the high ashing temperature or due to experimental error.

The percentage extractions of various elements with HNO_3 if compared with the percentage extractions with HCl for the same Coal, show a significant difference in the percentage extractions of Ca and Fe, which are elements present in highest amounts in Shahrigh Coal. The percentage extractions of Fe with HNO_3 are significantly high compared to its values with HCl. Some of the elements show values of their percentage extractions with HNO_3 quite comparable to their values with HCl, whereas the others show some variation of their

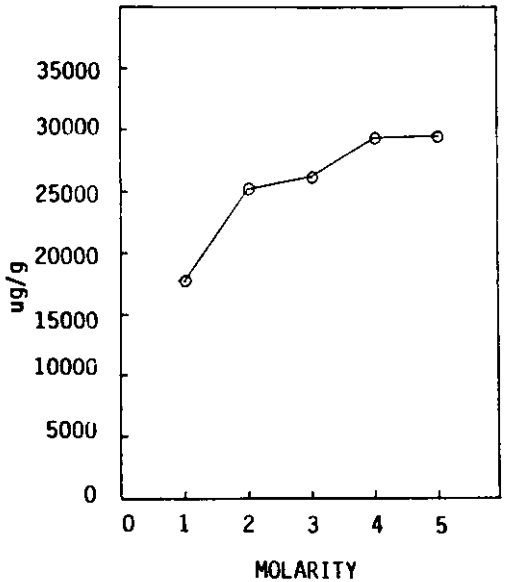

Fig.5: Fe Extracted by Different Molar HNO_3 from Shahrigh Coal, within 1 Day.

percentage extraction with HNO_3 compared to that with HCl. However these variations in the percentage extractions are not of much significance, because of their comparatively small amounts in coal as determined in the coal ash in our earlier study [1], where in small changes in the amounts of these trace elements in different determinations might appear as large changes in percentage extractions. Here it has to be pointed out that because of the quite heterogenous dispersion of mineral matter in coal, the difference in the amounts of trace elements from determination to determination under the same set of experimental conditions should be quite obvious.

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