CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Analysis of Sandstone

4.1.1 Chemical and Spectrophotometric Analysis

The compositions of the ore are shown in Table 4.1 .

Table 4.1 Sandstone analysis (assay percent)

Element	% (by weight)	Compound	% (by weight)
Si	28.19	SiO_2	60.30
Al	6.99	Al_2O_3	13.21
Cu	2.10	CuO	2.63
Fe	0.79	Fe_2O_3	1.13
Pb	0.056	PbO	0.06
Mn	0.12	MnO_2	0.19
K	2.55	P_2O_5	0.17
Mg	0.17		
Na	0.33		
Ca	0.05		
$CO_3^{=}$	0.60		

4.1.2 X—Ray Fluorescence Analysis

The compositions of the sandstone as analysed by X-ray fluorescence are illustrated in Table 4.2

Table 4.2 Compositions (%) of the sandstone sample.

Component	% (by weight)
U_3O_8	0.0364
U	0.0309
Fe_2O_3	1.6000
CuO	2.2000
PbO	0.0630
Y_2O_3	0.0600
ZrO_2	0.0610

The spectrophotometric analysis of Fe, Cu and Pb are in agreement with the results by X—ray fluorescence. As matrix effect plays an important role in X—ray fluorescence technique, differences in the results are to be expected.

4.1.3 Neutron Activation Analysis

A) The precision of INAA for uranium

The precision of the present method was checked by analysing the ore and the leach liquor repeatedly.   Five samples were taken from the ground ore for this purpose.   The results are given in Table 4.3 and Table 4.4 .

Table 4.3 Analysis of uranium in sandstone by neutron activation

Sample	% U from analysis		Mean and Standard deviation (σ)	% Error
1	0.02981,	0.0300		
	0.03071,	0.02807		
	0.03062,	0.03019	0.0293 ± 0.00135	4.61
	0.02782,	0.02913		
	0.02746,	0.02729		
2	0.02581,	0.02512		
	0.02641,	0.02520	0.02581 ± 0.00057	2.20
	0.02650,	0.02545		
	0.02616			
3	0.02531,	0.02526		
	0.02680,	0.02568	0.02597 ± 0.00067	2.59
4	0.02802,	0.02727	0.02830 ± 0.00120	4.42
	0.02962			
5	0.02762,	0.02701	0.02723 ± 0.00034	1.25
	0.02705			

Table 4.4 Analysis of uranium in acid leach liquors by
neutron activation.

Sample	ppm U from analysis		Mean and Standard deviation (δ)	% Error
A	215.29,	210.48	222.29 ± 8.36	3.76
	231.51,	226.90		
	231.03,	226.66		
	212.51,	223.89		
B	206.43,	205.55	205.5 ± 0.906	0.44
	204.62			
C	224.43,	205.11	215.61 ± 8.01	3.72
	215.06,	217.86		

It can be seen that the technique of neutron activation analysis
is very effective for the determination of uranium content in ores
and in leach solutions.   The precision of the method was found to be
excellent.   The results agree very well with those obtained from
X-ray fluorescence analysis.   Since the neutron activation analysis is
rapid and errors caused by matrix effect are significant compared to
X-ray fluorescence, the NAA was therefore chosen in the present
investigation.

B) Analysis of Vanadium

Vanadium content in sandstone and leach liquor was analysed by neutron activation, as shown in Table 4.5 .

Table 4.5 Analysis of Vanadium in sandstone and leach liquor.

Sample	Vanadium Content		Mean and Standard	% Error
	% V	ppm V	deviation (δ)	
Sandstone	0.0497 0.0562 0.0593 0.0625	—	0.0569 ± 0.0055	9.6
Leach liquor	—	224.54 231.26 221.55 226.49	225.96 ± 4.08	1.8

The results indicate that vanadium is easily analysed by neutron activation with reliable error not more than 10 % .

4.2   Acid Leaching of Sandstone

The effects of acid concentration, amount of oxidant, time of leaching, particle size and temperature on the sulphuric acid leaching of local sandstone were investigated. The uranium content in the ore prior to the leaching process as well as the uranium content in leach liquor were determined.

The percentage yield of leaching was evaluated as:

$$\text{Percent leaching} = \frac{\text{U concentration in leach liquor}}{\text{U concentration in sandstone}} \times 100$$

4.2.1   Effect of Acid Concentration on the Leaching of Uranium from Sandstone

In the study of the effect of acid concentration 100 g ore (-200 mesh) were mixed with concentrated sulphuric acid ranging from 22.5 - 360 g/kg of ore   which are equivalent to $1.26 - 20.24 \, cm^3$ H_2SO_4 . Water was added to make a liquid to solid ratio of 1:1 or a 50 % slurry. 0.55 g MnO_2 was added which equals to   5.6 g/kg of ore   .   The mixture was agitated at a constant temperature of $80 \pm 5 \, ^\circ C$ for 4 hours.

The results of this experiment are shown in Table 4.6 .

Table 4.6 Effect of Acid concentration on the

Leaching of sandstone

Conditions: weight of sandstone   100 g

particle size   − 200 mesh

solid:liquid ratio   1 : 1

amount of MnO_2 5.6 g/kg of ore

time of leaching   4   hours

temperature   80 ± 5 °C

Amount of H_2SO_4 (g/kg of ore)	% Leaching
22.5	1.5
45.0	11.5
67.5	48.4
90.0	62.1
135.0	76.9
180.0	89.4
270.0	94.3
360.0	92.7

The effect of acid concentration on the leaching of sandstone with sulphuric acid is shown in Figure 4.1 by plotting the percentage yield of leaching as a function of acid concentration. The obtained results indicated that, increasing the amount of acid from 22.5 to 270 g/kg of ore increased the uranium leachability to 94 %. Further addition of acid did not result in significant increase in leaching yield.

Excess of acid causes detrimental effects since it decomposes a fraction of the silica and the silicates. Silicic acid is colloidal and precipitates in the form of gel of which separation by vacuum filtration is extremely difficult (5).

4.2.2 Effect of Time on the Leaching of Uranium from the Sandstone

In the studying of the effect of extraction time, direct acid leaching had been applied to sandstone for time varied from 2 to 18 hours. The effect of leaching time on the uranium extraction is given in Table 4.7 and graphically shown in Figure 4.2 . A maximum yield of 90 % was approached in 4 hours. Leaching time longer than 4 hours doesnot cause significant increase in extraction.

Table 4.7 Effect of leaching time on the leaching uranium

from sandstone.

Conditions: weight of sandstone   100 g

particle size   200 mesh

liquid to solid ratio   1 : 1

amount of oxidant, MnO_2 5.6 g/kg of ore

amount of acid, H_2SO_4 180 g/kg of ore

temperature 80 ± 5 $^{\circ}C$

Time of Leaching	% Leaching		
(hr)	1	2	average
2	70.0	—	70.0
4	89.4	90.3	89.9
8	89.3	92.5	90.9
12	91.0	90.2	90.6
18	97.8	95.5	96.7

4.2.3 Effect of temperature on the leaching of uranium

from sandstone.

In the investigation of the effect of temperature, the reaction
temperature was allowed to vary from 30° C (room temperature) to
105 $^{\circ}C$, the latter being limited by the boiling temperature of the slurry.
After mixing the measured volume of sulphuric acid and

tri—distilled water with the ore, the temperature of the slurry rose to about 60°C. It was then placed on a hot—stirred plate. Approximately one hour of heating was required to bring the reaction temperature to required range. The results of the effect of temperature are given in Table4.8 . It is obvious that at the optimum temperature of 80±5°C a 90 percent leaching yield could be obtained, as the percent leaching temperature plotted in Figure 4.3 .

Table 4.8   Effect of temperature on acid leaching of sandstone

Conditions: weight of ore   100 g

              particle size   —200 mesh

              solid:liquid ratio   1 : 1

              amount of oxidant, MnO_2 11.25 g/kg of ore

              amount of acid, H_2SO_4 270   g/kg of ore

              time of leaching   8   hours

Temperature ($°C$)	%Leaching
30±3	80.4
60±5	86.7
80±5	92.1
100±5	94.4
105	94.3

4.2.4 Effect of Oxidant on Acid Leaching of Sandstone.

The influence of manganese dioxide was investigated in the hope that the presence of MnO_2 would accelerate the leaching of uranium into solution. A series of batch agitation was conducted by addition different amount of MnO_2 ranging from 0 to 45 g/kg of ore which are equivalent to 0 to 4.5 g MnO_2. The relative efficiency of this oxidizing agent is shown in Table 4.9 .

Table 4.9 Effect of MnO_2 on acid leaching of sandstone.

Conditions: weight of sandstone   100 g

particle size   -200 mesh

solid : liquid ratio   1 : 1

amount of acid, H_2SO_4 180 g/kg of ore

temperature   80 ± 5 °C

time of leaching   8   hours

Amount of MnO_2 (g/kg of ore)	% Leaching
0.00	73.6
5.60	87.4
11.25	86.3
22.50	92.4
45.00	94.7

The curve in Figure 4.4 illustrates the percentage uranium leaching as a function of oxidant content. An appreciable yield of 87 % has been obtained by using 5.6 g MnO_2/ kg of ore. The maintenance of oxidation conditions was necessary for quadrivalent uranium dissolution. It is interesting to point out that even without the addition of MnO_2, a leaching yield of approximately 70 percent could be obtained. This indicates that either the uranium is present mostly in the hexavalent state. To ensure complete oxidation into the hexavalent state, 11.25 g MnO_2 / kg of ore has been recommended the optimum condition.

4.2.5 Effect of Particle Size on the Leaching of Uranium from Sandstone.

Leach tests were performed to explore the effect of particle size on the leaching of uranium from sandstone. The ore with the grain size ranging from −48 to −200 mesh were investigated. The results are tabulated in Table 4.10 and the percent of leaching as a function of particle size is plotted in Figure 4.5 . Reducing the particle size to as small a value as possible may increase the percent of leaching. But the amount of uranium recovered might not compensate for the additional cost of grinding.

Table 4.10 Effect of particle size on the leaching of uranium
from sandstone.

Conditions:

weight of sandstone	100 g	
solid to liquid ratio	1 : 1	
amount of oxidant, MnO_2	11.25 g/kg of ore	
amount of acid, H_2SO_4	270 g/kg of ore	
temperature	$80 \pm 5\ ^{\circ}C$	
time of leaching	8 hours	

Mesh Size (mesh)	% Leaching
48	72.8
100	76.5
150	86.7
200	92.1

The effect of particle size on leaching yield agrees well
with the results on the study of particle size effect on leaching
rate by N.P. Galkin, et al. (5). It has been found that the
finer the ore, the faster is the consumption of reagents and the
faster the leaching rate. However, such a straight line relationship
is observed only down to a certain particle size.

4,2,6 Effect of Time on the Leaching of Uranium at Ambient Temperature

Several series of batch agitation leaching were performed at the ambient temperature to investigate the effect of time on leaching. Leaching at the ambient temperature may result in the decreasing of the operation cost, the saving being increasingly large, percentage-wise, as the grade of ore is lowered. As the reaction is extremely mild , it appears that the leaching time must be extended from 8 hours to 24 hours in order to achieve a similar leaching yield of 90%. The experiment was performed by a single stage batch agitation leaching of of -200 mesh sandstone at room temperature (approximately $30\,^{\circ}C$). The experimental results are tabulated in Table 4.11 and the effect is graphically shown in Figure 4:6 .

Table 4.11 Effect of time on the leaching of uranium from
sandstone at ambient temperature.

Conditions:
weight of sandstone	100	g
particle size	-200	mesh
solid to liquid ratio	1 : 1	
amount of oxidant, MnO_2	11.25	g/kg of ore
amount of acid, H_2SO_4	270	g/kg of ore
temperature	$30 \pm 2\,^\circ C$	

Time on Leaching	% Leaching		
(hours)	1	2	average
8	83.3	80.4	81.9
24	91.7	90.6	91.2
48	95.4	96.7	96.1

4.2.7 Process Precision Evaluation of Acid Leaching.

The precision of the process was determined by repeating the leaching experiment several times while all conditions were kept constant. The standard deviation was evaluated to determine the error of the experiments. The studies were performed at the optimum conditions obtained from the previous tests. The results are shown in Table 4.12.

Table 4.12 Replicate leaching yield at similar leaching conditions.

Conditions:

weight of sandstone	100 g	
particle size	— 200 mesh	
solid:liquid ratio	1 : 1	
amount of oxidant, MnO_2	11.25 g/kg	of ore
amount of acid, H_2SO_4	270 g/kg	of ore
temperature	$80 \pm 5\,^{\circ}C$	
time of leaching	8 hours	

Number of the Test	% leaching
1	94.5
2	91.2
3	94.4
4	85.9
5	94.6
average	92.1
standard deviation	3.8
percentage error	4.1
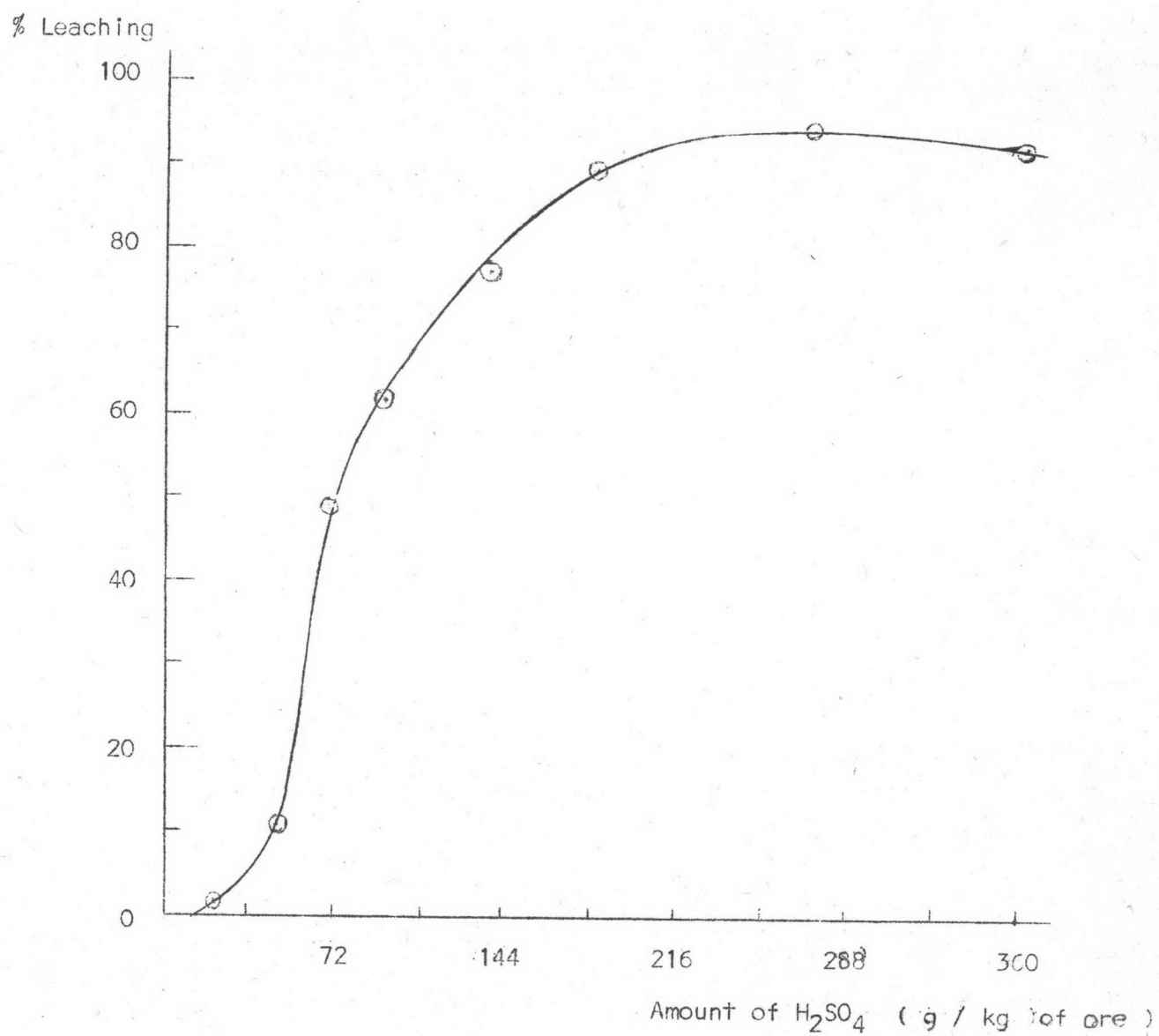
% Leaching

Figure 4.1   Effect of Acid Concentration on Leaching Yield
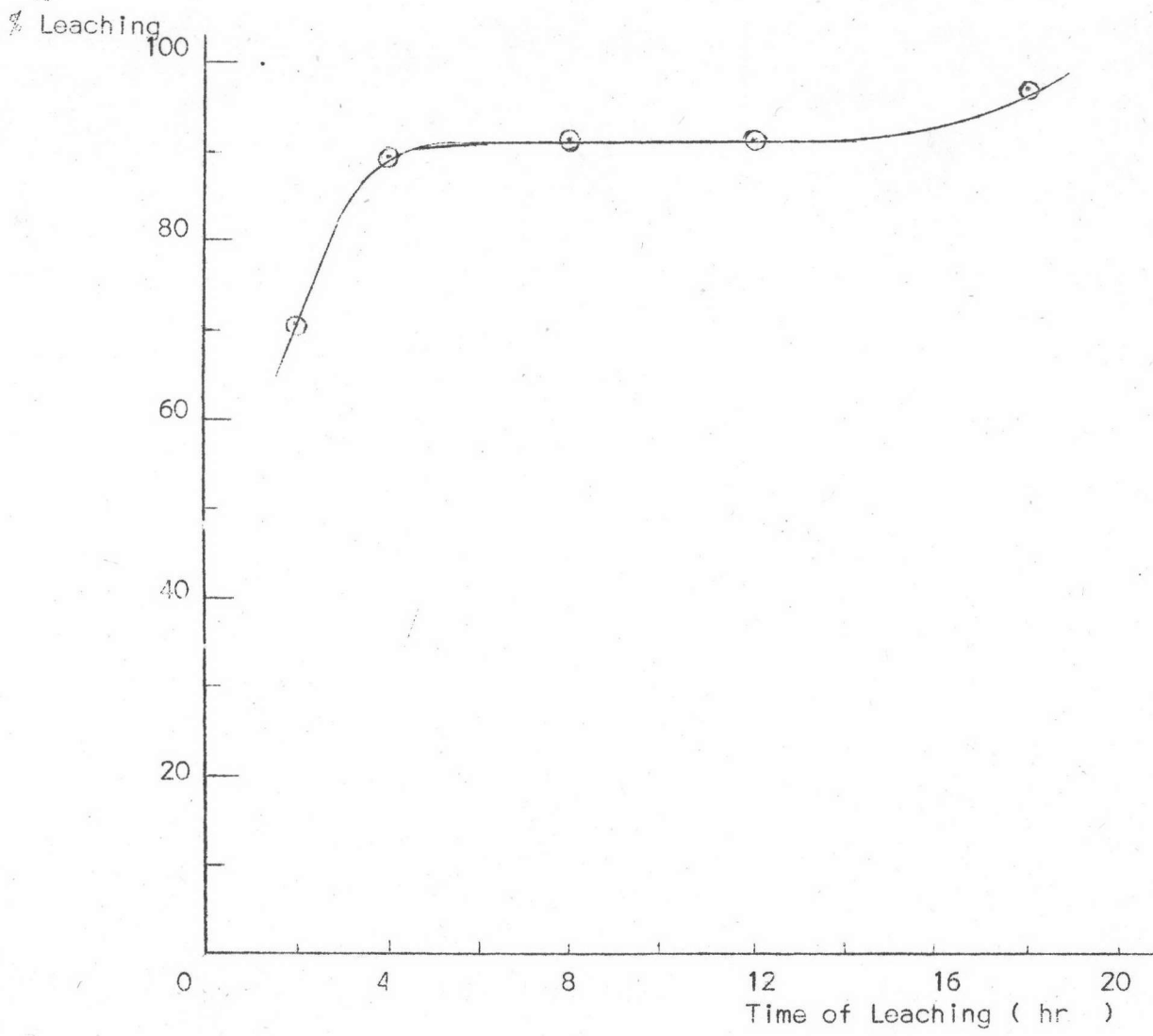
Figure 4.2   Effect of Time on Leaching Yield
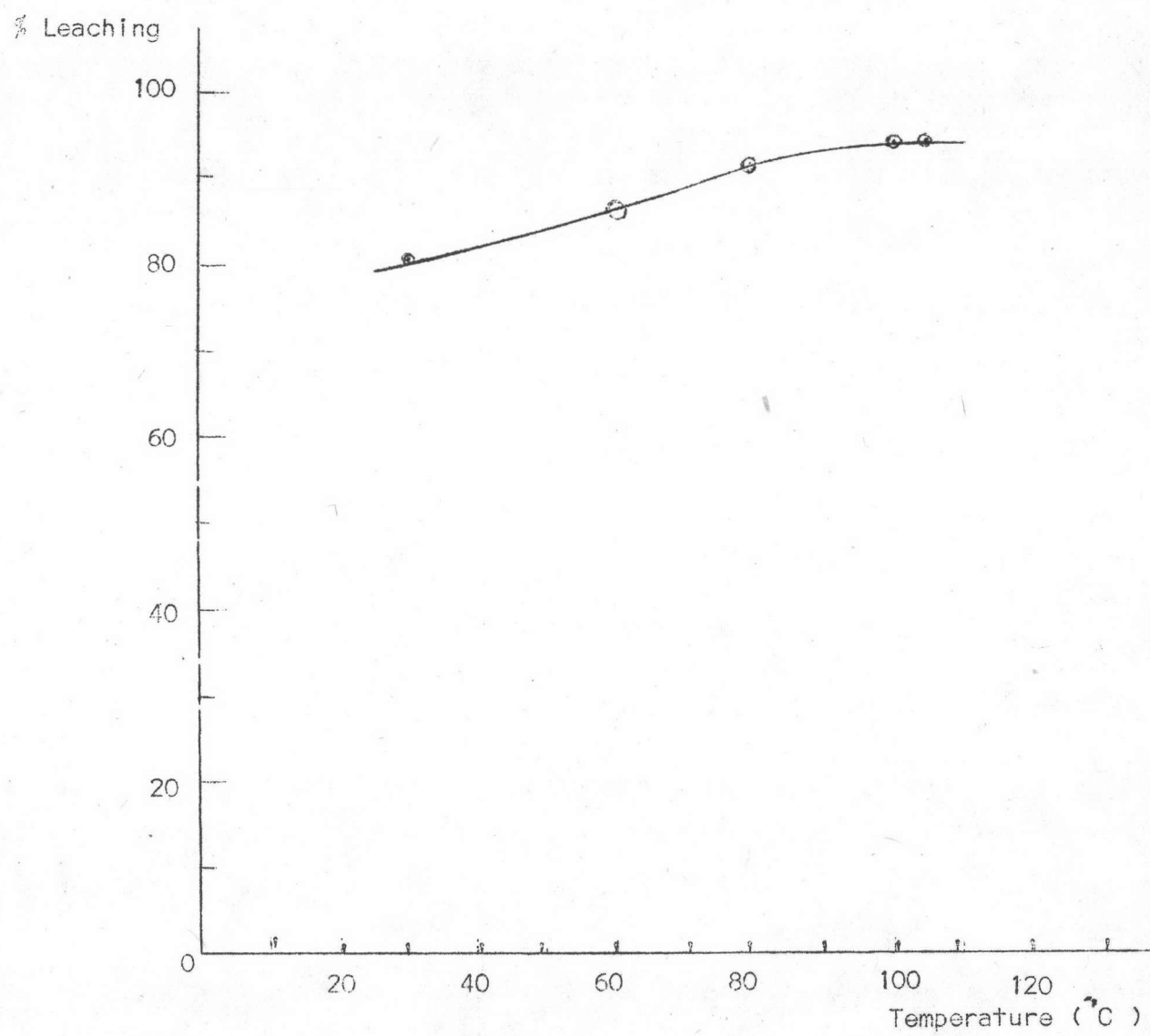
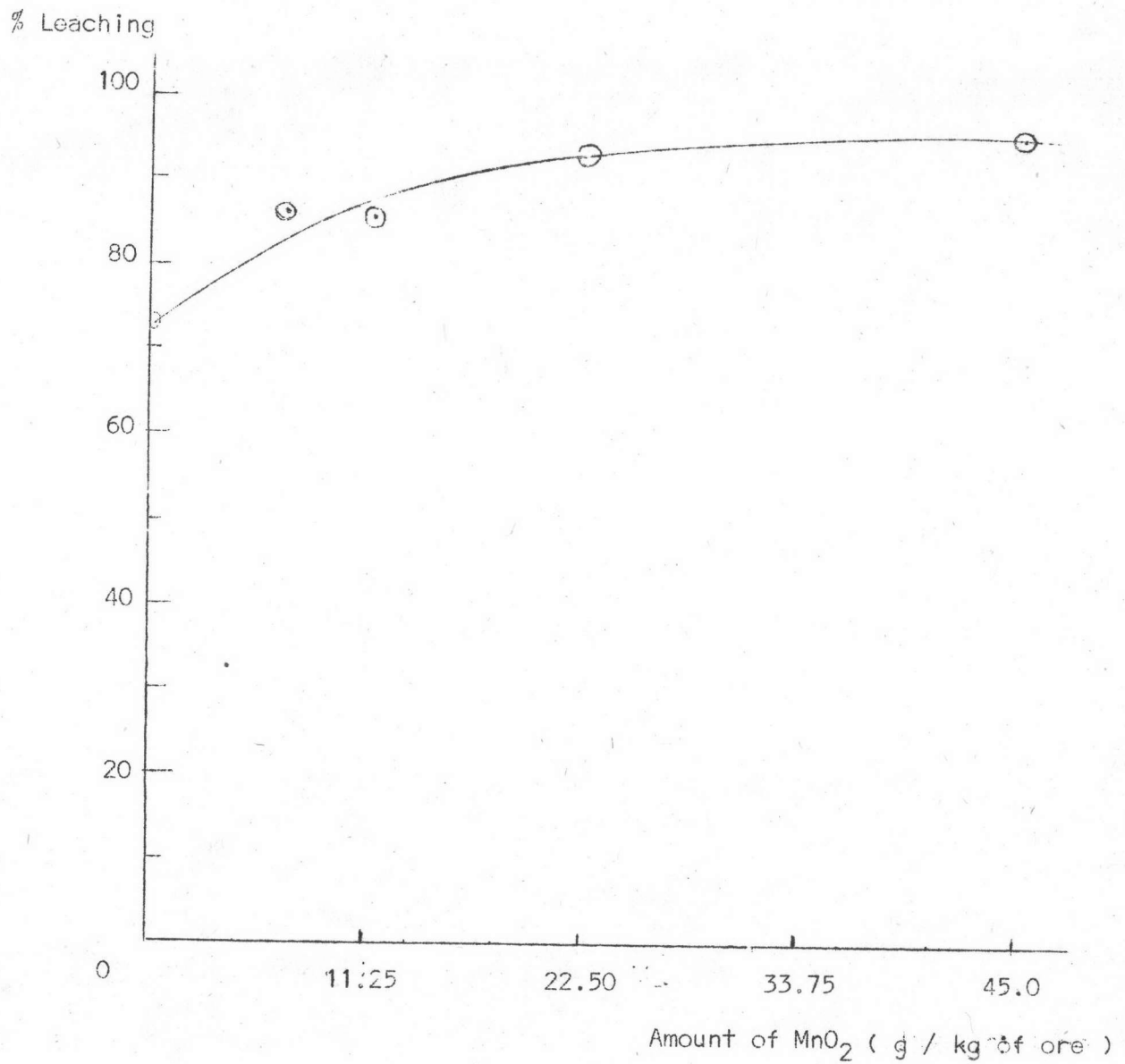Figure 4.3   Effect of Temperature of Leaching Yield

% Leaching

Figure 4.4   Effect of MnO$_2$ on Leaching Yield
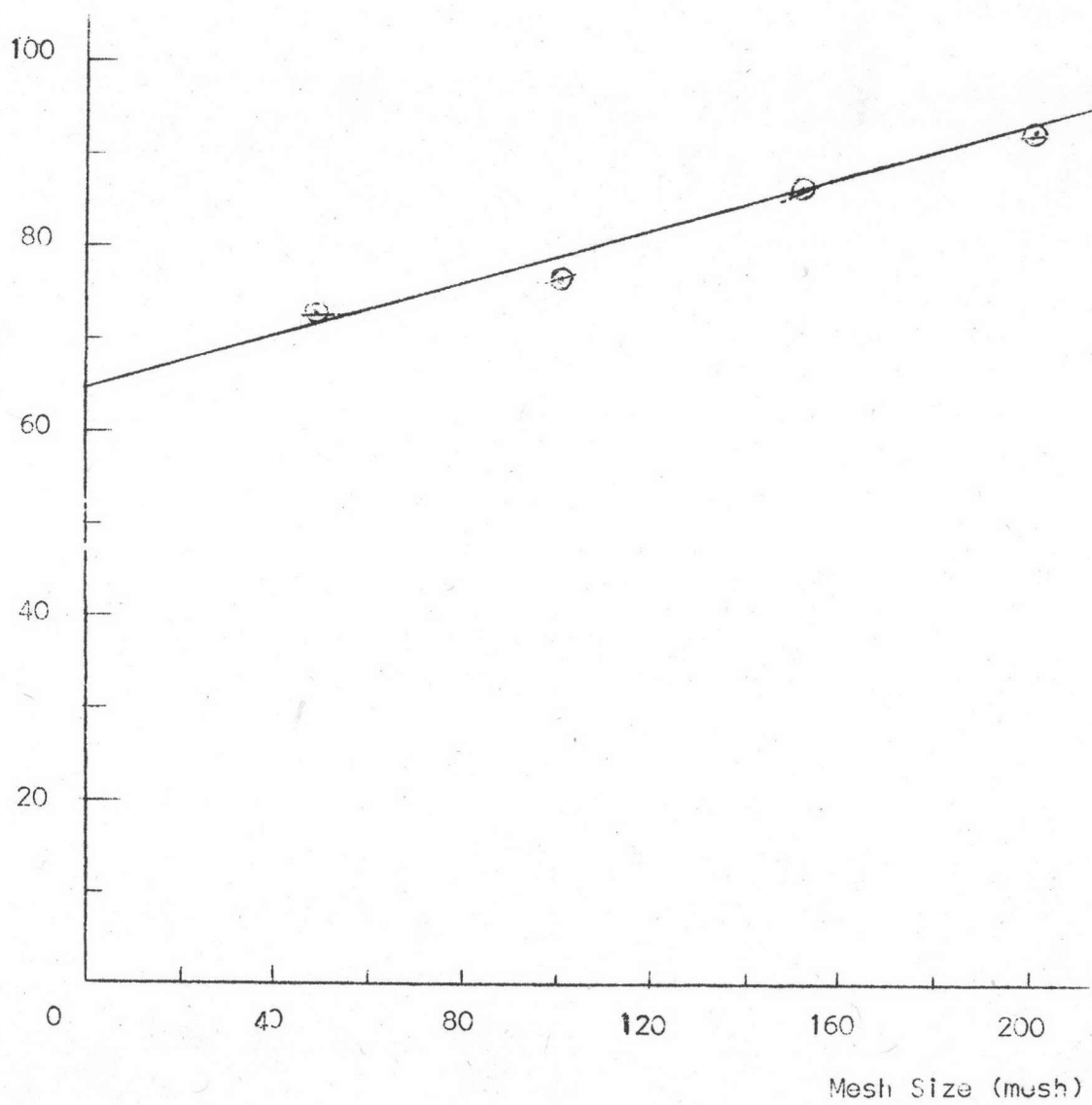
% Leaching

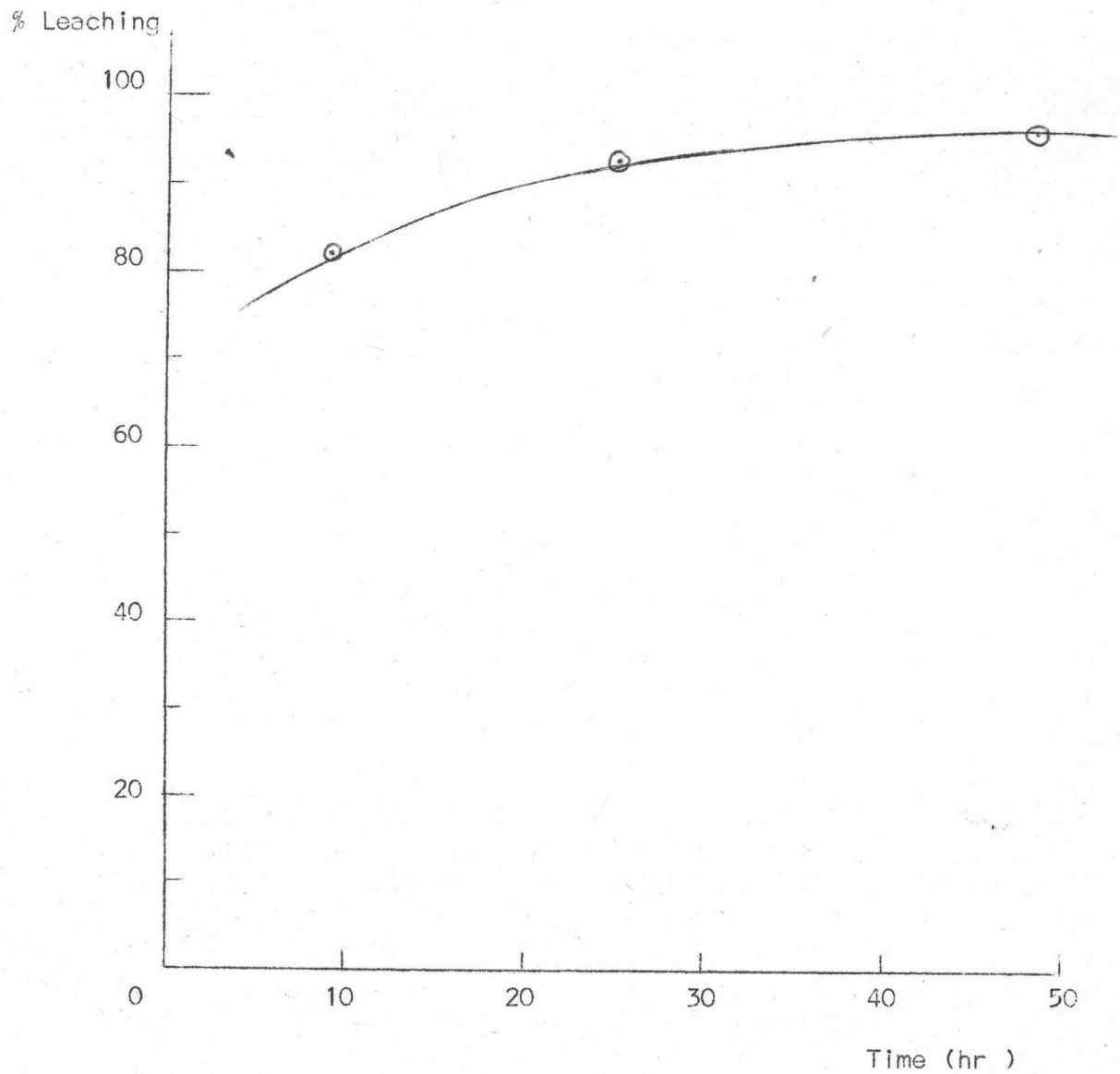Figure 4.5   Effect of Particle Size on Leaching

% Leaching

Figure 4.6 Effect of Time on Ambient Temperature Leaching

Investigation on precision of the leaching process has given excellent results. The experimental error was found to be about 4 %. In addition, it was confirmed that a maximum leaching was performed under optimum conditions.

4.2.8 Acid Leaching of Uranium from Sandstone in Scale of 1 kilogram per Batch.

In order to obtain more reliable data on the chemical yield and also to investigate the problems one would face in up—scaling, trial experiments, were performed in scale of 1 kg per batch. The leach liquor thus obtained, compositions of which are shown in Table 4.13, was used as feed material for solvent extraction purification. The ore contained 0.02581 % U.

Table 4.13 Compositions of leach liquor from large scale processing

Component	Concentration (%)	Method of analysis
Si	0.0025	AAS *
Al	1.500	AAS
Cu	1.340	AAS
Fe	0.610	AAS
Mn	0.260	AAS
Pb	0.061	AAS
Zn	0.008	XRFA
Y	0.018	XRFA
V	0.023	INAA
U	0.0222	INAA

The leach solution containing 0.0222 % U gave a leaching yield of 86 percent. The slight decrease in yield was expected as the mass of the slurry was larger and agitation could not be performed effectively.

4.3 Alkaline Leaching of Sandstone.

If the uranium ore contains larger amount of acid consuming components, the carbonate — hydrogencarbonate leaching system may prove to be more economical. Another advantage of carbonate leaching is that fewer undesirable elements such as iron are dissolved. Leaching with carbonate solutions, however does have disadvantages. The uranium dissolution normally takes longer time. The response of local sandstone to carbonate leaching has been evaluated in comparison to the acid process. The alkaline leaching conditions suggested by the UAR Atomic Energy Establishment (4) were followed.

The instrumental set — up and procedure were similar to those described under the acid process. The results of alkaline leaching of uranium from sandstone are given in Table 4.14 . It is apparent that more severe conditions are necessary for a higher leaching yield.

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AAS	Atomic Absorption Spectrophotometry
XRFA	X-Ray Fluorescence Analysis
INAA	Instrumental Neutron Activation Analysis

Table 4.14   Result of alkaline leaching of sandstone

Conditions: weight of sandstone   100   g

             particle size   −200   mesh

             amount of reagent, Na_2CO_3 60   g / kg of ore

             and $NaHCO_3$ 30   g / kg of ore

             amount of oxidant, $KMnO_4$ 10   g / kg of ore

             time of leaching   12   hours

             temperature of reaction $80\pm5\,^{\circ}C$

Number of the Test	% Leaching
1	20.3
2	19.0
average	19.7

4.4   Recovery of Uranium from Leach Liquor by Amine Solvent Extraction

The leach liquor containing 0.0222% U was used in the process of solvent extraction.   The extraction of a 0.025 % U standard solution was also performed to confirm the extraction yield.   The extraction efficiency was calculated from the content of uranium in the strip solution.   The results of a single stage extraction and two stages stripping are tabulated in Table 4.15.

The X-Ray spectra of the leach liquor, raffinate and strip solution is given in comparison to the pure uranium spectrum in Figure 4.7. It is obvious that Alamine 336 is a specific solvent for uranium. Higher extraction yield could be achieved by increasing the number of extraction stages.

Table 4.15 Results of Amine solvent extraction in the recovery

of uranium from acid leach liquor.

Fraction	Concentration (ppm U)	ml.	Total U (g U)	%Recovery
Standard solution	250	100	0.0250	
Acid leach liquor	222	100	0.0222	
Raffinate of standard	12.34	100	0.0012	
Raffinate of leach liquor	38.43	100	0.0038	
First strip of standard	420.99	50	0.0210	
First strip of leach liquor	375.43	50	0.0188	
Second strip of standard	11.82	50	0.0006	
Second strip of leach liquor	8.39	50	0.0004	
Total extraction of U in standard			0.0216	86.40
Total extraction of U in leach liquor			0.0192	86.45

4.5 Precipitation of Uranium as Yellow Cake

Uranium in the strip solution was precipitated as yellow cake.
Its low energy spectrum after 30 seconds of neutron irradiation is shown
in Figure 4.8 in comparison to the spectrum of U_3O_8 standard.   The
purity of the yellow cake was nearly 100 %.   No experiments were
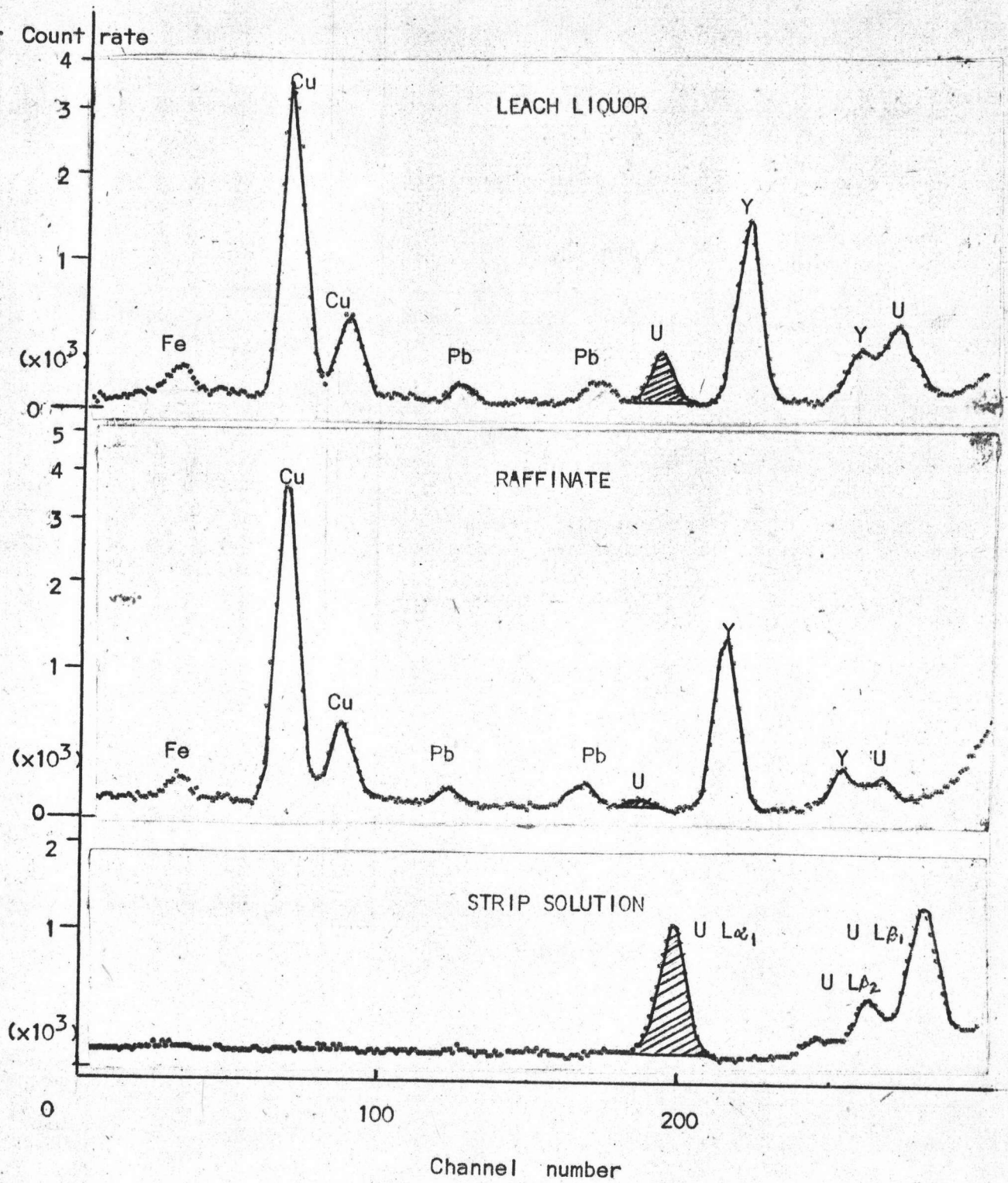performed to check the content of trace impurities.

Figure 4.7 Comparison of X-Ray fluorescence spectra of the solutions in solvent extraction.
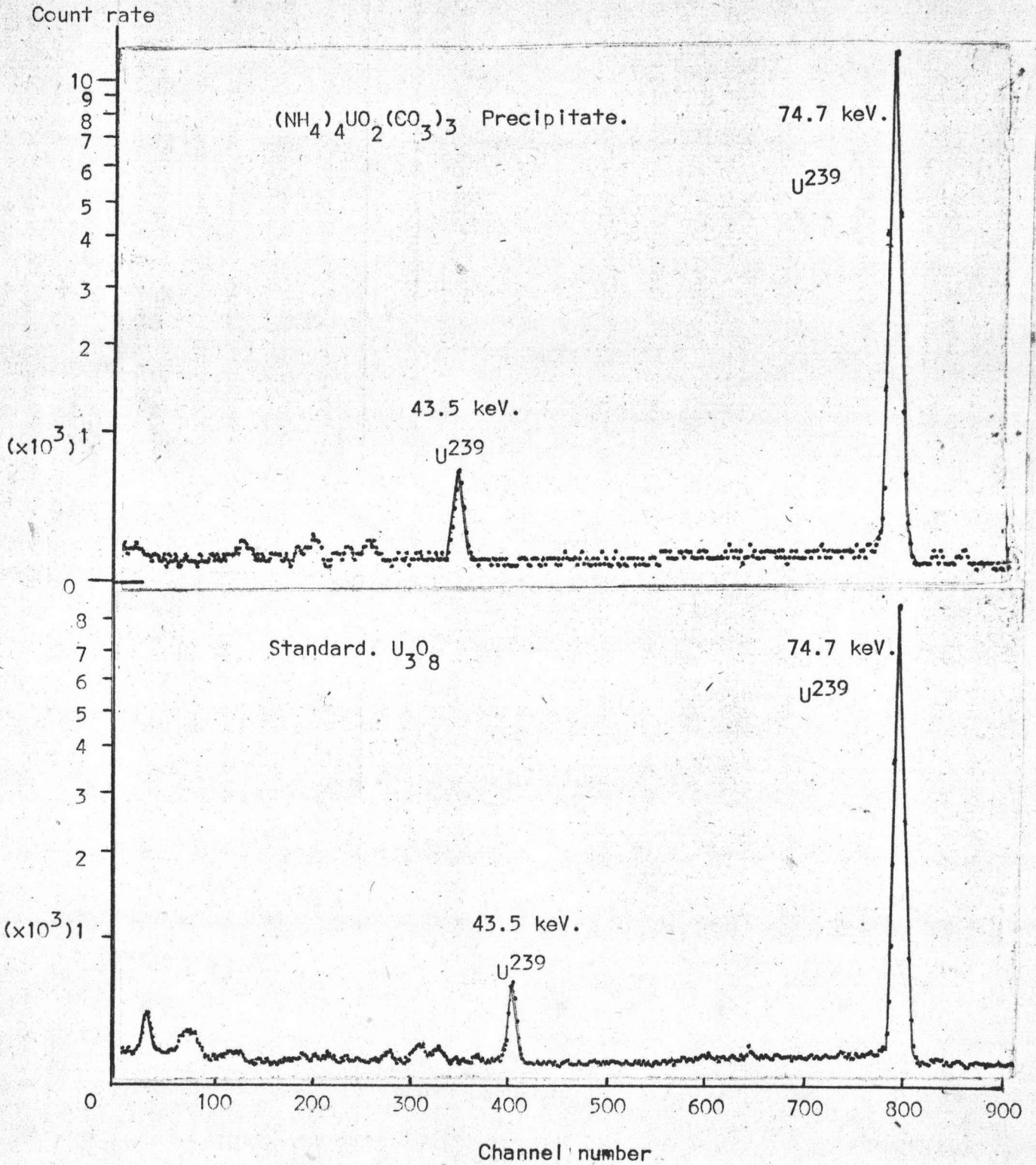
Figure 4.8   Gamma spectra of U_3O_8 and $(NH_4)_4UO_2(CO_3)_3$ precipitate.