Demineralization of Makarwal Coal with HCl and the Determination of Trace Elements in the Acid Extracts

M.A.KHAN*, M.I.MOHMAND AND KHADIM-UL-FAQIR,**
*Department of Chemistry, University of Peshawar, Peshawar, Pakistan
**N.W.F.P. University of Engineering & Technology, Peshawar, Pakistan.

[Received 9th February, 1986, revised 3rd June, 1986]

Summary: Demineralization of Makarwal Coal has been made with HCl solution and the trace elements present in the acid extracts have been determined using Atomic Absorption Spectrophotometer. It was found that a considerable increase occured in the amount of trace elements extracted by HCl solutions compared to that in the water extract. The amount of most of the trace elements in the acid extracts were, however quite low compared to their amounts in the coal ash.

The percentage extraction of most of the trace elements with HCl solution show a considerable increase compared to that with water. The order of percent extractability of trace elements with HCl solution are quite different compared to that with water. Moreover most of the elements show an increase in their percentage extraction with increase in time of equilibration or concentration of HCl solution.

Introduction

Demineralization of various Pakistani coals with water and the determination of trace elements in the water extracts has been performed in an earlier study [1]. The percentage extraction of the various trace elements showed that Ni was the most easily water extractable element, whereas Fe, Zn and K were comparatively the most difficult ones to be extracted. The amount of trace elements in ashes of the four coal samples were also determined and it was found that the amounts of trace elements in the coal ashes were very high compared to their respective values in the water extracts, which showed that extraction with water was not effective enough for demineralization.

In the present investigation demineralization of Makarwal coal with HCl solution has been made to compare its effectiveness with that of water. Demineralization of coal with acids has been reported in the literature [2-4].

Experimental

Determination of Trace Elements Extracted with HCl:

The coal sample obtained from Makarwal coal fields and used in an earlier study [1] were used in the current investigation, with a view to find out the effects of time and concentration of HCl on the extraction of various trace elements.

For the first set of experiments one gram each of coal sample were taken in conical flasks and to those were added 50 cm^3 of 1M HCl and were allowed to stand for different duration of time. The coal slurries

were filtered through Whatman No.540 filter paper and the coal residues were washed several times with hot distilled water and were later dried at 105°C in an oven. The total mineral matter extracted was then determined from the loss in weight of the coal sample. The filterate from all these extraction were diluted with distilled water to 100 cm^3 and were analysed for trace elements by Atomic Absorption Spectrophotometer. Each experiment was done in triplicate.

In the second set of experiments one gram portions each of coal sample were taken in conical flasks and to those were added different molar HCl solution and were allowed to stand for one day with occassional stirring. The coal slurries were filtered and washed several times with hot distilled water. The filterates were diluted with water and were used for trace elements determination using Atomic Absorption Spectrophotometer. Each experiment was done in triplicate.

Results and Discussion

The total mineral matter extracted with 1M HCl solution as the coal samples were allowed to stand with it for different duration of time is shown in Fig-1. It can be seen that the effect of time on the amount of mineral matter extracted is not very significant. Moreover the extraction with HCl is not significantly higher compared to that with water for the same coal sample.

The results of trace elements of the 1M HCl extracts obtained at different durations of time are shown in Table-1 and Figs.2-4. The Ca content found in the 1M HCl extract is the highest whereas Mn is the lowest similar to that observed in the water extracts [1].

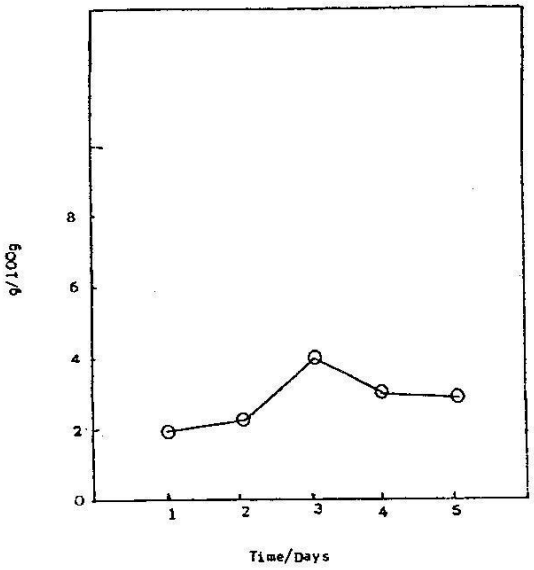

Fig-1: Total Mineral Matter extracted by 1 M HCl from Makarwal Coal.

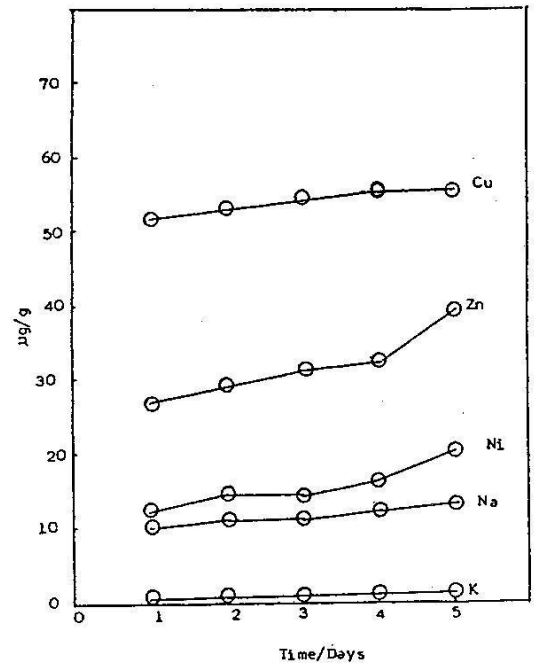

Fig-2: Trace Elements extracted by 1M HCl from Makarwal Coal.

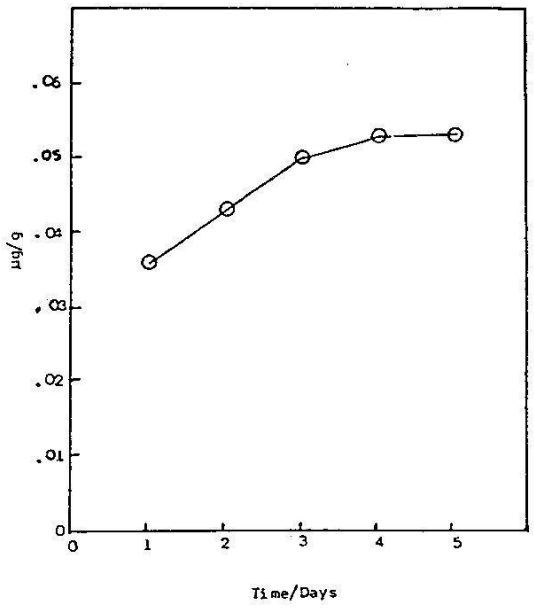

Fig-3: Mn extracted by 1M HCl from Makarwal Coal.

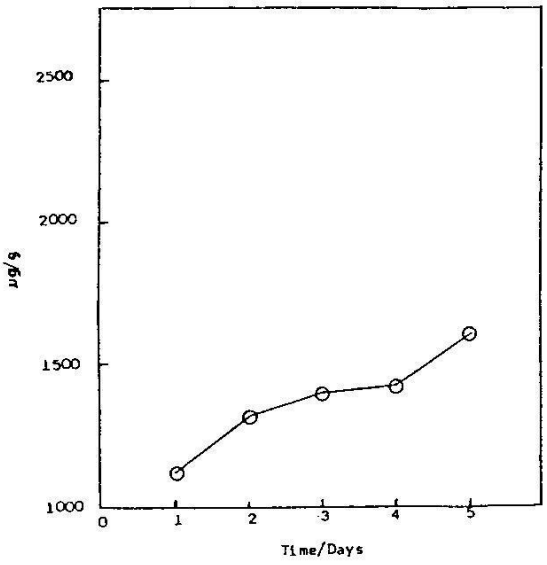

Fig-4: Fe extracted by 1M HCl from Makarwal Coal.

Table-1: Amount of Ca and Mg Extracted by 1MHCl from Makarwal Coal with in 3 and 5 days (µg/g)

Element \ Duration	3 days	5 days
Calcium	4110	4900
Magnesium	2.6	5.2

From Table-1 and Figs.2-4, it is also apparent that almost all elements show an increase with increase in the duration of time. Moreover there is an apparent increase in the values of all the elements compared to their respective values in the water extracts. This increase is quite predominant in the case of Ca, and Fe. However the value of various elements in the HCl extract are quite low compared to their respective values in the coal ash.

Table-2 and Figs.5-8 shows the amount of trace elements extracted when the coal samples were slurried for one day with different Molar solutions of HCl. An increase in the amounts of all the elements in the HCl extract with increase in concentration can be noticed. A considerable increase in the values of Ca, Fe, Zn, Mn and Mg in the 5MHCl extract compared to their respective values in the 5 days 1MHCl extract, can be noticed, whereas elements like Ni, Na, K and Cu did not show a considerable change. Most of the trace elements content in even the 5MHCl extract are quite low compared to their respective values in the coal ashes. However the value of Mn and Mg in the 5MHCl extract is a little higher compared to their respective value in the coal ash which might be due to some loss at the higher ashing temperature.

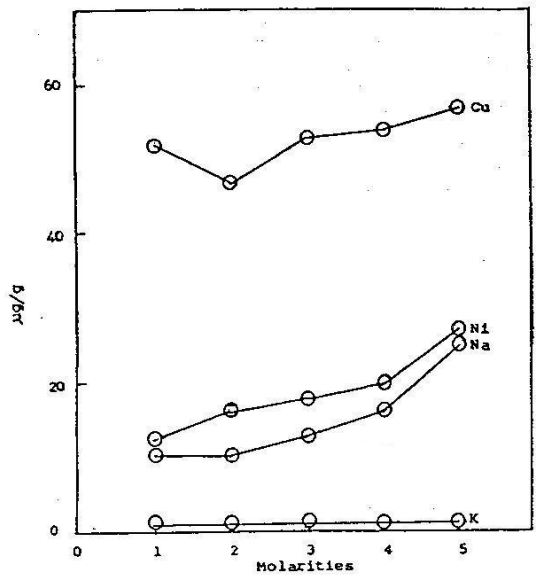

Fig-5: Trace element extracted by different Molar HCl from Makarwal Coal.

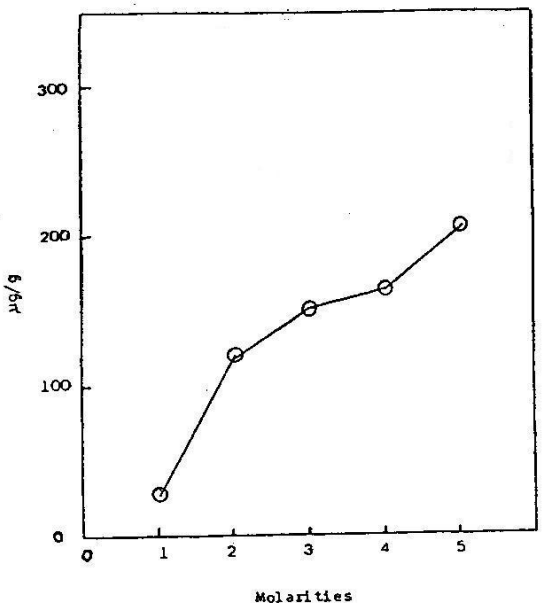

Fig-7: Zn extracted by different Molar HCl from Makarwal Coal.

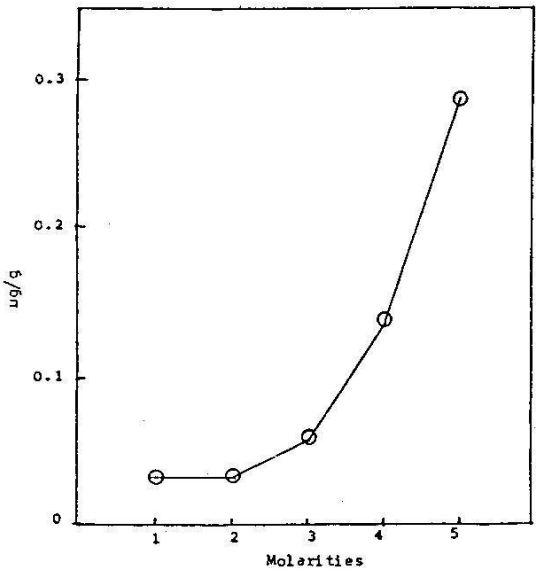

Fig-6: Mn extracted by different Molar HCl from Makarwal Coal.

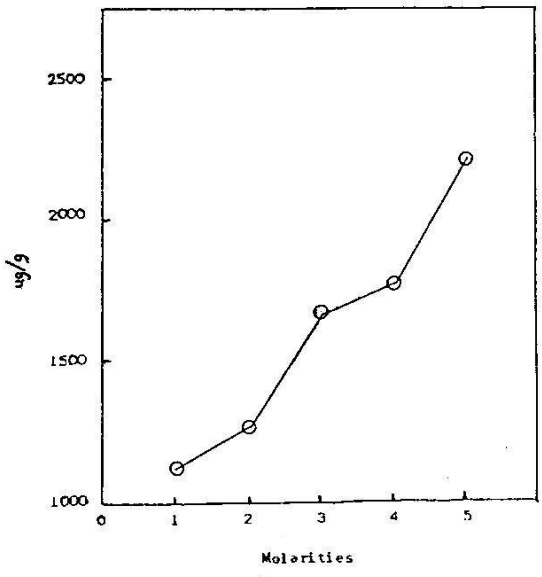

Fig-8: Fe extracted by different Molar HCl from Makarwal Coal.

Table-2: Amount of Ca and Mg Extracted by 3M and 5MHCl within 1 day (μg/g).

Molarity / Element	3 M HCl	5 M HCl
Calcium	5940	6660
Magnesium	9.2	11.6

In our previous work of demineralization with water [1], we found that the percentage extraction of Ni was the highest whereas elements like Fe, Zn and K have quite low values of percentage extraction. The percentage extraction of trace elements with 1M HCl solution within different duration of times is shown in Table-3 which shows a considerable increase of nearly all the elements compared to that with water, with the exception of Ni and K. Moreover there is an increase with time in the percentage extraction of nearly all the elements which is more pronounced in the case of Ni, Ca and Mg. Change with time in the percentage extraction of K is the least. The percent extractability of trace elements are quite different with HCl solution compared to that with water. The order of percent extractability of trace elements with water within 5 days for examples are : Ni(60.0%) Mn(37.5%) Mg(12.8%) Ca(11.9%) Cu(4.8%) Na(2.2%) Zn(1.1%) K(0.8%) Fe(0.1%), whereas that with

Table-3
Percentage Extraction of Trace Elements with 1MHCl within Different Durations of Time

Elements / Time days	Cu	Ni	Zn	Fe	Mn	Na	K	Ca	Mg
1	40.0	45.0	3.5	13.8	22.5	5.5	0.32	-	-
2	40.8	51.2	3.8	16.1	26.9	5.8	0.34	-	-
3	42.0	50.0	4.1	17.3	31.3	6.0	0.36	45.7	37.1
4	42.8	58.3	4.2	17.6	33.1	6.4	0.37	-	-
5	42.8	72.6	5.2	19.7	33.1	7.0	0.48	54.4	74.2

Table-4: Percentage Extraction of Trace Elements with HCl Solution of Different Concentrations within One Day.

Elements / Concentrt. Molarity)	Cu	Ni	Zn	Fe	Mn	Na	K	Ca	Mg
1	40.0	45.0	3.5	13.8	22.5	5.5	0.32	-	-
2	36.0	57.1	15.6	15.6	18.75	5.5	0.23	-	-
3	40.8	64.3	19.5	20.6	37.5	6.9	0.33	66.0	131.4
4	41.5	71.4	21.6	21.9	87.5	8.7	0.39	-	-
5	43.8	96.4	26.8	27.3	181.3	13.5	0.45	74.0	165.7

1MHCl solution within the same duration of time are Mg(74.2%) Ni(72.6%) Ca(54.4%) Cu(42.8%) Mn(33.1%) Fe(19.7%) Na(7.0%) Zn(5.2%) K(0.48%).

The percentage extraction of trace elements with HCl solution of different concentrations is shown in Table-4. Nearly all the elements with the exception of Cu and K show an increase with increase in concentration of HCl solution. This increase is quite pronounced in the case of Ni, Zn, Mn, Ca and Mg. The percentage extraction of Mn and Mg are above 100, which might be due to some loss of these elements in the ash at the higher ashing temperature.

References

1. M.A.Khan and M.I.Mohmand, *J.Chem.Soc.Pak.*, *7(4)*, *327 (1985)*.
2. R.G.Jenkins, S.P.Nandi and P.L.Walker Jr., *Fuel*, *52*, *288 (1973)*.
3. K.Otto, H.Sorek, L.Bartosiewicz and M.Shelef, *Proc. Int. Conf. Coal Science*, *739 (1983)*.
4. L.R.Radovic, K.Steczko, P.L. Walker Jr. and R.G.Jenkins, *Fuel Process Technol.*, *10(3)*, *321 (1985)*.