4. RESULTS AND DISCUSSION

4.1. Identification of the shale deposit sample:

4.1.1. Mineralogical analysis of the clay fraction separated from the shale sample.

The mineralogical composition of the clay fraction separated from the studied shale sample was carried out by X-ray diffraction analysis. This method is considered among the most essential tools for clay and minerals identification. The purpose of qualitative interpretation of X-ray diffraction pattern is to identify each of the crystalline species present in the clay fraction. The most characteristics diffraction spacing of layer silicate clay arises along the C-axis or in crystallographic symbols, the (001) spacing.

X-ray diffraction pattern is based on the presences of diffraction peaks characteristics for each of the crystalline species present in sample. The intensity of the sharpness of these peaks are dependent not only on the number and the corresponding diffraction plains present in the examined sample but also on the particle size, chemical composition, crystal imperfection, crystal orientation and pre-treatments during clay separation (**Whittig and Jackson 1965**). Identification of clay minerals by X-ray diffraction analysis was carried out following the essential principles established by **Jackson (1967) and Dixon and Weeds (1977)** as follows:

1 Koalinite mineral is identified by presences of very sharp peaks at about 7.1-7.2°A (001) and 3.54-3.57°A (002) in the Mg-saturated samples. These peaks are not effected by glycerolated solution and they disappear upon heating to 550°C for four hours.

2 Hydrous mica (illite) minerals are detected by the presence of the basal reflections at 9.9-10.28°A peaks upon Mg-saturation which remain constant throughout the diffraction treatments.

3 Quartz is detected from the presence of 4.26 and 3.35°A stable diffraction peaks throughout the diffraction treatments.

X-ray diffraction pattern of the clay fraction separated from shale sample representing Abo Thor area is shown in Fig. (6).

Data reveal that, X-ray diffraction patterns of the clay fraction separated from the studied sample are dominated by koalinite mineral followed by hydrous mica (illite), while accessory minerals are dominated by quartz.

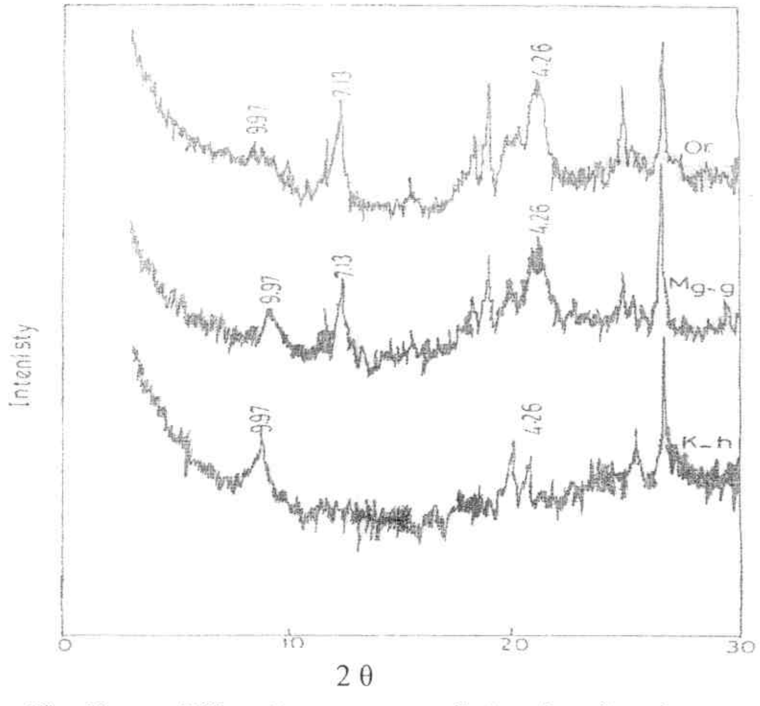

Fig. (6): X-ray diffraction pattern of the clay fraction separated from original sample.

4.1.2. Chemical composition:

In general, approaching of The soil chemical composition is used to obtain a general idea about the mineralogical composition of the various rock types especially by shale deposits, where the chemical constituents or elements are held in the mineral portion of soils and soil parent materials. Therefore, the contents of elements may give some information about nature of sediments and minerals forming the soil matrix. The studied shale deposit sample was analyzed for the major oxides of SiO_2, Al_2O_3, Fe_2O_3,TiO_2, CaO, MgO, K_2O, Na_2O and P_2O_5. Results of analysis are presented in Table (5).

Table (5):The average chemical composition of the studied shale sample.

Element oxid (%)										
Total	L.O.I.	P_2O_5	K_2O	Na_2O	CaO	MgO	TiO_2	Fe_2O_3	Al_2O_3	SiO_2
99.68	16.16	0.40	1.4	2.2	4.9	13..3	0.22	18.2	11.7	27.5

From these results the following characteristics can be outlined:

The SiO_2 content exceeded 27% of the shale deposit sample, this suggests that the SiO_2 is the main chemical constituent of the studied shale sample as well as it occupies the tetrahedral sites and may be found inserted inbetween as impurities. Also,quartz may occur as fine disseminated crystalline particles or deposited with tiny flasks of the clay mineral .

The percentage of Al_2O_3 was 11.71%. Alumina constitutes a considerable part of the clay mineral complex. Its percentage, generally, reflects the type and amounts of clay minerals present. Also, the data obtained reveal that SiO_2 / Al_2O_3 ratio in the studied sample is about 3/1, and this ratio indicates that the deposit under investigation consists mainly of koalinite and semictite, The Fe_2O_3 content reached 18.2% of the studied shale sample,and such relatively high iron oxide content could be attributed to four polygenetic phases :

1 - Secondary impregnation and staining by amourphous iron jel in the weathered samples.

2 -The presence of different iron oxides, mainly goethite.

3 -Iron substituting the Octahedral Al^{3+} and Mg^{2+} in the clay minerals structure.

4-Iron replacing Ca^{2+} in the carbonate minerals structure.**(Ahmed,1999)**

At the end, SiO_2 , Al_2O_3 and Fe_2O_3 constitute more than 50% of the chemical constituents of shale sample. This may indicate that the studied shale deposits has, in general, a ferruginous and argillaceous nature. Minor amount of TiO_2 were recorded in the studied sample and did not exceed 0.22% of its components. Two polygenetic phases may be suggested for the origin of TiO_2 in the studied sediments:

1) Titanium incorporated with detrital minerals such as rutile and ilmenite.

2) Titanium may be substantially concentrated in the octahedral Al^{3+} sites in clays, particularly those of terrestrial origin such as koalinite.

The percentage of MgO reached 13.3% of the studied shale sample, and it may be present as:

1) Octahedral and interlayer cations in the clay lattice, where it substitutes Al^{3+} in the octahedral sites of smectite and illite.

2) Substituting Ca^{2+} in the calcite to form dolomite.

The CaO content of the studied sample was 4.9%,and it may be distributed among the following polygenetic phases:

1) Ca^{2+} incorporated within the carbonate minerals (calcite and dolomite) structure.

2) Ca^{2+} occurs in the interlayer sites of the clay lattice.

The Na_2O content of the studied sample reached 2.2%,and it may be present in the shale sample into distinct forms:

- First, as a constituent of the clay minerals structure, especially Na smectite.

- Second, as water soluble salt.

The K_2O content in the shale deposite sample reached 1.4%, and its low content in the studied area may be due to the low content of K-bearing minerals.

P_2O_5 content reached 0.4% of the studied shale deposit sample,and its low content in the studied sample may be due to the natural of chemical components forming this shale deposit sample. In general, the variation in the SiO_2 and Al_2O_3 in the bulk sample may reflect the relative abundance of quartz and aluminium silicate bearing minerals. On the other hand, Na_2O and K_2O contents may reflect the type of feldspar present in the shale sample. The contents of CaO and Na_2O may be attributed to the presence of calcite and gypsum on one hand and presence of halite on the other hand, respectively.

The loss on ignition (L.O.I) is a measure of organic matter content, chemically combined water and CO_2 derived from carbonate. Its percentage was 16.6% of the studied shale deposit sample. This high value could be attributed to the presence of carbonates (calcite and dolomite) in substantial amount .

4.1.3. Physical and chemical properties:

Particle size distribution of the shale deposit sample revealed that clay fraction of the studied shale sample that was collected from Abo-Thor area is 17.25%, while the silt fraction was 24.95% and the sand fraction was 57.8%. The corresponding textural class of the studied shale deposit sample is sandy clay loam.

The analytical data in Table (6) reveal that the studied shale deposit sample is almost of a neutral pH (7.1). The salinity of the shale sample expressed as electrical conductivity (EC) and determined in the saturated shale paste extract is excessively high, (38.2 dSm^{-1}).

Table (6) . Some properties of the shale deposit extract.

Saturation percentage (SP) %	pH	EC dS/m	Soluble ions								$CaCO_3$
			Cations				Anions				
			Ca^{++}	Mg^{++}	Na^+	K^+	$CO_3^=$	HCO_3^-	Cl^-	$SO_4^=$	%
26	7.1	38.2	41.9	64.4	457.0	41.0	-	2.8	569.0	32.5	11.7

The dominant soluble cations followed the descending order:

Na+ > Mg2+ > Ca2+ > K+, while the dominant soluble anions could be generally arranged in the descending order: Cl- > SO4> HCO3.

4.2. Extraction of the poisonous elements:

It was an important goal of the current study to free the studied shale deposit from the toxic metal ions or at least reduce their concentrations in the shale deposit.

The main effective poisonous elements in the studied sediments are: U, Cu, Zn and Cl. The extraction of these four elements from the studied shale deposit depends on different solid/liquid ratios to obtain the optimum conditions for the leaching process. Two operations were carried out on a technological sample from Abu Thor locality (at w-8) mainly by tap water and H_2SO_4. The materials used and their specifications either in washing by Tap water or in leaching by acid solution are shown in Table (7).

Table (7). Contents of washing by Tap water and leaching by acid solution experiment.

S.No	Type	Specification
1.	Lithology of sample	Shale deposit
2.	Bulk Density of sample	1.6 g/cm^3
3.	Weight of sample	1 kg
4.	Volume of sample	625 cm^3
5.	Particle size	1 cm (10 mm)
6.	Height of the sample in the column	17.2 cm
7.	Number of column	6 column
8.	Material of column	PVC
9.	Height of the pebbles as a filter at the bottom of column	About 3-5 cm
10.	Pattern of the leaching	Heap
11.	Solid / liquid ratios	1: 1, 1: 2 and 1: 3
12.	Type of processes	1- washing by tap water. 2- Leaching by sulfuric acid solution (H_2SO_4)
13.	Concentrations of acid leaching solution	1- 2% or 20 g/L 2- 5% or 50 g/L
14.	Concentrations of the poisonous elements in the sample (Abu Thora Atw-8)	1- Uranium = 167 mg kg^{-1} 2- Copper = 6160.5 mg kg^{-1} 3- Zinc = 3826.4 mg kg^{-1} 4- Chloride = 19000 mg kg^{-1}

4.2.1. The washing by tap water process.

The washing process was carried out using 400mL of tap water , column with the specifications mentioned associated with Tables (8,9,10,11,12and 13)

Data presented in Table 8 and illustrated graphically in Figs. (7and8) reveal that the first outlet sample has 112.21 Cl g/L, while the last sample has 1.10 Cl g/L. The total washed Cl^- was 13.32g, thus the efficiency of Cl washing was 70.10%. Neither Cu nor Zn was detected in the outlet during washing this column. On the other hand, the first outlet sample showed a concentration of 2.02 mg U L^{-1}, while the last one showed 2.5 mg U L^{-1}. The efficiency of U washing was 0.50%. The Cl contents in the leachate of column (1) during the successive washing processes Nos.1,2,3 and 4 were 11.22, 1.80, 0.19and 0.11 g, respectively. The corresponding U contents were 0.20, 0.20, 0.20and 0.25 mg, respectively.

Table (8). Effect of washing by tap water on Cl^-, U, Cu and Zn contents in the successive water leachates (column No. 1) of the shale deposit.

S.No.	Sprinkling solution			The water leachate (pregnant solution)										
	Type	V_1, ml	R_1, ml/min	V_2, ml	pH	R_2, ml/min	Chloride		Uranium		Copper		Zinc	
							Cont. (g)	Eff., %	Cont., (mg)	Eff., %	Cont., (mg)	Eff., %	Cont. (mg)	Eff., %
1st	Tap water	400	1.0 – 1.5	100	7.86	0.25	11.22	70.1%	0.20	0.5%	Nil	Nil	Nil	Nil
2nd				100	7.97	0.30	1.80		0.20		Nil		Nil	
3rd				100	8.11	0.25	0.19		0.20		Nil		Nil	
4th				100	8.25	0.25	0.11		0.25		Nil		Nil	
							13.32		0.86					

S.No. = Serial Number of the leachate.

V_1 = Total volume of sprinkling solution

V_2 = Volume of washing sample

R_1 = Rate of sprinkling solution

R_2 = Rate of leachate flow out of the column

Cont. = Content

pH = pH of the water leachate

Eff.% = Efficiency

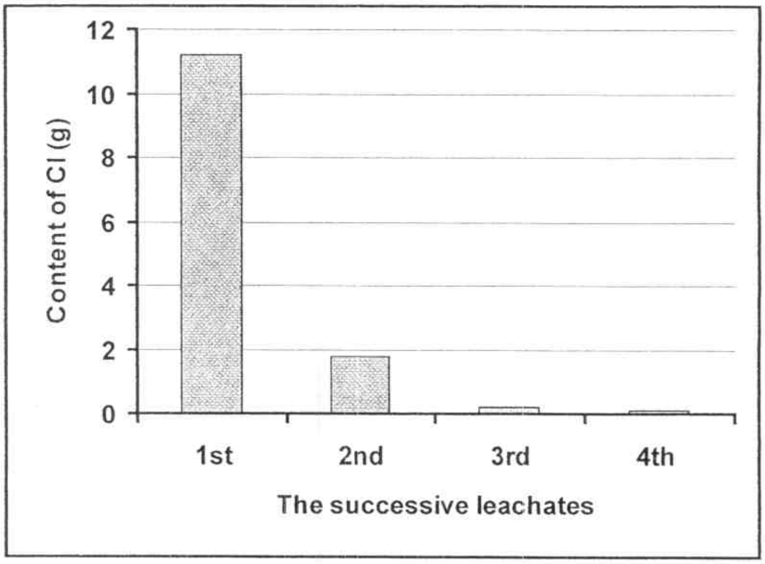

Fig. (7): Cl contents in the successive tap water leachates through column No. 1

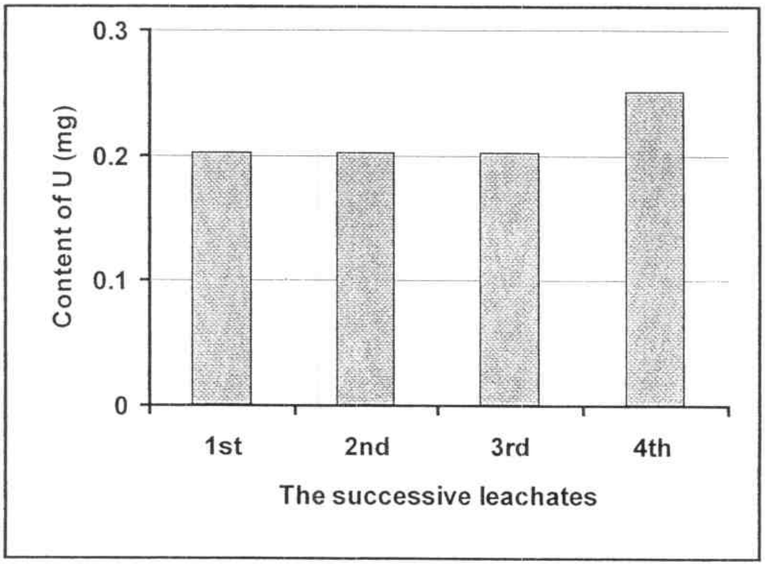

Fig.(8): U contents in the successive tap water leachates through column No. 1

In the column No. 2 which illustrated by Table 9 and Figs. (9 and 10) the concentration of Cl in first leachate sample was 97.1 g/L, while concentration of Cl in the last one was 1.3 g/L. The efficiency of Cl washing was 57.89%. Neither Cu nor Zn was presented in the outlet during washing in this column. Also, concentration of U in the first leachate was 2.02 mgUL^{-1}, while the corresponding concentration in the last one was 3.03 mgUL^{-1}. The efficiency of U washing was 0.66%. The chloride contents in the successive leachates of column (2) during the washing processes Nos.1,2,3and 4 as presented in Table(9) and illustrated by Fig(9and10) were 9.71, 0.94, 0.22 and 0.13, respectively, while the corresponding U contents were 0.20, 0.30, 0.30 and 0.30 mg, respectively.

Table (9). Effect of washing by tap water on Cl-, U, Cu and Zn contents in the successive water leachates (column No. 2) of the shale deposit.

S.No.	Sprinkling solution			The water leachate (pregnant solution)										
							Chloride		Uranium		Copper		Zinc	
	Type	V_1, ml	R_1, ml/min	V_2, ml	pH	R_2, ml/min	Cont. (g)	Eff., %	Cont., (mg)	Eff., %	Cont., (mg)	Eff., %	Cont. (mg)	Eff., %
1st	Tap water	400	1.0 – 1.5	100	6.91	0.40	9.71	57.61%	0.202	0.66%	Nil	Nil	Nil	Nil
2nd				100	7.40	0.43	0.94		0.303		Nil		Nil	
3rd				100	7.39	0.63	0.22		0.303		Nil		Nil	
4th				100	7.70	0.55	0.13		0.303		Nil		Nil	
							11.0		1.11					

- **See footnote Table (8).**

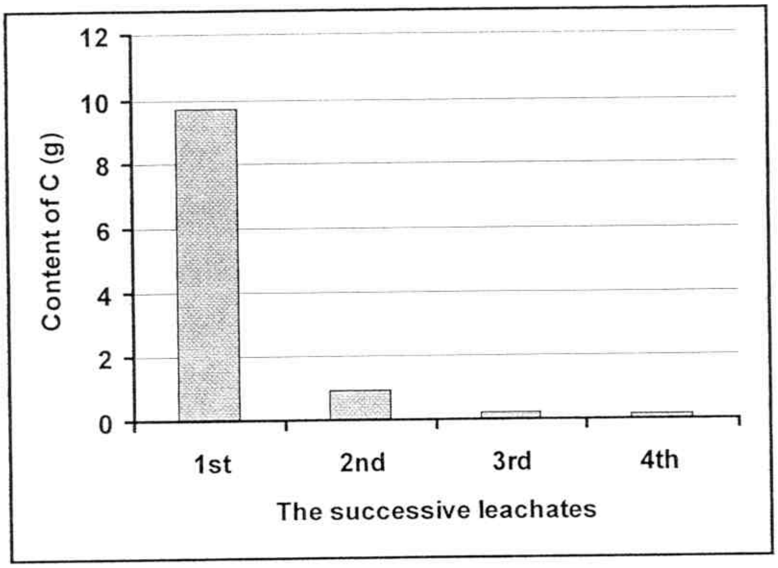

Fig. (9) Cl contents in the successive tap water leachates through Column No. 2.

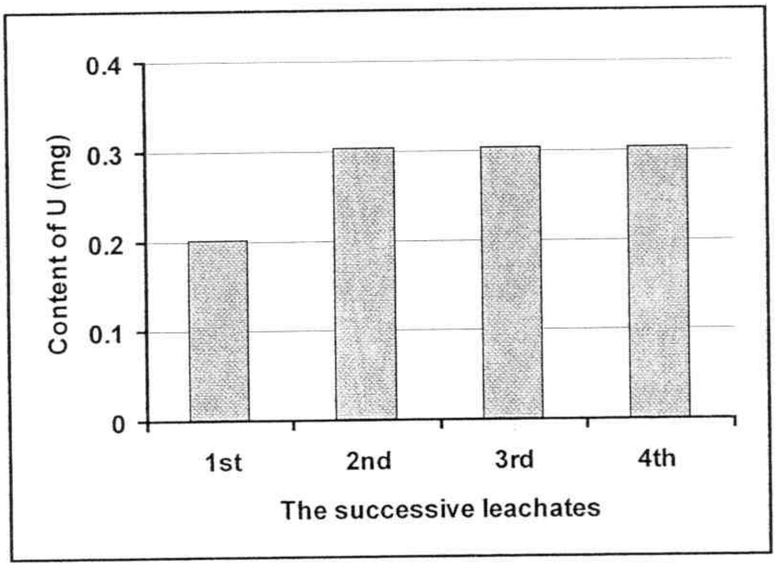

Fig. (10) U contents in the successive tap water leachates through column No. 2

Table 10 and Figs. (11 and 12) represent values of both Cl and U in the tap water leachate from column No. 3. The concentration of Cl in the first leachate was 123.74 g/L, while its concentration in the last one was 0.62 g/L. The efficiency of Cl washing was 68.31%. Neither Cu nor Zn was present in the outlet during washing in this column. Also, concentration of U in the first leachate was 3.03 mgUL^{-1}, while the corresponding concentration in the last one was 4.04 mgUL^{-1}. The efficiency of U washing was 0.86%. The chloride contents in successive leachates of column (3) during the washing processes Nos.1,2,3 and 4 were 12.37, 0.48, 0.40 and 0.40mg, respectively. Figs. (11 and 12) illustrate the relationships between the successive tap water leachates and their corresponding contents of Cl^- and U, respectively. It could be detected from these figures that while Cl^- content tended to decrease by increasing number of leachate,the opposite was true for U whose content increased with increasing number of leachate.

Table (10). Effect of washing by tap water on Cl-, U, Cu and Zn contents in the successive water leachates (column No. 3) of the shale deposit.

S.No.	Sprinkling solution			The water leachate (pregnant solution)										
	Type	V_1, ml	R_1, ml/min	V_2, ml	pH	R_2, ml/min	Chloride		Uranium		Copper		Zinc	
							Cont. (g)	Eff., %	Cont., (mg)	Eff., %	Cont., (mg)	Eff., %	Cont. (mg)	Eff., %
1st	Tap water	400	1.0 – 1.5	100	6.8	0.35	12.37	68.31%	0.30	0.86%	Nil	Nil	Nil	Nil
2nd				100	7.34	0.40	0.48		0.33		Nil		Nil	
3rd				100	7.7	0.45	0.07		0.40		Nil		Nil	
4th				100	7.8	0.45	0.06		0.40		Nil		Nil	
							12.98		1.43					

- See footnote Table (8).

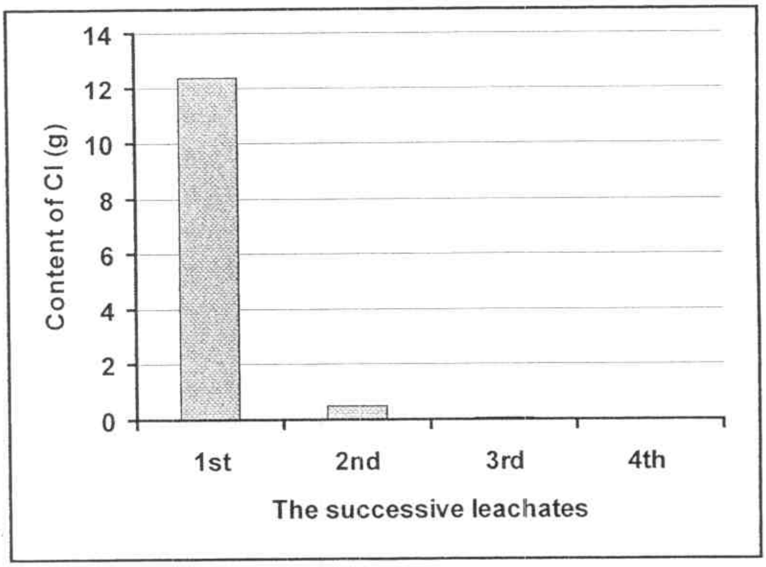

Fig. (11): Cl contents in the successive tap water leachates through column No. 3.

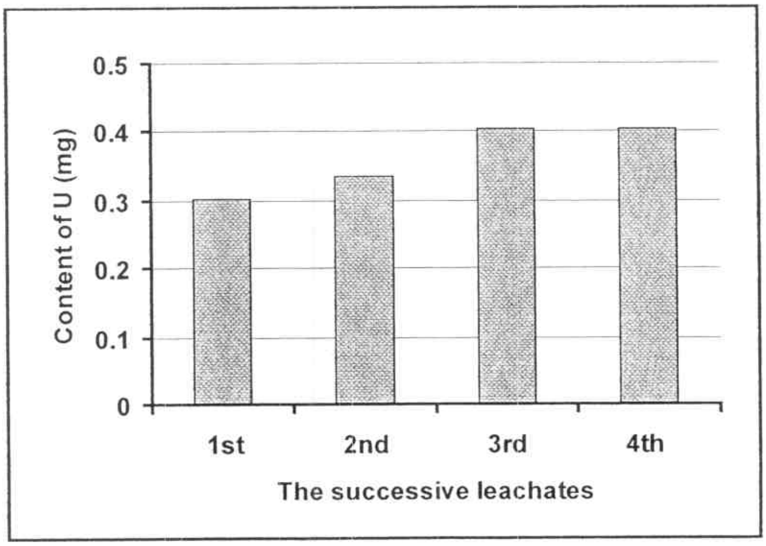

Fig. (12): U contents in the successive tap water leachates through column No. 3.

In the column No. 4, Table 11 and Figs. (13 and 14), the concentration of Cl^- in first leachate was 97.30 g/L, while in the last one it was 0.9 g/L. The efficiency of Cl^- washing was 66.6% Neither Cu nor Zn was present in the outlet during washing in this column. Also, concentration of U in the first leachate was 2.02 $mgUL^{-1}$, while the corresponding concentration in the last leachate sample was 3.03 $mgUL^{-1}$. The efficiency of U washing was 0.54%. The Cl contents in the successive leachate of column (4) during washing processesNo.s.1,2,3and 4 were 9.73, 2.29, 0.54 and 0.09g, respectively, while the corresponding U contents were 0.20, 0.20, 0.20 and 0.30 mg, respectively. Figs. (13 and 14) illustrate that both Cl^- and U contents although followed different patterns with increasing number of leachate, yet these patterns were ,to a great extent, similar to those achieved in columns Nos.1,2 and3.

Table (11). Effect of washing by tap water on Cl-, U, Cu and Zn contents in the successive water leachates (column No. 4) of the shale deposit.

S.No.	Sprinkling solution			The water leachate (pregnant solution)										
	Type	V_1, ml	R_1, ml/min	V_2, ml	pH	R_2, ml/min	Chloride		Uranium		Copper		Zinc	
							Cont. (g)	Eff., %	Cont., (mg)	Eff., %	Cont., (mg)	Eff., %	Cont. (mg)	Eff., %
1st	Tap water	400	1.0 – 1.5	100	6.25	0.30	9.73	66.16%	0.20	0.54%	Nil	Nil	Nil	Nil
2nd				100	6.82	0.35	2.29		0.20		Nil		Nil	
3rd				100	7.12	0.45	0.54		0.20		Nil		Nil	
4th				100	6.5	0.45	0.09		0.30		Nil		Nil	
							12.65		0.90					

- **See footnote Table (8).**

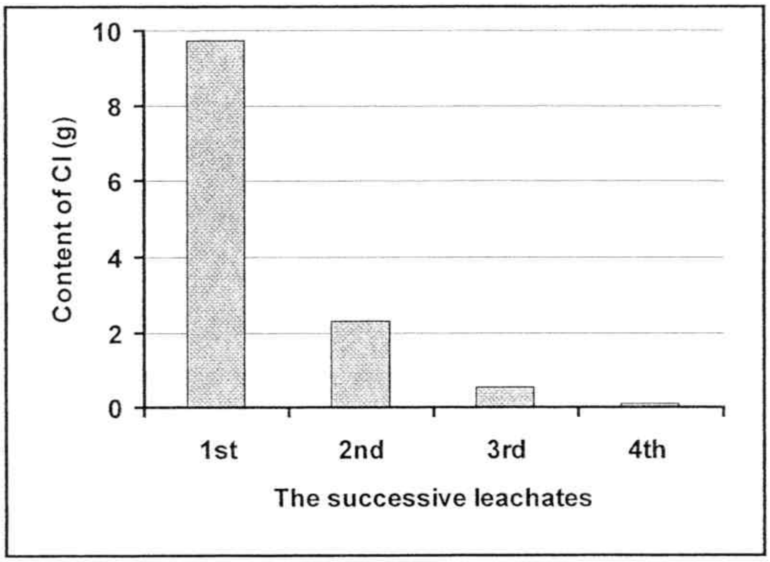

Fig.(13): Cl contents in the successive tap water leachates through column No. 4.

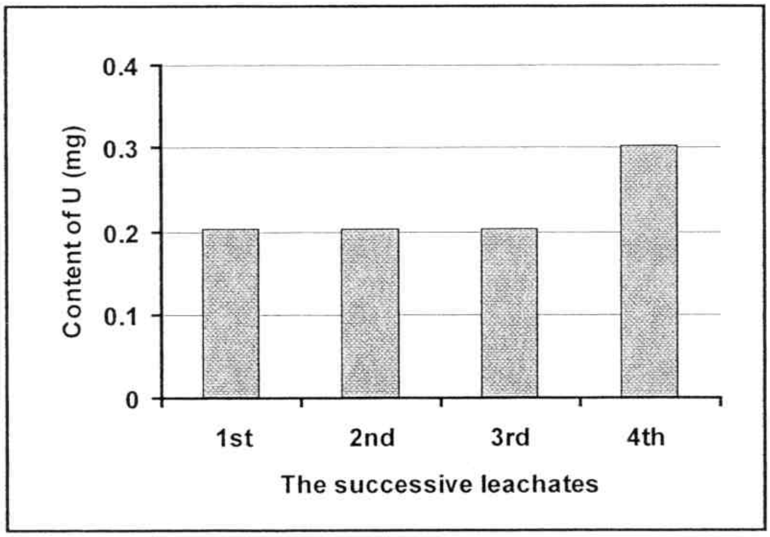

Fig. (14): U contents in the successive tap water leachates through column No. 4.

Data presented in Table 12 and illustrated graphically by Figs.(15and16) reveal that Cl^-content of first leachate was 5.8 g while that of the last leachate was 0.08 g. These Cl^- contents correspond Cl^- concentration in first leachate of 58.07 g/L, and Cl^- concentration of the last leachate of 0.8 g/L. The efficiency of Cl washing was 65.73%. Neither Cu nor Zn was present in the outlet during washing in this column. Also, U content of the first leachate was 0.20mg while the corresponding content of the last leachate was 0.30mg.These contents correspond to U concentration of 2.02 $mgUL^{-1}$ in the first leachate and U concentration of 3.03 $mgUL^{-1}$ in the last leachate. The efficiency of U washing was 0.55%. The Cl contents in the successive leachates of column (5) during the washing processes Nos.1,2,3and4 were 5.80, 2.73, 3.87 and 0.08g, respectively, while the corresponding U contents were 0.20, 0.20, 0.20 and 0.30mg, respectively. Figs. (15 and16) illustrate the relationships between No of the successive tap water leachate contents of Cl^- and U and the successive tap water leachates through column No.5.

Table (12). Effect of washing by tap water on Cl-, U, Cu and Zn contents in the successive water leachates (column No. 5) of the shale deposits.

S.No.	Sprinkling solution			The water leachate (pregnant solution)										
	Type	V_1, ml	R_1, ml/min	V_2, ml	pH	R_2, ml/min	Chloride		Uranium		Copper		Zinc	
							Cont. (g)	Eff., %	Cont., (mg)	Eff., %	Cont., (mg)	Eff., %	Cont. (mg)	Eff., %
1st	Tap water	400	1.0 – 1.5	100	6.22	0.30	5.80	65.73%	0.20	0.53%	Nil	Nil	Nil	Nil
2nd				100	6.38	0.35	2.73		0.20		Nil		Nil	
3rd				100	7.24	0.40	3.87		0.20		Nil		Nil	
4th				100	7.30	0.45	0.08		0.31		Nil		Nil	
							12.49		0.90					

- **See footnote Table (8).**

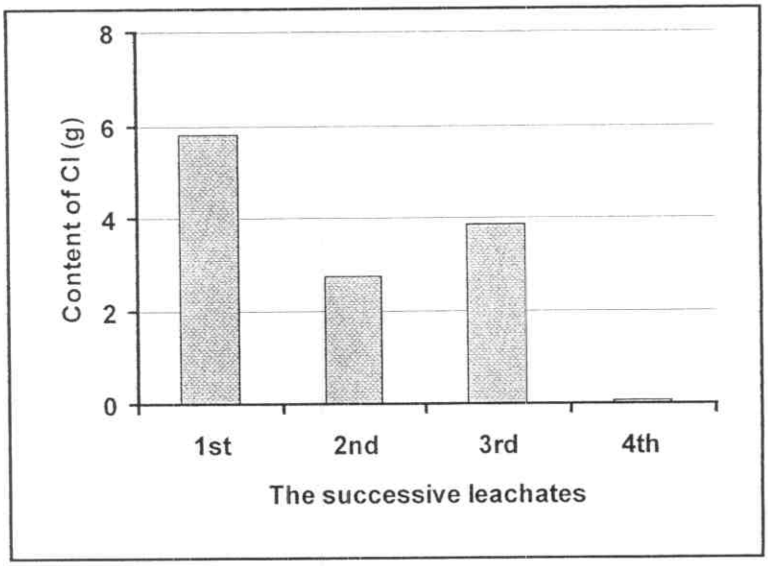

Fig. (15): Cl contents in the successive tap water leachates through column No. 5.

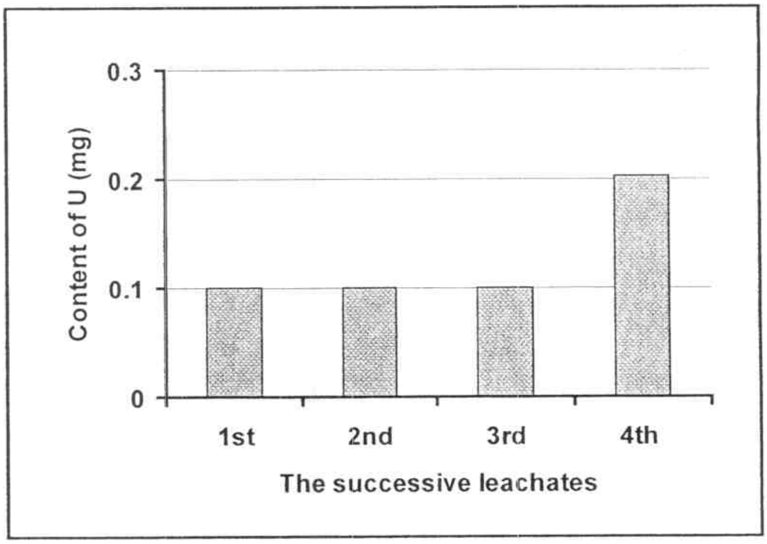

Fig. (16): U contents in the successive tap water leachates through column No. 5.

Similar to what occurred upon leaching of column No.5 with the tap water, leaching column No.6 with this water caused Cl content to be 9.41 g in the first leachate whereas it decreased it in the last leachate to 0.11 g. (Table 13 and Figs., 17 and 18). The corresponding Cl^- concentration of the first leachate was 94.10 g/L, while the concentration of Cl^- in the last leachate was 1.10 g/L. The efficiency of Cl washing was 59.58%. Neither Cu nor Zn was present in the outlet during washing in this column. Also,U concentration in the first leachate was 1.01 $mgUL^{-1}$, while the corresponding concentration the last leachate sample was 2.02 $mgUL^{-1}$. The efficiency of U washing was 0.42%. The Cl contents in successive leachates of the column No. (6) during the washing processes Nos.1,2,3 and 4 were 9.41, 1.405, 0.396 and 0.11 g, respectively, while the corresponding U contents were 0.101, 0.202, 0.202 and 0.202 mg, respectively. Figs. (17 and 18) illustrate the relationship between the Nos.of successive tap water leachates and the corresponding contents of each of Cl^- and U, respectively.

Table (13). Effect of washing by tap water on Cl-, U, Cu and Zn contents in the successive water leachates (column No. 6) of theshale deposit.

S.No.	Sprinkling solution			The water leachate (pregnant solution)										
	Type	V_1, ml	R_1, ml/min	V_2, ml	pH	R_2, ml/min	Chloride		Uranium		Copper		Zinc	
							Cont. (g)	Eff., %	Cont., (mg)	Eff., %	Cont., (mg)	Eff., %	Cont. (mg)	Eff., %
1st	Tap water	400	1.0 – 1.5	100	6.36	0.25	9.41	59.52%	0.10	0.42%	Nil	Nil	Nil	Nil
2nd				100	3.14	0.30	1.40		0.20		Nil		Nil	
3rd				100	6.39	0.35	0.39		0.20		Nil		Nil	
4th				100	6.89	0.35	0.11		0.20		Nil		Nil	
							11.31		0.70					

- **See footnote Table (8).**

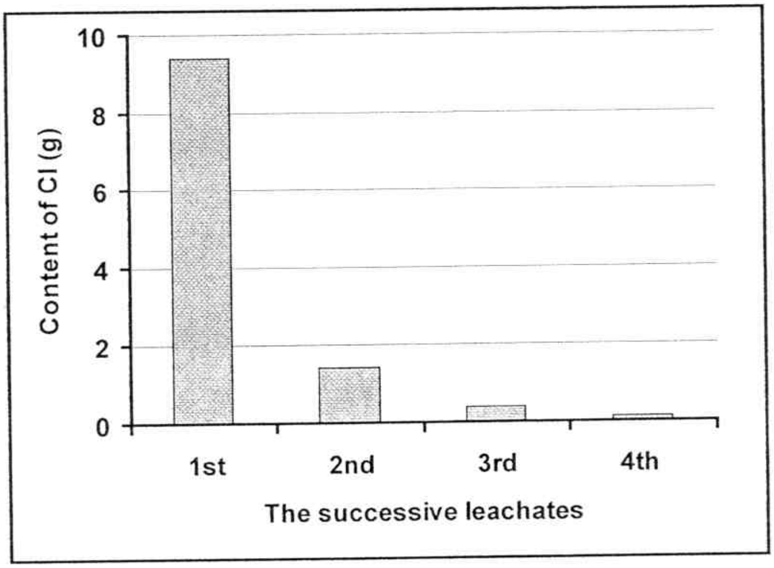

Fig. (17): Cl contents in the successive tap water leachates through column No. 6.

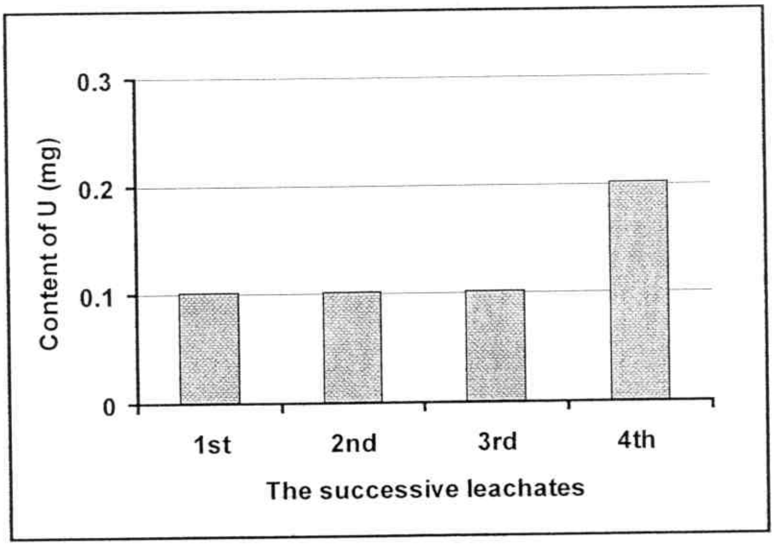

Fig. (18): U contents in the successive tap water leachates through column No. 6.

4.2.2. The leaching by H_2SO_4 process.

The leaching process by sulfuric acid was carried out on the six columns which were pre-washed with tap water as mentioned before. On these columns, sulfuric acid was used at different solid/liquid ratios and different acid concentrations:

Data present in Table 14 and illustrated graphically in Figs. (19) and (20) reveal that usage of H_2SO_4 acid at a ratio 1:1 and concentration of 2% was conducted downwards through column No.1 under the conditions presented in Table (14). The leach-liquor was collected five times, each of 200 mL volume. The U, Cu, Zn, Cl were measured in each volume, separately. Chloride leaching efficiency was 4.74%, while these of U, Cu and Zn were 1.7, 0.0015 and nile%, respectively.

The Cl contents in the leachates no.s.1,2,3and4 for column (1) were 0.158, 0.04, 0.024, 0.024 and 0.024 g, respectively. The corresponding U contents were 0.504, 0.504, 0.606, 0.606 and 0.606 mg, respectively.

Table (14). Effect of leaching by sulfuric acid at a concentration 2% and solid/liquid ratio of 1:1 on the successive acid leachate (column No. 1) of the shale deposit.

Chemical analysis of sample:
- Concentration of total chloride in the residual part = 5.630 g/kg.
- Concentration of total uranium in the residual part = 166.04 mg kg^{-1}
- Concentration of total Copper in the residual part = 6160.5mg kg^{-1}

S.No.	Sprinkling solution				The acid leachate (pregnant solution)										
	Type	Conc. of H_2SO_4 g/L	V_1, ml	R_1, ml/min	V_2, ml	pH	R_2, ml/min	Chloride		Uranium		Copper		Zinc	
								Cont. (g)	Eff., %	Cont., (mg)	Eff., %	Cont., (mg)	Eff., %	Cont. (mg)	Eff., %
1st	Sulfuric acid solution	20	1000	1.0 – 1.5	200	7.71	0.30	0.15	4.44%	0.50	1.68%	Nil	0.0015%	Nil	Nil
2nd					200	2.88	0.35	0.04		0.50		Nil		Nil	
3rd					200	2.01	0.25	0.02		0.60		0.05		Nil	
4th					200	1.88	0.30	0.02		0.60		0.04		Nil	
5th					200	1.85	0.30	0.02		0.60		Nil		Nil	
								0.25		2.8		0.09			

S.No. = Serial Number of the leachate.
V_1 = Total volume of sprinkling solution
R_1 = Rate of sprinkling solution
V_2 = Volume of leached sample
R_2 = Rate of leachate flow out of the column

Conc., = Concentration

Cont. = Content
pH = pH of the leachate
Eff.% = Efficiency

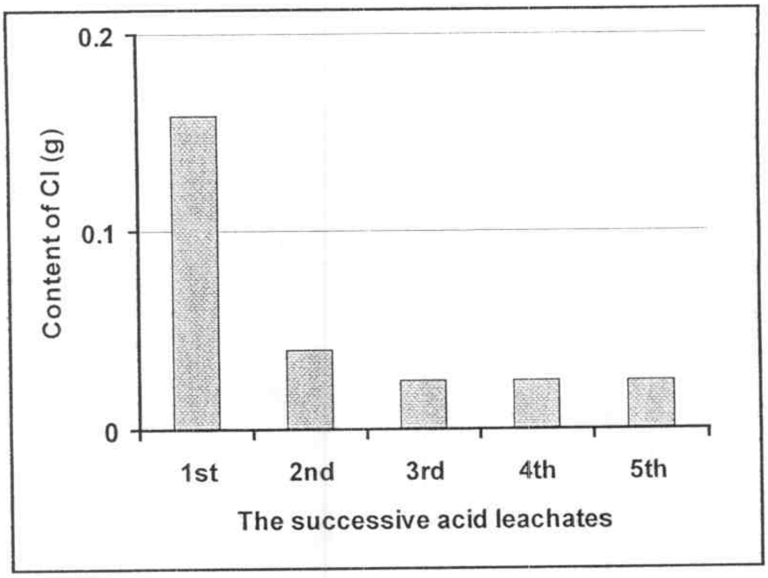

Fig. (19): Contents of Cl in the successive acid leachates (S/L ratio 1:1 and concentration 2%), Column No. 1

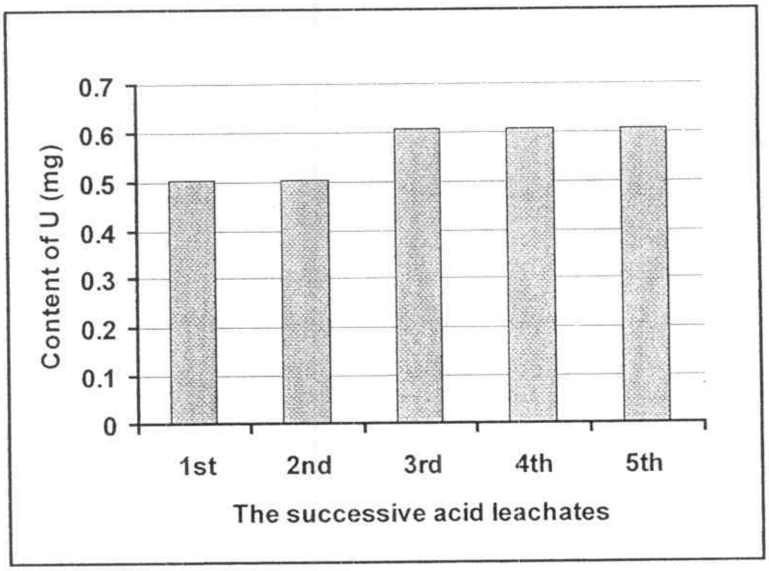

Fig. (20): Contents of U in the successive acid leachates (S/L ratio 1:1 and concentration 2%), Column No. 1

Data presented in Table (15) and illustrated graphically by Figs. (21, 22, 23 and 24) show effect of leaching by $H2SO_4$ acid at a ratio of 1:2 and concentration of 2% through column No.2 under the conditions presented in Table (15) on the contents of Cl , U, Cu and, Zn in the successive acid leachates. The leachliquor was collected ten times each of which is of 200 mL volume. The U , Cu , Zn Cl were measured in each volume separately.

Chloride leaching efficiency was 3.51% while those of U, Cu and Zn were 77.35, 5.34 and 33.37 %, respectively.

The Cl contents in the leachates Nos.1,2,3 and 4 for column (2) were 0.066, 0.052, 0.016, and 0.052g.In the leachates from No. 5 to No.10 the obtained values were almost costant and equal 0.016g, respectively. The corresponding U contents were 0.404, 0.404, 1.41, 1.41, 0.808, 3.03, 20.60, 45.36, 40.0 and 15.75mg, respectively. Also, the Cu contents in leachates No.1 to10 were 0.078, 0.108, 0.208,0.1050.147, 4.916, 57.30, 188.72, 40.94and 37.04mg,respectively.The corresponding Zn content was nil in sample No.1 to sample No.5, contents were ,186.19,451.14,302.7,182.01and 154.9mg Zn in leachates of Nos. 6 to 10,respectively.The aforementioned results illustrate that Cl content tended to decrease sharply by progressing leaching by sulfuric acid to an almost content of about o.o16 g. The content of U in the successive leachates took another pattern since it tended to increase by progressing leaching.The former pattern can be explained on the basis of leachability of Cl whether by water or acid. U compounds, on the other hand ,might interacted with sulfuric acid whose effect become more pronounced by progressing leaching.

Table (15). Effect of leaching by sulfuric acid at a concentration 2% and solid/liquid ratio of 1:2 on the successive acid leachate (Column 2) of the shale deposit.

* Chemical analysis of sample:
- Concentration of total chloride in the residual part = 7.95g/kg.
- Concentration of total uranium in the residual part = 165.78 mg kg^{-1}.
- Concentration of total Copper in the residual part = 6160.5 mg kg^{-1}.
- Concentration of total Zinc in the residual part = 3826.4 mg kg^{-1} .

S.No.	Sprinkling solution				The acid leachate (pregnant solution)										
								Chloride		Uranium		Copper		Zinc	
	Type	Conc. of H_2SO_4 g/L	V_1, ml	R_1, ml/min	V_2, ml	pH	R_2, ml/min	Cont. (g)	Eff., %	Cont., (mg)	Eff., %	Cont., (mg)	Eff., %	Cont. (mg)	Eff., %
1st	Sulfuric acid solution	20	2000	1.0 – 1.5	200	7.54	0.45	0.06	3.77%	0.40	77.9%	0.078	5.34%	Nil	33.37%
2nd					200	7.67	0.54	0.05		0.40		0.108		Nil	
3rd					200	8.16	0.51	0.02		1.41		0.208		Nil	
4th					200	8.10	0.50	0.05		1.41		0.105		Nil	
5th					200	7.74	0.45	0.02		0.2		0.147		Nil	
6th					200	6.79	0.51	0.02		3.03		4.916		186.19	
7th					200	4.32	0.51	0.02		20.60		57.30		451.14	
8th					200	4.16	0.50	0.02		45.36		188.72		302.70	
9th					200	3.89	0.50	0.02		40.0		40.94		182.01	
10th					200	3.80	0.50	0.02		15.75		37.04		154.9	
							0.3			129.17		329.59		1276.94	

- See footnote Table (14).

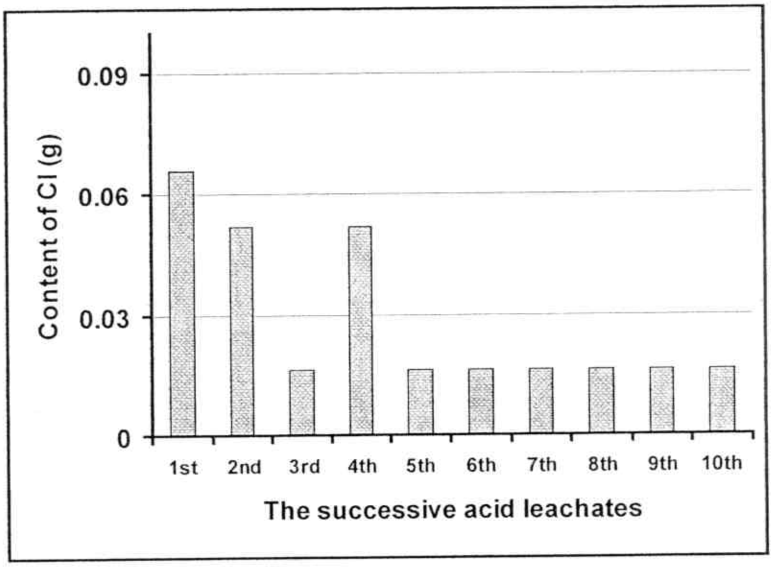

Fig. (21) Contents of Cl in the successive acid leachates (S/L ratio 1:2 and concentration 2%), Column No. 2.

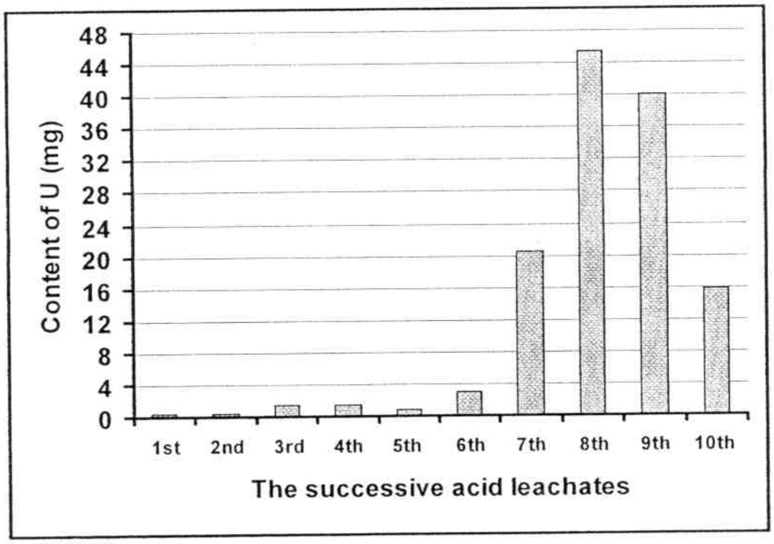

Fig. (22) Contents of U in the successive acid leachates (S/L ratio 1:2 and concentration 2%), Column No. 2.

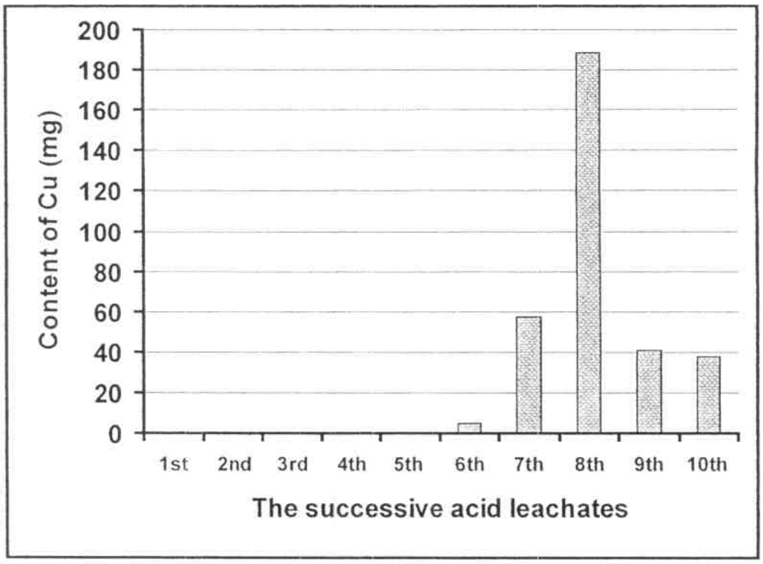

Fig. (23) Contents of Cu in the successive acid leachates (S/L ratio 1:2 and concentration 2%), Column No. 2.

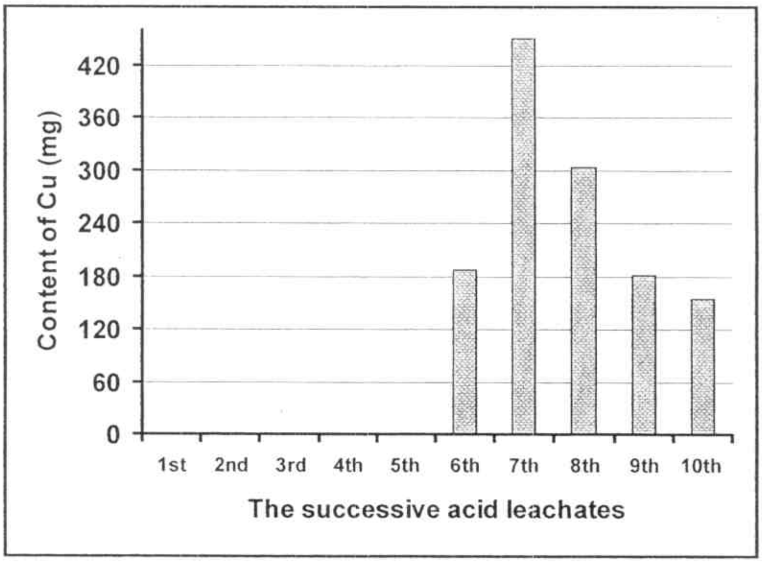

Fig. (24) Contents of Zn in the successive acid leachates (S/L ratio 1:2 and concentration 2%), Column No. 2.

Data presented in Table (16) and illustrated graphically in Figs. (25,26,27 and28) reveal that usage of $H2SO_4$ acid at a ratio of 1:3 and concentration 2% for washing the shale deposit downwards column No.3 caused various contents of U, Cu, Zn and Cl in each washing volume.The efficiency of leaching these elements ,therefore, varied widely Chloride leaching efficiency for example was 10.16%, while those of U, Cu and Zn were 86.22, 35.74 and 47.76%, respectively.

The Cl content in the leachates of column (3) were 0.12, 0.12, 0.09, 0.07, 0.06, 0.04, 0.024, 0.024, 0.024, 0.024 ,0.01 ,0.01 ,0.01 ,0.01 ,0.01 and 0.01g from sample No. 10 to sample 15 respectively. The corresponding U content were 0.808, 1.01, 1.1, 1.61, 2.22, 1.01, 1.81, 4.04, 4.04, 29.29, 22.3, 14.14, 10.50, 7.67 and 4.84mg, respectively.

The corresponding Cu content were 0.380, 0.694, 0.766, 1.46, 1.662, 0.26,0.220,1.87,78,37.52,261.84,456.0,457.52,455and453.6mg, respectively ,aswellas6.89, 8.35 ,2.93 ,7.32 ,9.12 ,7.01 ,22.25 ,440.8 ,411.23 ,301.12 ,144.14 ,132.76,126.59,93.0 and 76.0 mg ,for the Zn contents in this column ,respectively.The aforementioned results indicated to the higher efficiency of extraction U by Sulfuric acid at aconcentration of 2% and a ratio of 1:3 Solid/liquid than the other stuied toxic elements.

Table (16). Effect of leaching by sulfuric acid at a concentration 2% and solid/liquid ratio of 1:3 on the successive acid leachate (Column 3) of the shale deposit.

Chemical analysis of sample:
- Concentration of total chloride in the residual part = 5.94 g/kg.
- Concentration of total uranium in the residual part = 165.35 mg kg^{-}.

S.No.	Sprinkling solution				The acid leachate (pregnant solution)											
								Chloride		Uranium		Copper		Zinc	
	Type	Conc. of H_2SO_4 g/L	V_1, ml	R_1, ml/min	V_2, ml	pH	R_2, ml/min	Cont. (g)	Eff., %	Cont., mg)	Eff., %	Cont., (mg)	Eff., %	Cont. (mg)	Eff., %
1st	Sulfuric acid solution	20	3000 ml	1.0 – 1.5	200	7.5	0.40	0.12	10.3%	0.808	86.32%	0.380	35.79%	6.89	46.76%
2nd					200	2.72	0.40	0.12		1.01		0.694		8.35	
3rd					200	1.86	0.50	0.09		1.1		0.7660		2.93	
4th					200	7.2	0.50	0.07		1.61		1.460		7.32	
5th					200	7.13	0.40	0.06		2.22		1.662		9.12	
6th					200	7.73	0.38	0.04		1.01		0.26		7.01	
7th					200	6.68	0.50	0.024		1.81		0.220		22.25	
8th					200	5.52	0.38	0.024		4.04		0.187		440.8	
9th					200	2.32	0.45	0.024		40.4		78		411.23	
10th					200	2.69	0.50	0.01		29.29		37.52		301.12	
11th					200	2.12	0.40	0.01		22.3		261.84		144.14	
12th					200	2.19	0.40	0.01		14.14		456.0		132.76	
13th					200	3.5	0.40	0.01		10.50		457.52		126.59	
14th					200	3.5	0.40	0.01		7.67		455		93.0	
15th					200	3.5	0.40	0.01		4.84		453.6		76.0	
								0.612		142.74		2205.1		1789.46	

- **See footnote Table (14).**

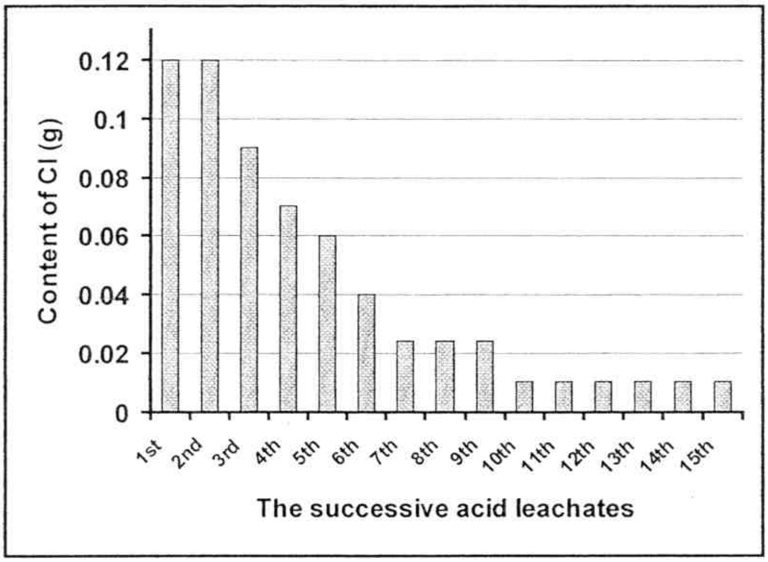

Fig. (25) Contents of Cl in the successive acid leachates (S/L ratio 1:3 and concentration 2%), Column No. 3

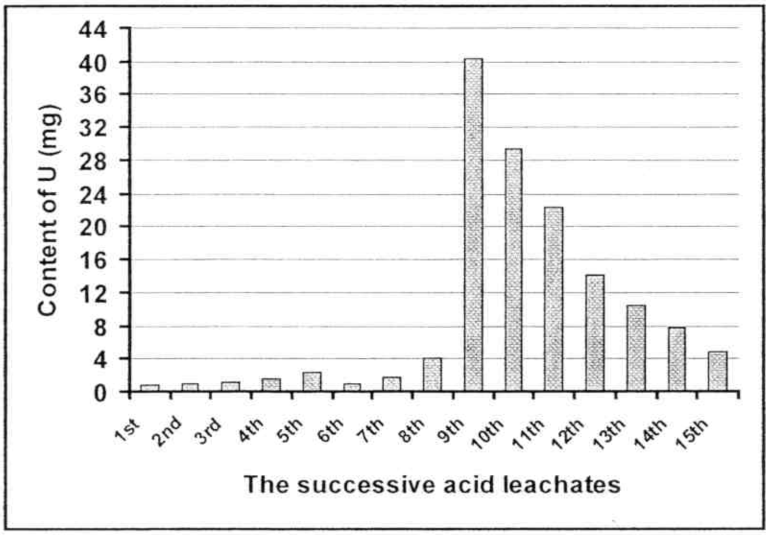

Fig. (26)Contents of U in the successive acid leachates (S/L ratio 1:3 and concentration 2%), Column No. 3

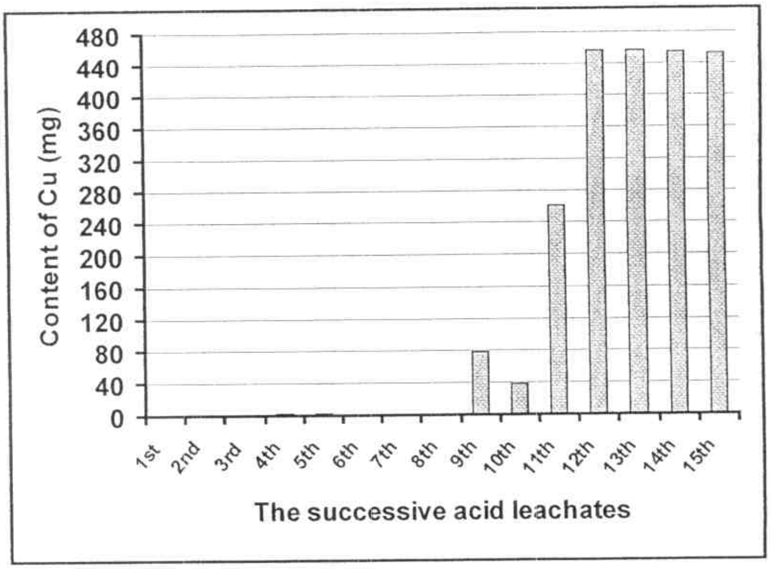

Fig. (27) Contents of Cu in the successive acid leachates (S/L ratio 1:3 and concentration 2%), Column No. 3.

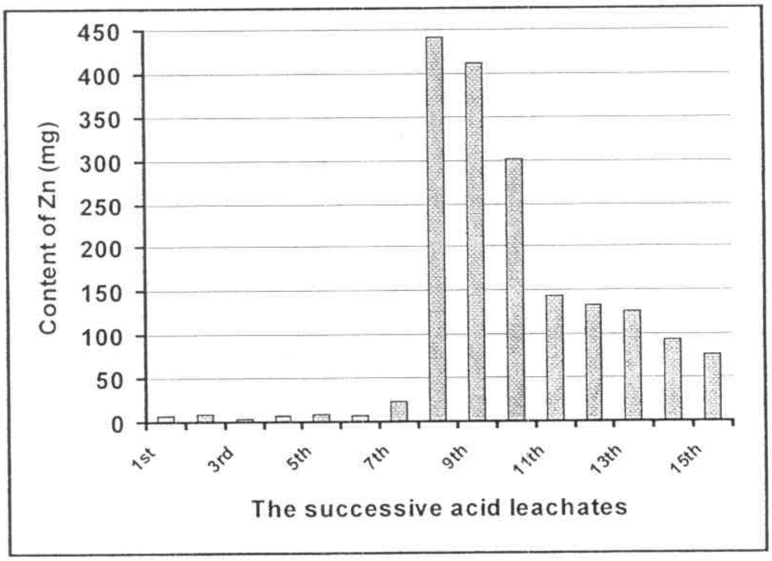

Fig. (28) Contents of Zn in the successive acid leachates (S/L ratio 1:3 and concentration 2%), Column No. 3

The procedure was carried out for other three columns, with 5% H2SO$_4$acid concentration.

Data presented in Table (17) and illustrated graphically in Figs. (29,30 and 31) reveal that leaching the shale deposit in column No.4 by H2SO$_4$ acid at a ratio of 1:1 and a concentration of 5% under the conditions presented in Table (17) resulted in different contents of U, Cu, Zn and Cl in each 200 mL collected leachliqure. As a final product of the successive leaching, chloride leaching efficiency was 3.31% while those of U, Cu and Zn were 8.73, 0.032 and nil%, respectively.

The Cl contents in the five leachates of column (4) were 0.158, 0.07, 0.04, 0.05 and 0.05g, respectively. The corresponding U contents were 0.606, 6.86, 0.70, 1.07 and 11.51 mg, respectively while those of Cu were 0.28 ,0.17 , 504 ,0.36 and 0.62 mg, resepectivey.These results indicate that sulfuric acid at a concentration of 5% and a solid/liquid ratio of 1:1 was not quite enough for extracting the poisonous elements out of the used shale deposit sample.

Table (17). Effect of leaching by sulfuric acid at a concentration 5% and solid/liquid ratio of 1:1 on the successive acid leachate (Column 3).

* Chemical analysis of sample:
- Concentration of total chloride in the residual part = 6.24 g/kg.
- Concentration of total uranium in the residual part = 166.01 mg kg^{-1}
- Concentration of total copper in the residual part = 6160.5 mg kg-1
- Concentration of total zinc in the residual par = 3826.5 mg kg-1

S.No.	Sprinkling solution				The acid leachate (pregnant solution)										
	Type	Conc. of H_2SO_4 g/L	V_1, ml	R_1, m/min	V_2, ml	pH	R_2, ml/min	Chloride		Uranium		Copper		Zinc	
								Cont. (g)	Eff., %	Cont., (mg)	Eff., %	Cont., (mg)	Eff., %	Cont. (mg)	Eff., %
1st	Sulfuric acid solution	50	1000	1.0 – 1.5	200	5.32	0.45	0.15	5.76%	0.60	8.73%	0.28	0.03%	Nil	Nil
2nd					200	5.15	0.40	0.07		0.68		0.17		Nil	
3rd					200	2.63	0.40	0.04		0.70		0.50		Nil	
4th					200	3.55	0.40	0.05		1.01		0.36		Nil	
5th					200	3.38	0.40	0.05		11.51		0.62		Nil	
								0.36		14.51		1.93		Nil	

- **See See footnote Table (14).**

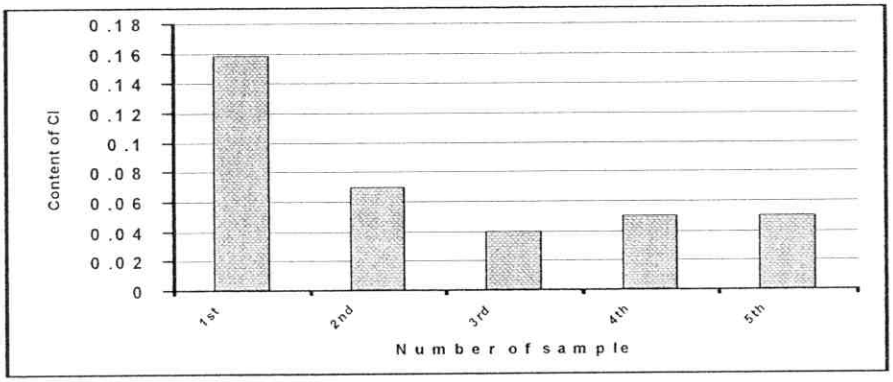

Fig. (29) Contents of Cl in the successive acid leaching (solid/liquid ratio 1:3 and acid concentration 5%) column No. 4.

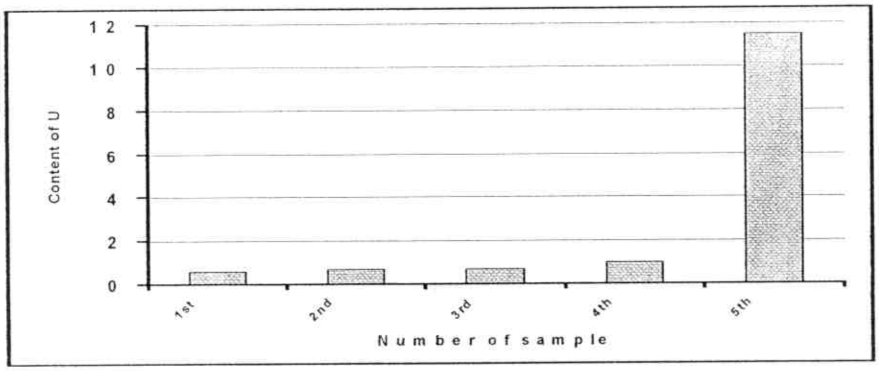

Fig. (30) Contents of U in the successive acid leaching (solid/liquid ratio 1:3 and acid concentration 5%) column No. 4.

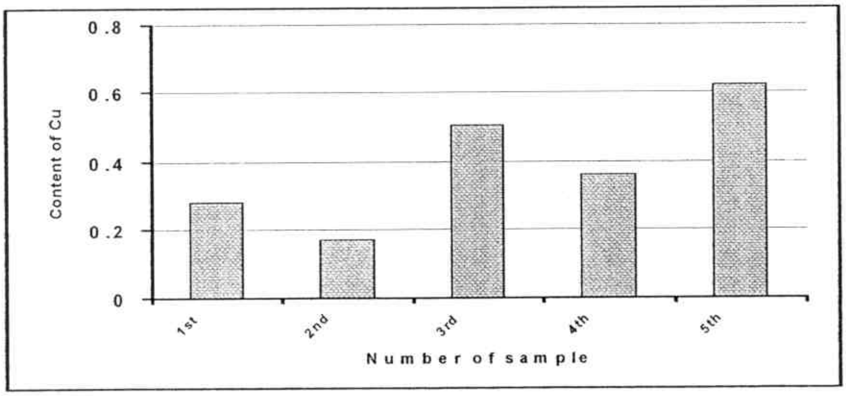

Fig. (31) Contents of Cu in the successive acid leaching (solid/liquid ratio 1:3 and acid concentration 5%) column No. 4.

Data presented in Table (18) and Figs. (32,33,34 and 35), reveal the effect of leaching by H2SO$_4$ acid at ratio of 1:2 and concentration 5% on extraction of the poisonous elements out of the shale deposit placed in column No.5 under the condition presented in Table (18). The leachliquir was collected ten times each of 200mL volume. The U, Cu, Zn and Cl were measured in each volume separately. Chloride leaching efficiency was 13.76%, while those of U, Cu and Zn were 71.98, 62.48 and 47.09%, respectively. The Cl contents in column (5) during leaching processes Nos.1to10 were 0.16, 0.142, 0.138, 0.106, 0.09, 0.06, 0.05, 0.05, 0.05 and 0.05 g, respectively. The corresponding U contents were 0.62, 0.79, 1.01, 1.41, 37.16, 23.02, 25.04, 16.06, 8.08 and 6.26 mg, respectively, Also, the Cu contents were 0.064, 0.11, 0.48, 0.256, 80.77, 529.46, 1080.2, 880.42, 707.6 and 570.0 mg, while the corresponding contents of Zn were nil, nil, nil, 17.158, 627.84, 469.24, 235.92, 170.0, 137.33 and 144 mg, respectively. It is obvious, generally, that in spite of usage of the same concentration of sulfuric acid, yet increasing the solid/liquid ratio to 1:2 caused the efficiency of the extraction process to increase as compared with the solid /liquid ratio of 1:1 Such a finding might by attributed to providing conditions more suitable for extraction of the studied elements by increasing amount of the applied acid.

Table (18). Effect of leaching by sulfuric acid at a concentration 5% and solid/liquid ratio of 1:2 on the successive acid leachate (Column 5).

* Chemical analysis of sample:
- Concentration of total chloride in the residual part = 6.35 g/kg.
- Concentration of total uranium in the residual part = 165.88 mg kg^{-1}.

S.No.	Sprinkling solution				The acid leachate (pregnant solution)										
								Chloride		Uranium		Copper		Zinc	
	Type	Conc. of H_2SO_4 g/L	V_1, ml	R_1, m/min	V_2, ml	pH	R_2, ml/min	Cont. (g)	Eff., %	Cont., (mg)	Eff. , %	Cont., (mg)	Eff. , %	Cont. (mg)	Eff., %
1st	Sulfuric acid solution	50	2000	1.0 – 1.5	200	7.55	0.40	0.16	14.11%	0.62	71.985%	0.064	62.48%	Nil	47.09%
2nd					200	7.20	0.45	0.14		0.79		0.110		Nil	
3rd					200	6.95	0.50	0.14		1.01		0.482		Nil	
4th					200	2.30	0.45	0.11		1.41		0.256		17.158	
5th					200	3.98	0.45	0.09		37.10		80.77		627.84	
6th					200	3.63	0.45	0.06		23.02		529.46		469.24	
7th					200	3.45	0.45	0.05		25.04		1080.2		235.92	
8th					200	2.34	0.45	0.05		16.16		880.42		170.41	
9th					200	2.30	0.45	0.05		8.08		707.6		137.33	
10th					200	2.20	0.45	0.05		6.26		570.0		144	
								0.89		119.55		3849.4		1801.9	

- **See See footnote Table (14).**

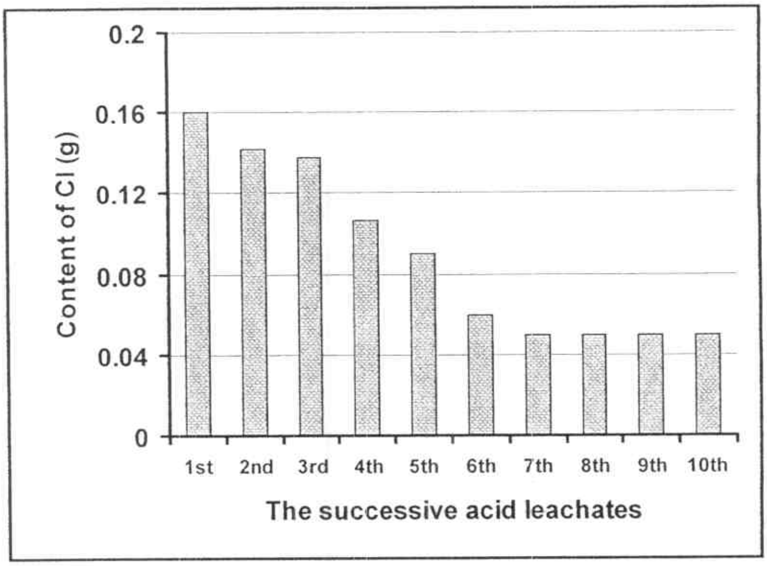

Fig. (32) Contents of Cl in the successive acid leaching (solid/liquid ratio 1:2 and acid concentration 5%) column No. 5.

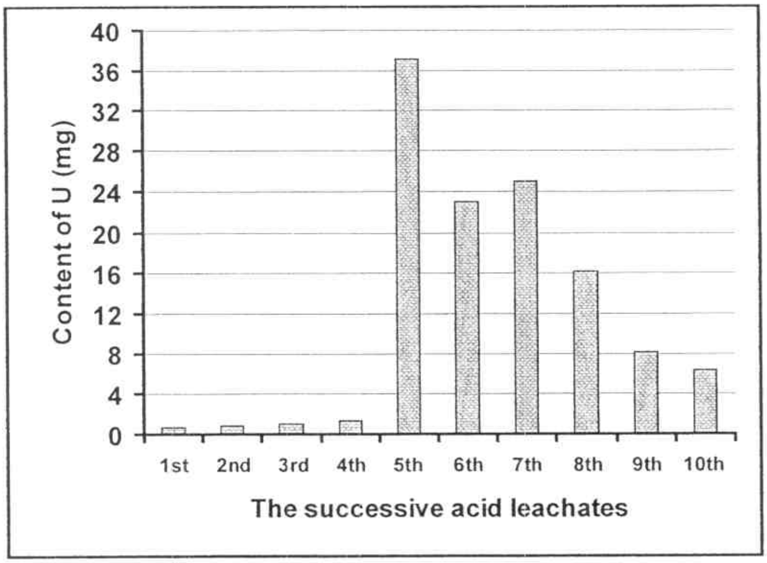

Fig. (33) Contents of U in the successive acid leaching (solid/liquid ratio 1:2 and acid concentration 5%) column No. 5.

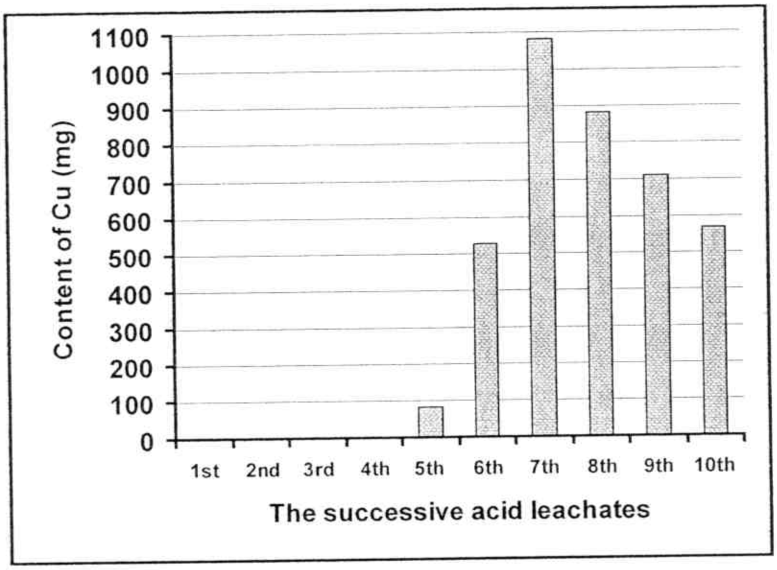

Fig. (34) Contents of Cu in the successive acid leaching (solid/liquid ratio 1:2 and acid concentration 5%) column No. 5.

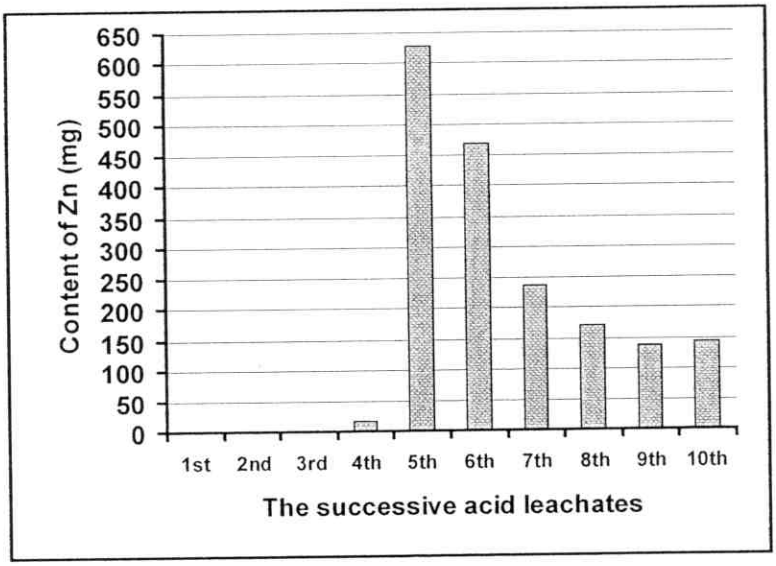

Fig. (35) Contents of Zn in the successive acid leaching (solid/liquid ratio 1:2 and acid concentration 5%) column No. 5.

Effect of $H2SO_4$ at a concentration of 5% and solid/liquid ratio of 1:3 on extraction of the poisonous studied elements is illustrated by data presented in Table (19) and Figs. (36,37,38 and39). The leachliquor was collected fifteen times, each of 200mL volume and used for measuring the studied poisonous elements. Chloride leaching efficiency was 16.40% Cl. while those of U, Cu and Zn were 83.27, 84.21 and 55.01% , respectively. The Cl contents in the leachates of column No.6 were 0.18, 0.16, 0.14, 0.11, 0.09, 0.07, 0.06, 0.07, 0.07, 0.07 and 0.06g for the leachates No.1 to No.11 and tended to be almost constant of. o,o6 g up to leachate No.15 The corresponding U contents were0.40 ,0.62 ,0.80 ,1.01 ,1.41 ,4.64 ,40.84 ,27.06 ,18.89 ,10.1 ,8.88 ,8.48 ,6.06 ,4.64 and 4.64 mgvs 0.009 ,0.334 ,0.606 ,0.442 ,0.720 ,3.908 ,644.4 ,915.5 ,562.32 ,592.72 ,665.4 ,456 ,457.4 ,455.1 and 432.52 mg for C , and. Nil ,23.17 ,21.98 ,5.97 ,nil ,238.54 ,739.2 ,270 ,7.17 ,172.08 ,146.1 ,138.02 ,140 ,116 and 87 mg for Zn, respectively. It is of importance to indicate that efficiency of extraction of all the studied poisonous elements increased by increasing the solid/liquid ratio. However, the comparison between the results obtained by acid at a concentration of 2% and those obtained by the same acid but at a concentration of 5% reveal that the former concentration showed higher efficiency values for extraction of uranium while the latter concentration was of higher superiority for extraction of Cl, Cu and Zn

Table (19). Effect of leaching by sulfuric acid at a concentration 5% and solid/liquid ratio of 1:3 on the successive acid leachate (Column 6).

* Chemical analysis of sample: - Concentration of total chloride in the residual part =7.6g/kg.
- Concentration of total uranium in the residual part = 166.09 mg kg^{-1}.

S.No.	Sprinkling solution				The acid leachate (pregnant solution)										
								Chloride		Uranium		Copper		Zinc	
	Type	Conc. of H_2SO_4 g/L	V_1, ml	R_1, ml/min	V_2, ml	pH	R_2, ml/min	Cont. (g)	Eff., %	Cont., (mg)	Eff., %	Cont., (mg)	Eff., %	Cont. (mg)	Eff., %
1st	Sulfuric acid solution	50	3000 ml	1.0 – 1.5	200	7.52	0.45	0.18	16.40%	0.404	83.27%	0.009	84.21%	Nil	55.01%
2nd					200	7.42	0.45	0.16		0.620		0.334		23.17	
3rd					200	2.67	0.50	0.14		0.808		0606		21.98	
4th					200	2.44	0.50	0.11		1.01		0.442		5.97	
5th					200	6.80	0.50	0.09		1.41		0.720		Nil	
6th					200	1.50	0.50	0.07		4.64		3.908		23845	
7th					200	2.41	0.45	0.06		40.84		644.4		739.2	
8th					200	1.81	0.45	0.07		27.06		915.52		270	
9th					200	3.51	0.50	0.07		18.89		562.32		7.17	
10th					200	3.50	0.50	0.07		10.1		592.72		172.08	
11th					200	3.42	0.55	0.06		8.88		665.4		146.10	
12th					200	2.87	0.65	0.06		8.48		456		138.02	
13th					200	2.27	0.55	0.06		6.06		457.4		140.0	
14th					200	2.38	0.50	0.06		4.64		455.1		116.0	
15th					200	2.35	0.50	0.06		4.64		432.5		87	
								1.26		138.5		5187.85		2104.9	

- See See footnote Table (14).

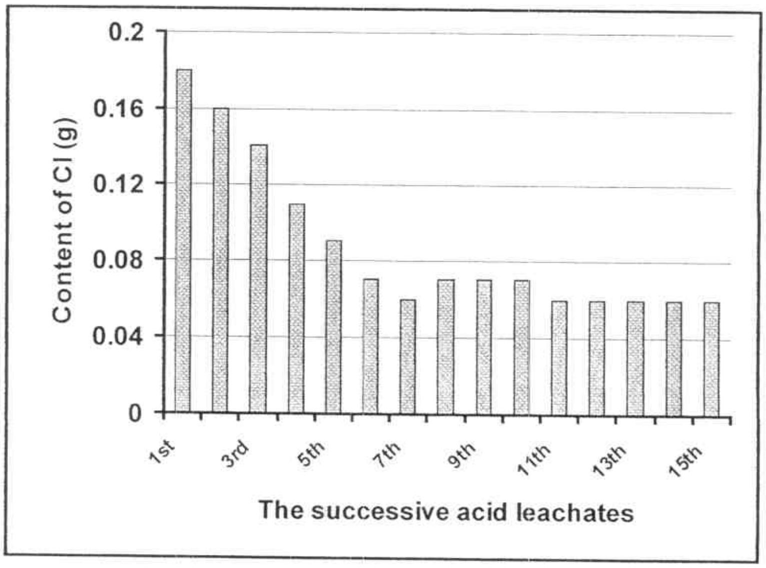

Fig. (36) Contents of Cl in the successive acid leaching (solid/liquid ratio 1:3 and acid concentration 5%) column No. 6.

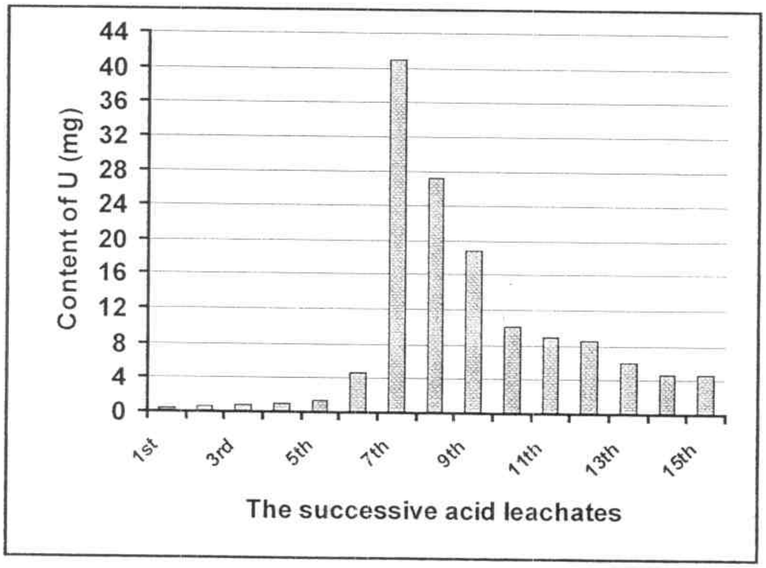

Fig. (37) Contents of U in the successive acid leaching (solid/liquid ratio 1:3 and acid concentration 5%) column No. 6.

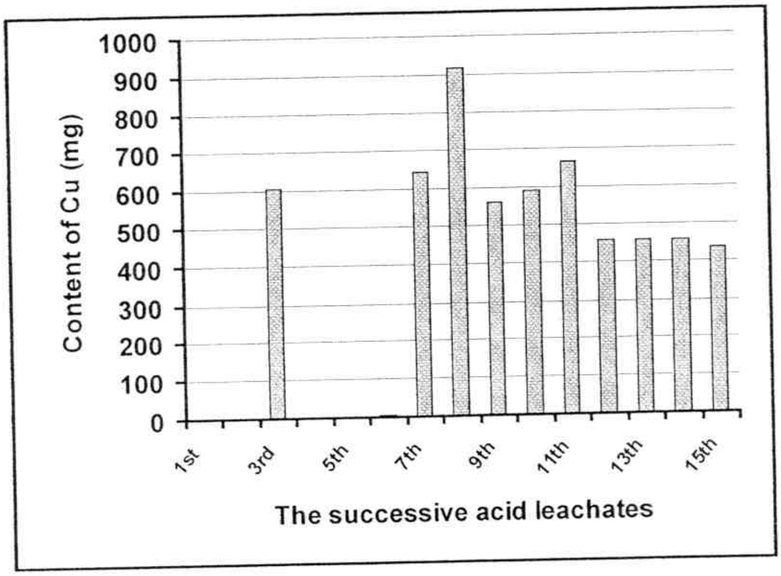

Fig. (38) Contents of Cu in the successive acid leaching (solid/liquid ratio 1:3 and acid concentration 5%) column No. 6.

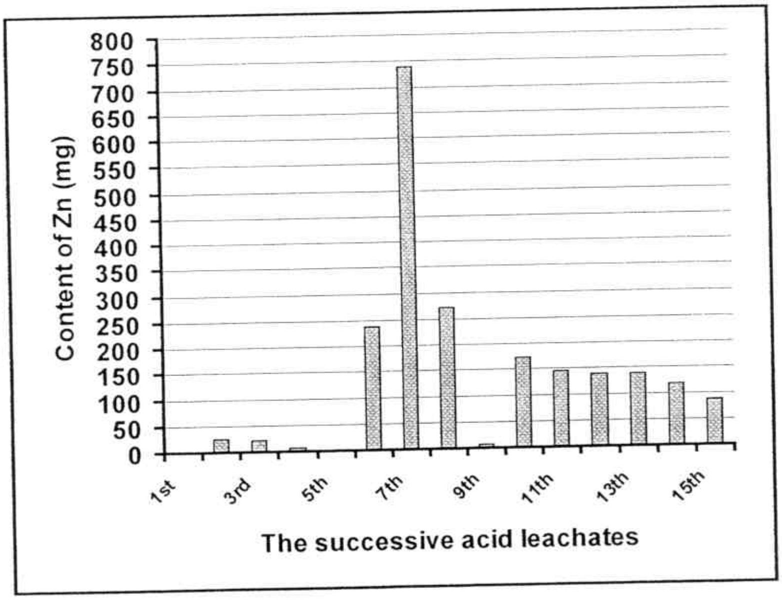

Fig. (39) Contents of Zn in the successive acid leaching (solid/liquid ratio 1:3 and acid concentration 5%) column No. 6

4.3.Effect of H2SO$_4$ acid concentration and solid : liquid ratio on the mineralogical properties of the shale deposit sample:

X-ray diffraction analysis was undertaken for 6 shale subsamples representing the different acid concentration and solid / liquid ratios.

X-ray diffraction patterns of clay fraction separated from the shale subsamples after being leached using the different acid concentrations and the different solid/liquid ratios are given in Table (20) and Figs. (40, 41 ,42 ,43 ,44 and 45).

Table (20). Semi-quantitative estimation of the clay fraction separated from the studied shale sample.

Conc. of acid leaching solution	Solid / liquid ratios	Clay minerals%		
		Kaolinite	Illite	Quartz
2%	1 : 1	70.0	15.0	15.0
	1 : 2	65.0	12.0	23.0
	1 : 3	60.0	10.0	30.0
5%	1 : 1	69.0	12.0	19.0
	1 : 2	60.0	10.0	30.0
	1 : 3	57.0	8.0	35.0

Data reveal that kaolinite as a clay mineral dominated among the clay minerals in the studied shale subsamples followed by illite while quartz was the dominant associated mineral.

With regard to effect of the acid concentration and the different solid/liquid ratios, data in Table (20) show that increasing the acid concentration and solid/liquid ratio resulted in decreaseing the percentage of both koalinite and illite minerals. This finding might be due to the effect of the added acid on increasing solubilization of the silicate minerals. While,the revers was true for quartz,since its percentages tended to increase by increasing both acid concentration and solid/liquid ratio due to its resistant to be weathered under the applied acid concentrations and solid/liquid ratios.on one hand and the relative decrease in percentages of the both kaolinite and on the other one.

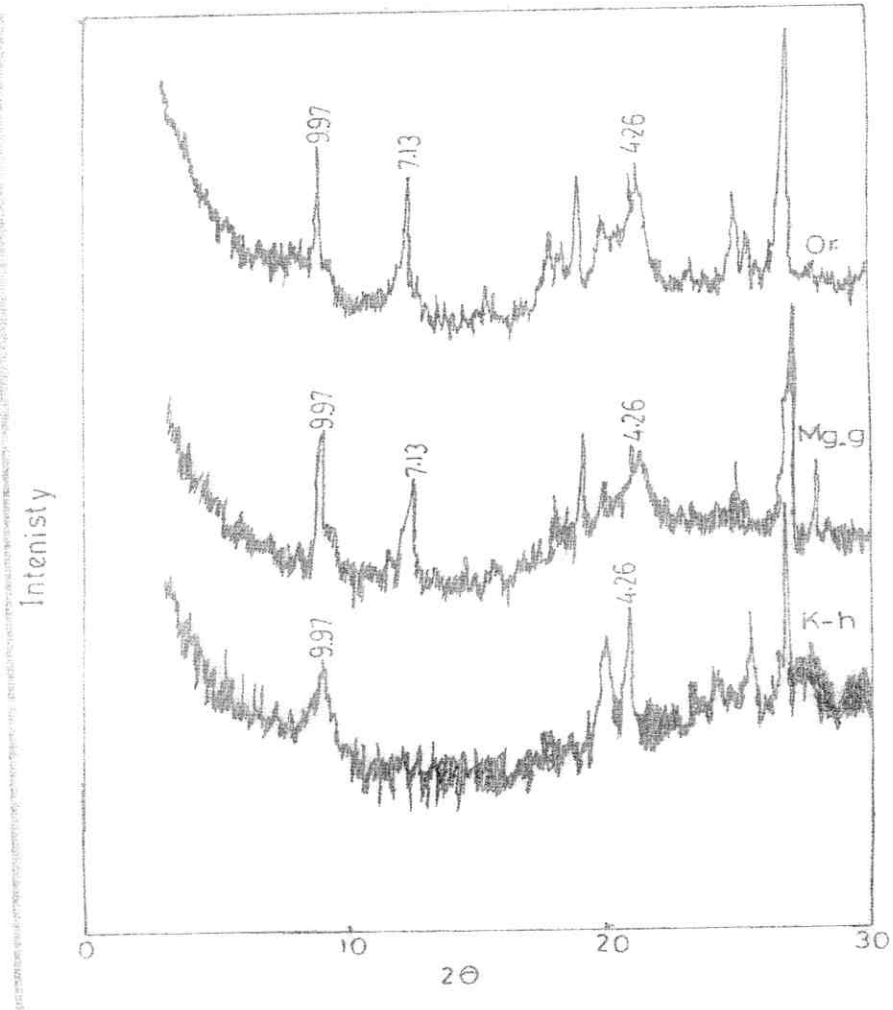

Fig. (40): X-ray diffraction pattern of the clay fraction separated from 2% acid concentration (S/L 1:1) sample.

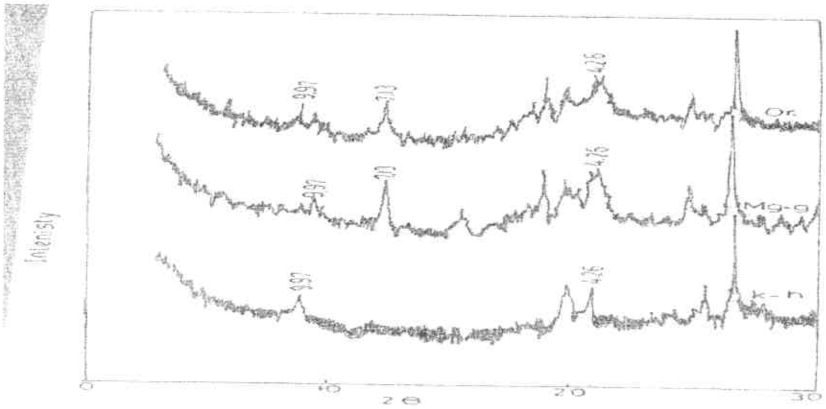

Fig. (41): X-ray diffraction pattern of the clay fraction separated from 2% acid concentration (S/L 1:2) sample.

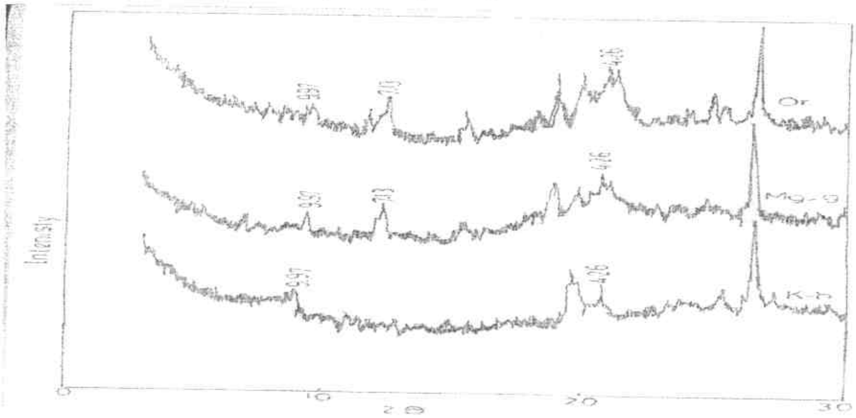

Fig. (42): X-ray diffraction pattern of the clay fraction separated from 2% acid concentration (S/L 1:3) sample.

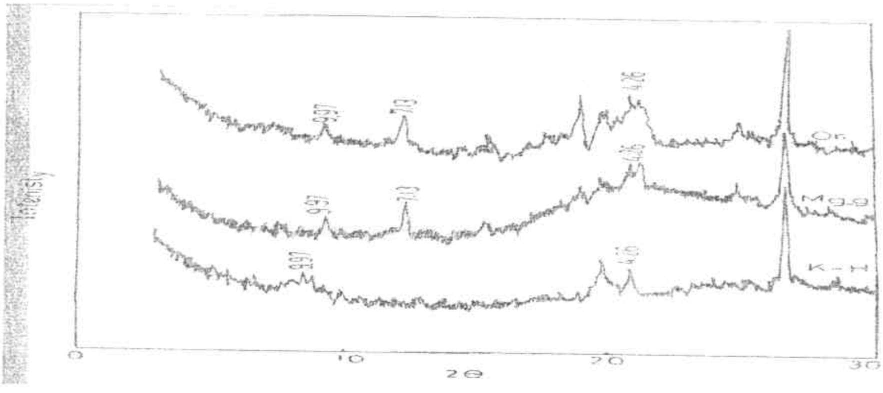

Fig. (43): X-ray diffraction pattern of the clay fraction separated from 5% acid concentration (S/L 1:1) sample.

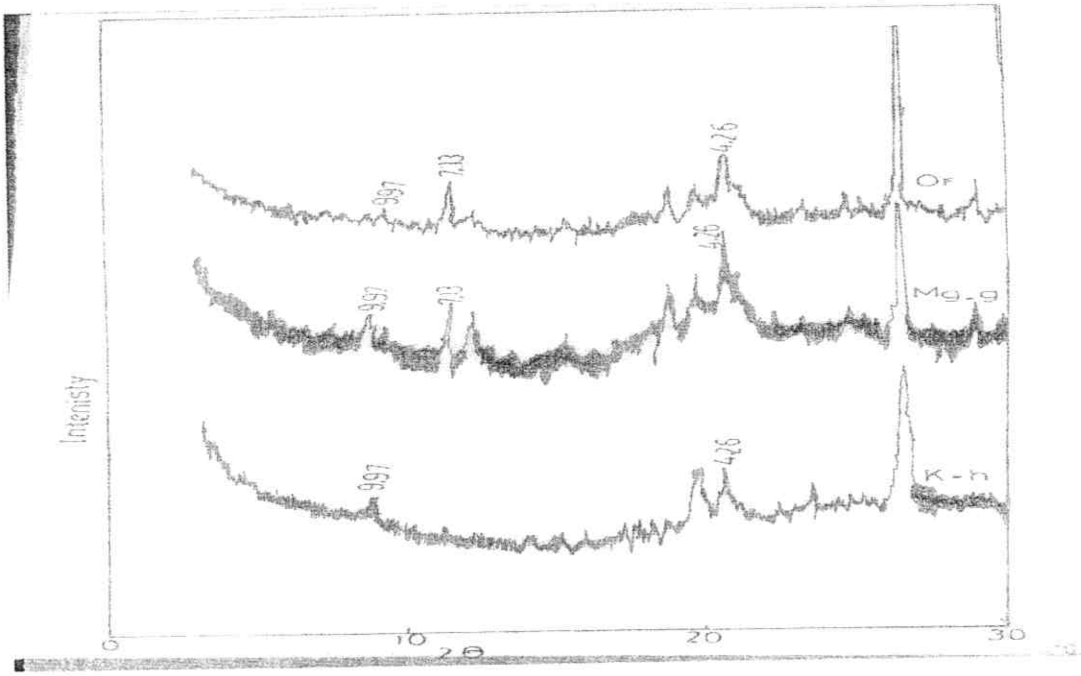

Fig. (44): X-ray diffraction pattern of the clay fraction separated from 5% acid concentration (S/L 1:2) sample.

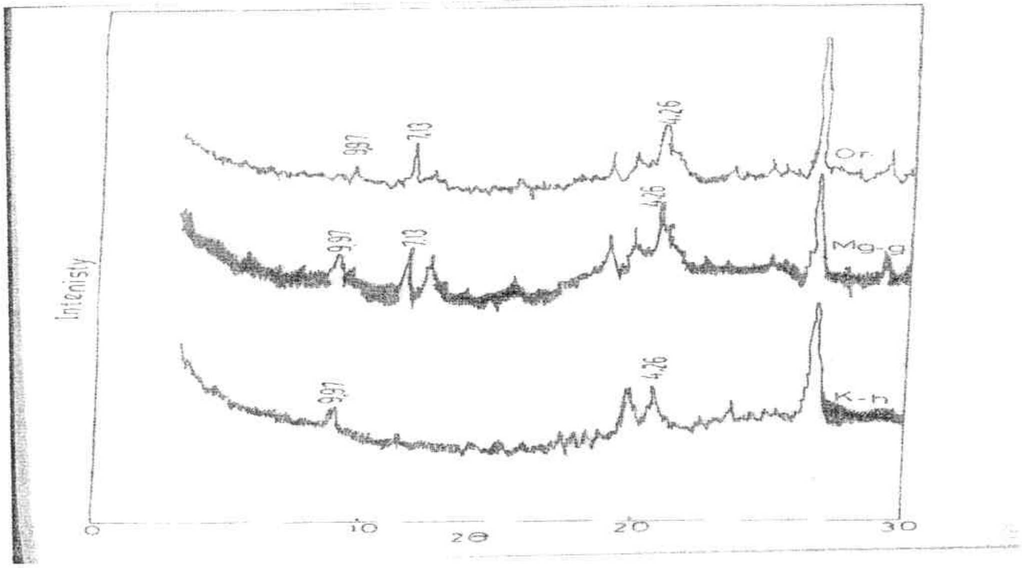

Fig. (45): X-ray diffraction pattern of the clay fraction separated from 5% acid concentration (S/L 1:3) sample.

4.4. Effect of acid concentration and solid : liquid ratio on the chemical properties of the shale deposit sample.

Data presented in Table (21) indicate that electrical conductivity (EC) of the shale sample collected from Abu Thor area and subjected to leaching by $H2SO_4$acid at different concentrations and different solid/liquid ratios decreased as compared with the corresponding EC value of the original shale deposit sample before leaching process.

Table (21). Chemical compositions of the saturation paste extract of the subsamples leached with $H2SO_4$ acid at different concentrations and different solid/liquids.

Sample No.	Conc. of acid leading solutes (%)	Solid / liquid ratio	pH	EC (dS/m)	Soluble ions($mmol_C\ L^{-1}$)							
					Cations				Anions			
					Ca^{++}	Mg^{++}	Na^+	K^+	$CO_3^=$	HCO_3^-	Cl^-	$SO_4^=$
1	2%	1 : 1	3.6	7.62	50	18.36	9.52	2.14	-	1.20	12.00	66.82
2		1 : 2	2.9	9.97	75	11.2	10.79	3.21	-	1.20	15.0	84.0
3		1 : 3	2.8	9.64	65	20.84	9.52	4.64	-	1.0	12.0	87.0
4	5%	1 : 1	3.0	15.32	100	57.43	24.12	2.49	-	1.0	26.0	157.04
5		1 : 2	2.2	18.41	75	136.63	8.89	0.71	-	1.30	10.0	209.93
6		1 : 3	1.9	19.24	70	148.79	11.43	0.71	-	1.20	13.0	216.73

These decreases were more obvious by decreasing both $H2SO_4$ concentrations and the solid / liquid ratio where the EC values of the leached subsamples were 7.62, 9.97 and 9.64 dSm^{-1} upon using the acid at a concentration of 2% and 1:1, 1: 2 and 1: 3 solid / liquid ratios, respectively. The corresponding EC values raised up to 15.32, 18.41 and 19.24 dSm^{-1} upon using the acid concentration of 5% at 1: 1, 1: 2 and 1: 3 solid/liquid ratios, respectively. The more remarkable decrease in EC value of the shale deposits by increasing acid concentration and solid/liquid ratio may be attributed to the ability of the higher concentration of acid to dissolve and leach more ions out of the soil columns.

Data in Table (21) reveal also that, soil reaction (pH) of the studied shale sample decreased by increasing the acid concentration and solid / liquid ratio. This might be attributed to the more concentration of H+ ions introduced to the shale deposit sample as a result of applying $H2SO_4$.

Regarding the soluble cations, data in Table (21) show that soluble cations of Ca^{2+}, Mg^{2+}, Na^+ and K^+ increased, generally, with increasing concentration of the applied acid. They could be arranged in the following descending order. $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ upon using the acid at a concentration of 2%, while the sequence and $Mg^{2+} > Ca^{2+} > Na^+ > K^+$ characterized, generally, the distribution of the soluble cations upon using the acid at a concentration of 5%.

With regard to the soluble anions, data in Table (21) reveal that soluble anions of the studied shale sample were dominated by SO_4^{2-} followed by Cl^- and the HCO_3^-. Also, the values of soluble SO_4^{2-} increased with increasing both acid concentration and solid/liquid ratio. This is probable because solubility of some rarely soluble Ca- components such as $CaCO_3$increases with increasing acidity **(Balba,1995).**