Selection of Lixiviant System for the Alkaline in-Situ Leaching of Uranium from an Arkosic Type of Sandstone and Measuring the Dissolution Behaviour of some Metals and Non-Metals

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Summary: A laboratory simulation study was carried out to check the possibility of alkaline in-situ leaching of uranium from an arkosic type of sandstone recovered from a specific location at a depth of 300-500 m. The ore body was overlaying impervious clay shale below the water table. Different CO_3^{-2} containing soluble salts were tested as complexing agent of the UO^{+2} ions along with H_2O_2 as oxidizing agent. The lixiviant system, comprising NH_4HCO_3 as complexing agent along with H_2O_2 as oxidizing agent in concentrations of 5 g/L and 0.5 g/L respectively, was found to be the most efficient for the leaching of uranium among the 25 different compositions employed. Along with uranium, the dissolution behaviour of 15 other metals, non-metals and radicals, including eight transition metals, was also observed in the lixiviant employed. These were Na, K, Ca, Mg, Cl, SO_4^{-2}, CO_3^{-2}, Ti, V, Cr, Mn, Fe, Cu, Zn and Mo. It was found that the leaching of uranium compared to non-transition metals/radicals followed the trend $Cl^- > SO_4^{-2} > U > Na^+ > K^+ > Mg^{+2} > Ca^{+2} > CO_3^{-2}$. The comparison of uranium leaching to the transition metals was in the order U > Cr > Mo > V > Ti > Cu > Zn > Mn > Fe. Physical parameters like pH, oxidation reduction potential (ORP) and conductivity were also measured for the fresh and pregnant lixiviants. It was found that the leaching of uranium is directly related to the concentration of native soluble hexavalent uranium, contact time of the lixiviant and ore and to some extent with the total concentration of uranium as well as the porosity and permeability of the ore.

Introduction

Leaching is a process by which a soluble substance is removed / extracted from gangue (undesirable matter) by the action of a percolating liquid, called lixiviant [1]. Uranium ores are treated by either acid or alkaline reagents with sulphuric acid or sodium carbonate – sodium bicarbonate systems used almost exclusively for commercial uranium recovery. In general, alkaline leaching is milder but more selective for uranium than acid leaching and is used for the treatment of high carbonate ores which would consume excessive amounts of acid. As acidic leaching is a rapid process so the majority of uranium mills employ it but the fundamental advantage of the alkaline leaching is that most of the gangue is not attacked and the carbonate solutions can be regenerated [2].

In carbonate leaching, uranyl tricarbonate $[UO_2(CO_3)_3^{-4}]$ ion is formed which is stable and soluble although, the number of CO_3^{-2} ions attached to the UO_2^{+2} ion is a function of pH and ORP (oxidation-reduction potential) of the solution [3]. Alongside these advantages, there are some limitations which include the sluggishness of the process, the suitable porosity and permeability requirement of the ore and the poor attack of the mild carbonate solutions on refractory ores.

In the present study, an ore was recovered in a specific area of Pakistan from a depth of 300 – 500 m and below the water table. The ore was found to be ~ 0.07 % in U_3O_8 and overlaying impervious clay shale. Due to the high depth and low grade of the ore a laboratory simulation study was carried out to look into the possibility of in-situ leaching of uranium from the ore. In the in-situ leaching process, the ore body is not physically removed / displaced from its native position. Instead, holes are bored in the ore body and proper reagents are injected to dissolve the uranium or any other target metal. The solution is then recovered and the target metal is separated from the gangue in the pregnant solution. The solution mining is rather slow process [4] but economical as no digging up or haulage of the ore is required, especially when the ore grade is low as in our case. The process is also environment friendly, particularly, in case of alkaline leaching where least amount of gangue metals are dissolved from the ore body so the water table is not appreciably contaminated.

Several CO_3^{-2} containing soluble salts were tested as complexing agent of the soluble UO_2^{+2} ion. Along with a suitable complexing agent, oxidizing agent is always required as in most of the cases, only a fraction of uranium in the underground ore bodies

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exists in the oxidized form (soluble hexavalent form, U^{+6}) while a large portion exists in the insoluble tetravalent (U^{+4}) form that must be oxidized. H_2O_2 was employed as oxidizing agent as it is miscible with water and decomposes into oxygen and water leaving no hazardous residue. The rate of leaching in case of carbonate leaching is controlled by the oxidation of U^{+4} [5]. For the reaction with oxygen, an electrochemical mechanism has been proposed [6]. Tap water was used as solvent. Among the five complexing agents tested, NH_4HCO_3 was found to be the most suitable for the ore under study. The reactions are;

$UO_2 + ½ O_2 \rightarrow UO_3$ Oxidation (1)

$UO_3+3CO_3^{-2}+H_2O\rightarrow UO_2(CO_3)_3^{-4}+2NaOH$ Complexation (2)

The leaching behavior of Uranium along with 15 other metals, non-metals and radicals was also studied. These included Na^+, K^+, Ca^{+2}, Mg^{+2}, Cl^-, SO_4^{-2} and CO_3^{-2} along with eight transition metals Ti, V, Cr, Mn, Fe, Cu, Zn and Mo.

It was found that uranium can be effectively leached by the lixiviant system of NH_4HCO_3 and H_2O_2. Among the 25 different compositions of this lixiviant used, the highest efficiency was shown by the system comprising 5 g/L NH_4HCO_3 and 0.5 g/L H_2O_2. The dissolution of gangue metals / non-metals was low compared to the acidic leaching, where almost complete dissolution of these would take place. Thus, comparatively purest product solution can be obtained by the carbonate leaching process from the ore under study.

Results and Discussion

Mineralogical Study of the Ore Body

The mineralogical study of the sink of the ore revealed that no uranium mineralization existed in this portion. The analysis results of the sink minerals are given in Table-1. As no uranium was found in this portion of the ore, it would be obviously present in the float.

The chemical analysis results of the float, regarding U_3O_8, and sorted out by sieve analysis are given in Table-2. It is clear from these results that uranium octoxide (U_3O_8) is present throughout the ore float but the highest concentration is present in the -200 # mesh. It means that uranium mineralization took place in the fine sand grains.

Selection of Lixiviant

A variety of carbonate compounds can be used as complexing agents in the leaching/extraction of uranium from the ore body. The selection of a particular complexing agent depends upon its leaching efficiency, suitability for a particular ore type, easy availability as well as the economical load incurred in its use. The complexing agents tried in the present study are;

(1)$NaHCO_3$ (2) Na_2CO_3 (3) $(NH_4)_2SO_4$ (4) $(NH_4)_2CO_3$ (5) NH_4HCO_3

One sulphate containing soluble salt was used as like CO_3^{-2}, UO_2^{+2} ion also complexes with SO_4^{-2}, forming stable uranyl sulphates. Keeping in view the concentration of uranium in the ore that is only ~0.07 % U_3O_8, 4 g/L of each salt was used along with a fixed amount (0.5 g/L) of hydrogen peroxide as oxidizing agent. The results are given in Table-3. The highest leaching efficiency for uranium was found to be that of $(NH_4)_2CO_3$ followed by NH_4HCO_3. However, in case of $(NH_4)_2CO_3$, precipitation of solid material started which could be seen in the drain pipes carrying the lixiviant discharge from the sample to the collection flasks (Fig. 1). The precipitate when analyzed contained more than 50 % $CaCO_3$. This can be explained by observing the dissociation reactions of $(NH_4)_2CO_3$ which are;

$(NH_4)_2 CO_3 \rightarrow 2NH_4^+ + CO_3^{-2}$ (3)

$CO_3^{-2} + H_2O \leftrightarrow HCO_3^- + OH$ (4)

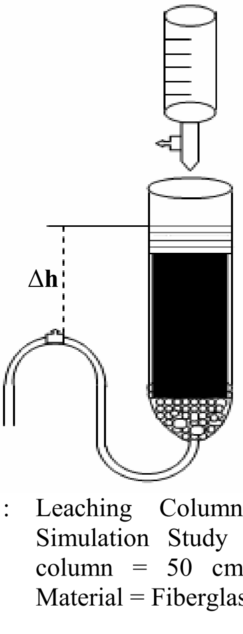

Fig. 1: Leaching Column for the Laboratory Simulation Study of the Ore.(Length of column = 50 cm, Diameter = 10 cm, Material = Fiberglass).

Table-1: Heavy Minerals (sink) Analysis of the Ore (Average) [7]*.

Name of Mineral	Ave. %
Magnetite ($Fe^{+2}Fe^{+3}{}_2O_4$)	**0.18**
Hematite (Fe_2O_3)	**0.03**
Ilmenite ($Fe^{+2}TiO_3$)	**0.16**
Garnet [$X_3Y_2(SiO_4)_3$] X = Ca^{+2},Mg^{+2},Fe^{+2}, Y = Al^{+3},Fe^{+3},Cr^{+3}	**1.12**
Amphibole [$Ca_2(Fe, Mg)_5Si_8O_{22}(OH)_2$]	**6.39**
Epidote [$Ca_2(Fe, Al)Al_2(SiO_4)$ $(Si_2O_7)O(OH)$]	**4.06**
Tourmaline [$XY_3Z_6(T_6O_{18})$ $(BO_3)_3V_3W$] X = Ca, Na, K, vacancy Y = Li,Mg,Fe^{+2},Mn^{+2}, Zn, Al, Cr^{+3},V^{+3},Fe^{+3},Ti^{+4},vacancy Z = Mg, Al, Fe^{+3},Cr^{+3},V^{+3} T = Si, Al, B B = B, vacancy V = OH,O W = OH, F, O	**0.03**
Biotite [$K(Mg,Fe^{+2})_3(AlSi_3O_{10})$ $(OH,F)_2$]	**0.41**
Calcite ($CaCO_3$)	**2.56**
Quartz / feldspar (Ave. Quartz content =17.5 %, rest is feldspar)	**85.19**

*The chemical formulae have been verified from the reference

Table-2: Conc. of U_3O_8 in the Different light portions (float) of Ore, along with Mesh Nos.

S. No	Sample No.	U_3O_8 (ppm)					
		+ 60 #	- 60 # +100 #	- 100 # + 150 #	- 150 # + 200 #	- 200 # + 250 #	- 250 #
1	A	407	532	906	1198	1776	1360
2	B	479	674	738	1074	2010	1587

Due to these hydrolysis reactions, the aqueous solutions of $(NH_4)_2CO_3$ are alkaline [8]. Calcium is present in the tap water being used as a solvent (Table-4) and also mobilized from the ore. The carbonate is present in a large amount in the ore (~ 4 – 8 %), but is not soluble in the lixiviants used. However, carbonate is formed in the dissociation reaction of the salt as shown in reaction-3 and 4. The leaching column with sample inside and lixiviant running through becomes almost an airtight system with little exposure to the atmospheric carbon dioxide (Fig. 1). In these circumstances, the internal pH of the sample loaded column may rise to such a value at which precipitation of calcium carbonate takes place in accordance with reaction-5.

$$Ca^{++} + CO_3^{-2} \rightarrow CaCO_{3\,(ppt)} \qquad (5)$$

Reaction (5) takes place in neutral or alkaline medium forming precipitate of $CaCO_3$. The in-situ leaching is a slow process often continued for years and the pipe lines etc. are also very long and may be up to several hundred meters in length. Hence, if such type of precipitation is started in the initial stages of the experiment, then it is ominous for the future of the process. Because, it would be almost impossible to stop the process after few weeks, the lines are dismantled and cleaned off the precipitate. Thus, on these grounds, in spite of the high leaching efficiency of the compound $(NH_4)_2CO_3$ as complexing agent, it was not selected for the process.

The lowest leaching efficiency of $(NH_4)_2SO_4$ among the five complexing agents employed can be explained on the grounds that the complex formed, $UO_2(SO_4)_3^{-4}$, has lower formation constant of the order of $1x10^4$ (much lower as compared to that of $UO_2(CO_3)_3^{-4}$ which is of the order of $1x10^{23}$, as given in Table-5 [9]. Moreover, $UO_2(SO_4)_3^{-4}$ complex is stable at a pH value of ~2.6 while here, the initial pH of the $(NH_4)_2SO_4$ lixiviant used is ~ 7.5.

The sodium salts $NaHCO_3$ and Na_2CO_3 both gave almost the same recovery of uranium. However, in case of Na_2CO_3 there was a permeability loss i.e. the rate of discharge from the column slowed down with the passage of time and a bit of swelling of the sample was observed. This phenomenon has been reported in the literature for the so called sodium clays or sodic (sodium rich) soils [10]. The clay minerals found in soils belong to the layer lattice alumino-silicates. Each clay crystal has an overall permanent negative charge which results when ions in the crystal lattice are replaced i.e. divalent magnesium replaces trivalent aluminium and trivalent aluminium replaces tetravalent silicon. This type of replacement is called isomorphous replacement and essentially develops a permanent negative charge on the clay surface which is balanced by positive ions (counter ions). The counter ions are predominantly calcium and magnesium. Under certain conditions, these latter types of ions are replaced (exchanged) with a significant degree of sodium ions. If the pores of the soil are filled with water, as in wet conditions, the counter ions balancing the negative charge on the clay surface, are in equilibrium with the cations in the soil solution which contains varying amounts of calcium, magnesium, sodium and potassium as well as the anions chloride, sulphate, bicarbonate and small quantities of other cations and anions.

If the counter ion is calcium it is tightly bound to the clay surface forming a very thin electrical double layer. However, if in some way, it is replaced (exchanged) with sodium from the solution entrapped in the soil (or ore) pores, the electrical double layer formed by the latter ion is diffused and loose due to its low charge. Hence, this may be one reason for a bit of swelling and loss of permeability. Calcium when replaced by sodium and mobilized can precipitate as $CaCO_3$, further reducing the permeability. No significant swelling or loss of permeability was observed in case of $NaHCO_3$. Solution pH may be playing some role in the loss of permeability or certainly in calcium precipitation. This may be due to the fact that the pH of the carbonate solutions is high as compared to those of the bicarbonate solutions since HCO_3^- ion is a consumer of OH^- ion. Thus, calcium precipitation is more expected in carbonate solutions than in bicarbonate solutions.

Table-3: Selection of a Suitable Complexing Agent for Uranium Leaching.

NH_4HCO_3 (4 g/L) + H_2O_2 (0.5 g/L), Solvent = Tap Water
Total U_3O_8 in the sample (U_3O_8 Leached + U_3O_8 in Residue) = 0.8339451 gm

No.of Irrg.	Lixt passed in one Irrig (ml)	Total Lixiviant passed (ml)	Lixt collected (ml)	Leached U_3O_8 (gm)	(%) Leaching
20	1000	20,000	19865	0.64171	76.95
$(NH_4)_2CO_3$ (4 g/L) + H_2O_2 (0.5 g/L), Solvent = Tap Water **Total U_3O_8 in the sample (U_3O_8 Leached + U_3O_8 in Residue) = 1.07 gm**					
20	1000	20000	19858	0.86884	81.20
$(NH_4)_2SO_4$ (4 g/L) + H_2O_2 (0.5 g/L), Solvent = Tap Water **Total U_3O_8 in the sample (U_3O_8 Leached + U_3O_8 in Residue) = 1.20113 gm**					
20	1000	20000	19870	0.375	31.22
$NaHCO_3$ (4 g/L) + H_2O_2 (0.5 g/L), Solvent = Tap Water **Total U_3O_8 in the sample (U_3O_8 Leached + U_3O_8 in Residue) = 0.73117 gm**					
20	1000	20000	19855	0.511	69.89
Na_2CO_3 (4 g/L) + H_2O_2 (0.5 g/L), Solvent = Tap Water **Total U_3O_8 in the sample (U_3O_8 Leached + U_3O_8 in Residue) = 0.83027 gm**					
20	1000	20000	19872	0.579	69.69

(%) Leaching = [U Leached x100] / Total U

Table-4: Tap Water Analysis, used as Solvent in the Leaching Study.

S.No	Element / Radical etc.	Conc. (ppm)	S.No	Element / Radical etc	Conc. (ppm)
1	Na^+	146	10	Fe	451 ppb
2	K^+	02	11	Mn	626 ppb
3	Ca^{++}	18	12	Cu	79 ppb
4	Mg^{++}	10	13	Zn	70 ppb
5	NH_4^+	Nil	14	V	468 ppb
6	SO_4^{-2}	231	15	Mo	<1 ppb
7	Cl^-	162	16	Cr	01
8	CO_3^{--}	11	17	Ti	03
9	HCO_3^-	218	-----	--------	------

TDS=700 ppm, ORP=170 mV, pH=8.35, Conductivity=6350μS/cm, Temperature=25 $\pm$1 C°.

Table-5: Stability Constants (Formation Constants) of the Compounds / Complexes of Uranyl Ion with Different Anions in Aqueous Solutions at Unit Ionic Strength.

S.No	Type of Complex	Stability Constant of the complex (~ 25 C°)
1	$UO_2(CO_3)_3^{-4}$	10^{23}
2	UO_2F_2	10^8
3	$UO_2(SO_4)_3^{-4}$	10^4
4	$UO_2H_2PO_4^+$	10^3

Among the five complexing agents, NH_4HCO_3 gave the second highest recovery of uranium after $(NH_4)_2CO_3$. No swelling or loss of permeability was observed in this case. Hence it was selected as complexing agent along with H_2O_2 as oxidizing agent for carrying out the leaching of uranium from the particular type of ore targeted in the present work.

Dependence of Uranium Leaching on the Lixiviant Concentration and other parameters of the Ore

After selection of the complexing and oxidizing agents (NH_4HCO_3 and H_2O_2), 25 types of lixiviant compositions were tested for the leaching of uranium from the ore under study (Table-6).

The basic idea of selecting these compositions was that uranium was only ~0.07 % in the ore and going for a higher concentration would be uneconomical although, use of much higher concentrations have been reported in the literature [11]. Also, any excess of bicarbonate used must be neutralized with some stronger base such as NaOH during uranium precipitation [12]. A further approach was to look at the trend of the ore body with regard to ejection of its values (uranium and other metals / non-metals) with changing concentration of the lixiviant.

Table-6: Lixiviant Compositions in Tap Water Solvent, Employed in the Leaching Study of Uranium from the Selected Ore.

S. No	NH_4HCO_3 (g/L)	H_2O_2 (g/L)
1	0	0
2	0	0.5
3	0.5	0.5
4	1	0.5
5	1.5	0.5
6	2	0.5
7	2.5	0.5
8	3	0.5
9	3.5	0.5
10	4	0.5
11	4.5	0.5
12	5	0.5
13	1	0
14	2	0
15	3	0
16	4	0
17	4	1
18	4	1.5
19	4	2
20	4	2.5
21	4	3
22	4	3.5
23	4	4
24	4	4.5
25	4	5

It has been reported in the literature [13] that leaching tests conducted on actual ore samples usually give anomalous results, due in part to differences among samples, even from the same deposit and possible complicating effects of metals other than uranium as well as other components in the samples. This is obvious because the ore body is a heterogeneous system and so in addition to the above-mentioned factors the difference in porosity and permeability and the content of the existing oxidized uranium from one point to another point within the ore body would affect the leaching process (Table-7). Another difficulty is that one sample from a specific point in the body can be used only once for a specific lixiviant system and the response of the same sample for another lixiviant system cannot be established. Hence, only a general overall response of the ore body can be obtained from the laboratory simulation study of the ore samples by using different lixiviant systems with respect to the concentration of the oxidizing and reducing agents. Thus, a more empirical approach would be to use a substantially pure uranium compound for laboratory simulation study such as uranium dioxide (UO_2). However, laboratory simulation studies of the actual ore bodies are valuable as there is no other way to know the response of the ore towards different lixiviant systems or to different concentrations of the same type of lixiviant system. It is because that the extent to which a particular type of leaching solution is effective or relatively ineffective in solubilizing a pure uranium compound will obviously have the same effect on the ore containing the same type of uranium compound.

Twenty five (25) samples were taken at different spots from the ore body under study. The maximum distance between these spots was 27.5 m. By looking at the Tables-7 and 8, it is clear that the total uranium concentration changes in about similar weights of the samples in the range of 270 – 687 ppm. Similarly, the oxidized uranium content (U^{+6}) ranges from 8 – 37 %. The other parameters, such as porosity and permeability also change significantly at different points showing the heterogeneity of the ore body. However, at the same spot and by just changing the depth, a small difference is observed in the porosity and permeability of the ore (the central figure in the Sample No. represents the same spot i.e. 46, 22 etc. in Table-7). But the difference in uranium can be observed in the samples from the same spot, with changing depth, showing the lack of uniformity in uranium mineralization within the ore body. Thus, the leaching efficiency of the different lixiviant concentrations for uranium would be certainly dependent to some extent, among other factors, on the concentration of uranium in a particular sample.

Tap water was used as solvent in all the lixiviants. When this was used as lixiviant without adding any complexing and oxidizing agent, about 40 % leaching of uranium was obtained (Table-7). Since, tap water contains HCO_3^- (218 ppm, Table-4) which is the complexing agent and also part of the uranium was already in oxidized form in the sample used (12 % U^{+6}) so this much amount (~ 40%) was leached by tap water only. A general trend of increase in leaching of uranium was observed for samples at S.No.1 - 5 in Table-7 with the increasing concentration of complexing agent at constant concentration of oxidizing agent in the lixiviant. This is understandable as HCO_3^- enhances leaching [14]. These are the samples from the same spot in the ore body (Spot No.46) which differs from each other only in the depth of their recovery. That is why these samples have close values of porosity and permeability. The small anomalies in leaching can be attributed to the difference in the oxidized content of uranium (U^{+6}) which is a ready fraction of the metal for dissolution.

Again the two samples at S.No.6 and 7 are from the same spot but the leaching of uranium has not increased with the increasing concentration of the complexing agent at constant concentration of oxidant. Although, the oxidized content of uranium is twofold for sample at S.No.7 but the smaller leaching of uranium can be attributed to the originally smaller concentration of total uranium and possibly to the presence of some refractory material that is inert to the rather mild lixiviant. The somewhat dry nature of this latter sample (smaller porosity and low moisture content) might have played its part in the low uranium recovery. Similar is the case with other samples taken from different spots of the ore bodies. A general overview of the samples studied shows that the anomalies in leaching of uranium are due to the difference in the existing oxidized form of uranium, the total uranium content of the sample or to the possibility of the presence of refractory material that may or may not be reflected in the permeability parameter. It is because that sometimes, there is a fault or fracture in the ore which allows a quick exit of the lixiviant (high flow rate, resulting in high permeability) but poor leaching of uranium.

The highest leaching of uranium (90.38%) was obtained by the lixiviant composition of 5 and 0.5 g/L while the lowest leaching (18.19%) was noted for the lixiviant composition of 3 and 0 g/L with respect to complexing and oxidizing agent pair respectively. Now the two samples involved here have almost the same content of uranium. The difference is in the content of the oxidized uranium which is almost twice for the sample giving the highest leaching (20 % compared to 9 %). Moreover, no oxidant was added to the sample giving the lowest leaching so this factor has been reflected in the substantial difference between the oxidation-reduction potential (ORP) of the two samples as shown in Table-8. The importance of a high value of ORP is essential for the effective leaching of uranium [1].

One other interesting feature appearing from Table-7 and Fig. 2 is that the uranium leaching is higher for the lixiviant having 2 g/L complexing agent as compared to 3 g/L while in both cases no oxidant has been added. The other factors in case of the two samples are comparable but the significant difference lies again in the content of the original oxidized uranium. The sample receiving the 2 g/L complexing agent has almost twofold hexavalent uranium (20 %) than the other sample receiving 3 g/L complexing agent (9 % only), a factor which essentially overshadowed the higher content of complexing agent for the recovery of uranium.

The relationship between the lixiviant components and leaching of uranium is also elaborated in Fig. 2. The leaching of uranium during the passage of all the 20 irrigations has been shown in Tables-9 and 10, only for the extreme cases i.e. highest and lowest recovery of uranium. An overview of the tabulated data shows that uranium leaching is higher in the initial irrigations because large content of the existing oxidized metal (hexavalent uranium) is available. In addition, the more exposed and so easily oxidizable uranium in the sample results in higher uranium leaching with increasing concen-tration of the oxidant and complexing agent. The anomalies may probably be due to the presence of some refractory material in the heterogeneous ore body as well as the insufficient time for the decomposition of the oxidant hydrogen peroxide at higher concentrations, resulting in the poor release of oxygen.

Table-7: Relationship of Uranium Leaching with Lixiviant Conc. and Some Physical Parameters.

S. No	Sample No.	(NH_4HCO_3) gm/L	(H_2O_2) gm/L	(%) Leaching of U_3O_8	Total U_3O_8 (U^{+4}+ U^{+6}) ppm*	% U_3O_8 (U^{+6} only)	% age Porosity	permeability m / day	Recovery Depth (feet)**
1	B-46-23	0	0	40.17	644	12	36.24	1.53	396 - 397'
2	B-46-19	0	0.5	50.6	405	18	30.56	1.4	392 - 393'
3	B-46-20	0.5	0.5	76.41	534	22	27.75	1.38	393 - 394'
4	B-46-21	1	0.5	86.32	672	16	33.6	1.48	394 - 395'
5	B-46-22	1.5	0.5	85.22	555	13	33.42	1.47	395 - 396'
6	B-21-16	2	0.5	76.56	550	11	46.56	0.52	357- 358'
7	B-21-18	2.5	0.5	68.32	300	22	27.27	0.4	359 - 360'
8	B-22-8	3	0.5	75.05	678	22	38.26	0.35	427 - 428'
9	B-22-11	3.5	0.5	84.45	572	16	39.03	0.71	430 - 431'
10	B-22-14	4	0.5	76.95	525	37	36.56	0.68	433 - 434'
11	B-21-14	4.5	0.5	87.6	484	34	27.91	0.41	355 - 356'
12	B-42-10	5	0.5	90.38	385	20	30.18	1.22	428 -429'
13	B-46-24	1	0	37.93	686	12	29.76	1.39	397 - 398'
14	B-46-25	2	0	48.65	687	18	33.88	1.48	398 - 399'
15	B-46-16	3	0	18.19	380	9	43.63	1.61	389 - 390'
16	B-22-15	4	0	78.62	337	18	28.19	0.63	434 - 435'
17	B-39-15	4	1	88.29	393	9	36.78	1.47	384 - 385'
18	B-39-17	4	1.5	86.02	515	8	38.38	1.48	386 - 387'
19	B-39-14	4	2	84.32	274	11	37	1.48	383 - 384'
20	B-40-4	4	2.5	81.08	270	31	31.06	1.31	452 - 453'
21	B-40-5	4	3	78.91	370	37	33.25	1.37	453 - 454'
22	B-40-7	4	3.5	84.73	393	25	33.15	1.35	455 - 456'
23	B-40-9	4	4	88.19	483	19	33.46	1.42	457 - 458'
24	B-40-10	4	4.5	83.37	433	17	31.53	1.32	458 - 459'
25	B-40-11	4	5	72.93	414	20	29.77	1.28	459 - 460'

* [gms U_3O_8 in the sample x 10^6 / sample actual wt in gms] ** Underground depth of the ore body from where the sample was recovered

Table-8: Relationship of Uranium Leaching with Lixiviant Conc. and Some Physical Parameters.

S.No	Sample No.	(NH_4HCO_3) gm/L	(H_2O_2) gm/L	Sample actual wt (gm)*	Total U_3O_8 (U^{+4}+ U^{+6}) ppm [gms U_3O_8 x 10^6 / sample actual wt in gms]	Beeta Counts /second (cps)	Sample initial Moisture Content (%)	Initial pH of Solution (Lixiviant)	Initial ORP of Solution (Lixiviant)
1	B-46-23	0	0	1656.01	644	644	12.55	8.22	196
2	B-46-19	0	0.5	1731.91	405	504	11.56	8.19	208.1
3	B-46-20	0.5	0.5	1728.9	534	504	11.69	7.77	214.6
4	B-46-21	1	0.5	1664.85	672	532	11.55	7.74	210.4
5	B-46-22	1.5	0.5	1692.35	555	616	12.26	7.73	197.1
6	B-21-16	2	0.5	1605.596	550	476	14.28	8.11	181
7	B-21-18	2.5	0.5	1586.15	300	224	12.54	8.12	165.7
8	B-22-8	3	0.5	1464.75	678	616	13.17	8.07	159.4
9	B-22-11	3.5	0.5	1391.17	572	588	7.89	8.09	156.2
10	B-22-14	4	0.5	1588.72	525	504	11.27	8.09	156.7
11	B-21-14	4.5	0.5	1727.63	484	420	10.9	7.61	204.6
12	B-42-10	5	0.5	1759.47	385	308	11.06	7.69	192.4
13	B-46-24	1	0	1733.39	686	616	9.72	7.75	176.9
14	B-46-25	2	0	1779.23	687	560	11.33	7.66	167
15	B-46-16	3	0	1572.49	380	224	16.34	7.72	157.2
16	B-22-15	4	0	1656.48	337	476	7.58	7.68	188.2
17	B-39-15	4	1	1810.19	393	392	14.17	7.78	181.8
18	B-39-17	4	1.5	1810.69	515	476	14.35	7.77	181.3
19	B-39-14	4	2	1745.86	274	280	14.07	7.79	185.1
20	B-40-4	4	2.5	1659.995	270	196	14.26	7.82	180.5
21	B-40-5	4	3	1752.8358	370	224	14.52	7.84	177.8
22	B-40-7	4	3.5	1708.6353	393	336	14.37	7.87	172.9
23	B-40-9	4	4	1784.3827	483	420	12.28	7.91	182.1
24	B-40-10	4	4.5	1695.7506	433	392	14.42	7.92	172.4
25	B-40-11	4	5	1768.7081	414	392	11.66	7.96	170.4

Table-9: Extraction of Uranium from the Selected Ore Samples (T = 25 ±1 C°)*

S. No	Vol. collected (ml)	U_3O_8 (ppm)	U_3O_8 (gm)	U_3O_8 Leaching (%)	Ca^{+2} (ppm)	Mg^{+2} (ppm)	Cl^- (ppm)	SO_4^{-2} (ppm)	Na^+ (ppm)	K^+ (ppm)	CO_3^{-2} (ppm)	pH 7.69^a	ORP (mV) 192.4	Cond. µS/cm 11500
1	960	228	0.21888	32.3519	95	97	164	187	195	61	N.D	8.08	186.7	12600
2	990	110	0.1089	16.0961	36	33	107	207	141	26	N.D	8.08	189.8	12300
3	995	64	0.06368	9.4123	18	24	116	198	141	15	N.D	8.16	157.9	12500
4	1000	41	0.041	6.0601	15	18	138	193	141	13	N.D	8.14	174.5	12800
5	------	28	0.028	4.1386	15	15	133	194	141	10	N.D	8.12	146.8	11800
6	------	29	0.029	4.2864	17	13	142	235	141	10	N.D	8.19	136.6	12600
7	------	18	0.018	2.6605	14	12	154	246	136	09	N.D	8.19	132.8	12100
8	------	20	0.020	2.9561	13	12	155	204	150	08	N.D	8.15	136.7	12100
9	------	13	0.013	1.9215	13	10	148	216	141	05	N.D	8.16	131.1	12200
10	------	14	0.014	2.0693	09	14	149	208	155	06	N.D	8.11	126.0	12300
11	------	11	0.011	1.6259	08	13	154	211	150	05	N.D	7.87	162.8	11800
12	------	08	0.008	1.1825	09	11	144	225	145	05	N.D	7.88	173.1	12700
13	------	07	0.007	1.0346	08	12	125	222	155	04	N.D	7.85	166.2	12100
14	------	06	0.006	0.8868	12	09	168	209	141	04	N.D	7.88	148.3	12500
15	------	06	0.006	0.8868	09	11	169	166	145	04	N.D	7.87	164.8	12600
16	------	04	0.004	0.5912	12	08	130	255	150	04	N.D	7.88	177.0	12600
17	------	04	0.004	0.5912	11	09	146	263	137	04	N.D	7.86	165.2	12500
18	------	04	0.004	0.5912	11	08	147	246	141	04	N.D	7.85	172.4	12200
19	------	04	0.004	0.5912	10	09	109	243	146	04	N.D	7.90	164.6	12200
20	------	03	0.003	0.4434	12	09	131	222	145	04	N.D	7.92	123.0	12100
Leached (U_3O_8)			0.61146 gm	90.38 %	0.70 %	3.39 %	94.52 %	82.35 %	72.61 %	8.81 %	7.26 %			
Residue (U_3O_8)		37 ppm		% Leaching	2.40 %	0.55 %	96 ppm	554 ppm	600 ppm	1168 ppm	4.49 %			

***Conditions:** Lixiviant Composition {NH_4HCO_3 (g/L) = 5.0, H_2O_2 (g/L) = 0.5} in Tap Water
Total Uranium Content of the Ore Sample (U_3O_8) = 0.67656039 gm
Volume of Lixiviant used in One Irrigation = 01 Lit.
Contact Time of Lixiviant and Ore Sample = 01 Hr
a: Values of Physical Parameters for the Fresh Lixiviant

Leaching of Non-Transition Metals / Radicals along with Uranium from the Ore

The leaching behaviour of seven number non-transition metals and radicals was observed along with uranium in the laboratory simulation study. Uranium forms strong di- and tricarbonate complexes in alkaline medium in the presence of carbonate with high formation constants [15-16]. Along with extraction of uranium from the ore, one of the purpose of the laboratory simulation study was to observe the leaching behaviour of some of the elements / radicals, whatever their concentration was in the ore, in the employed lixiviant systems. These metals / radicals included two alkali metals Na and K, two alkaline earths Ca and Mg, one known corrosive element Cl and two other radicals SO_4^{-2} that is a complexing agent for uranium [2] and CO_3^{-2} which is also a complexing agent of uranium [17-23].

CO_3^{-2} is also a precipitating agent, most importantly of Ca and Mg at high pH values. The leaching behaviour of the non-transition metals / radicals is shown in Fig. 3 and 4.

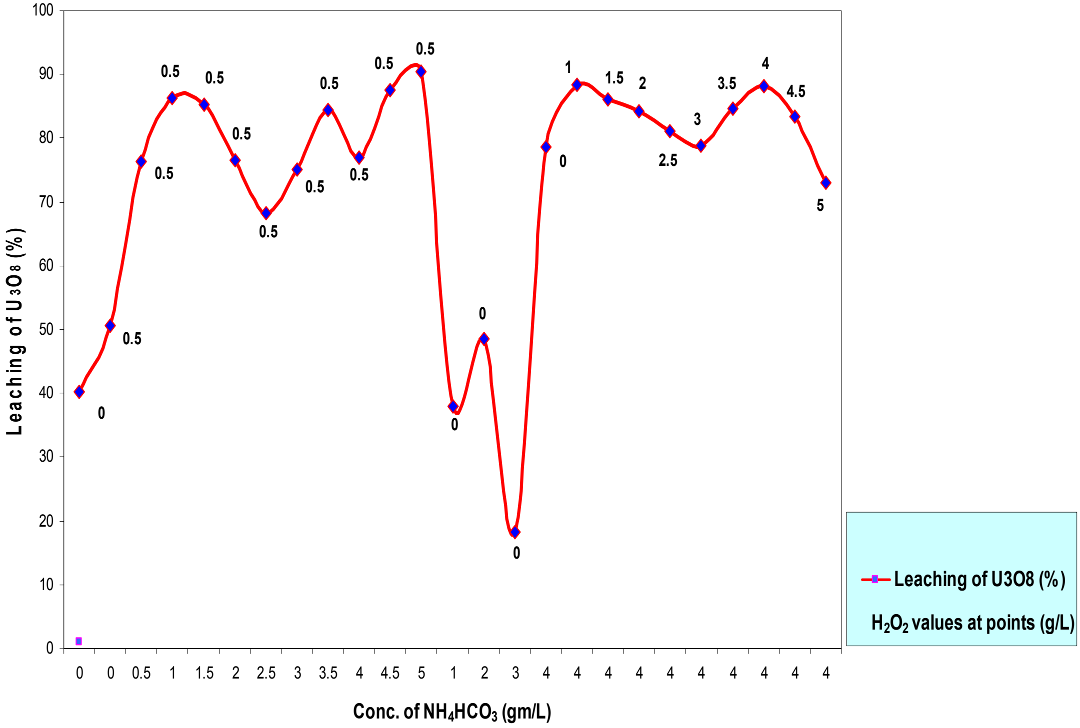

Fig. 2: Extraction of Uranium Vs Conc. of Ammonium Bicarbonate (g/L).

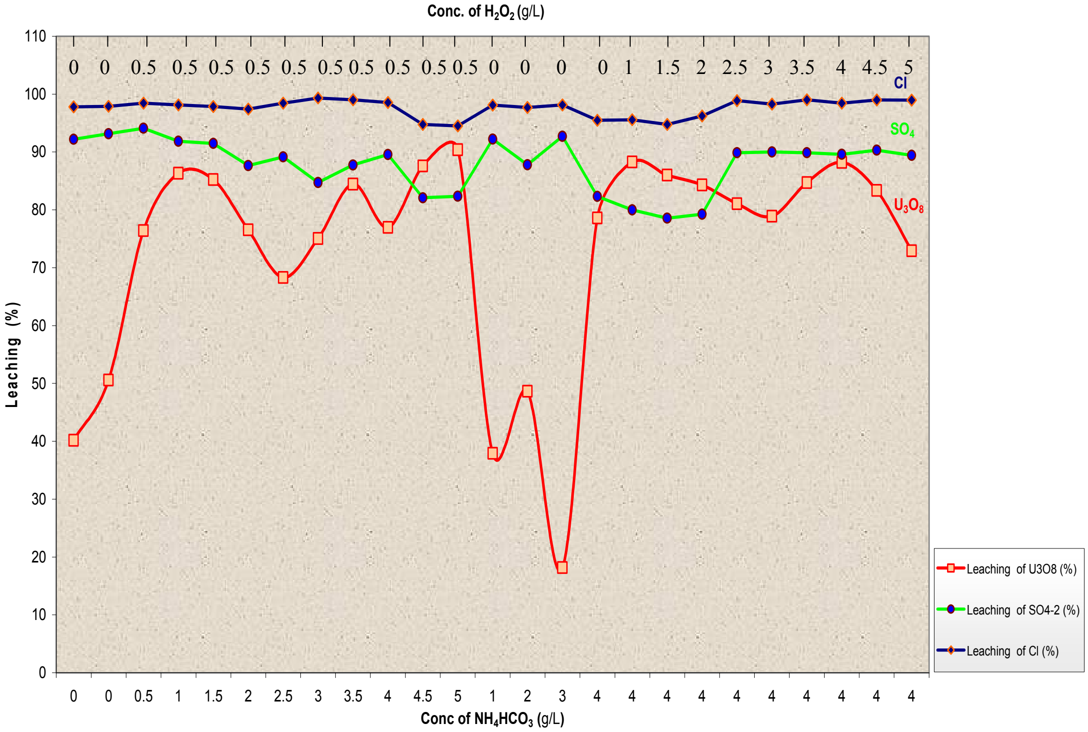

Fig. 3: Comparison of the Leaching of Uranium with Cl and SO_4^{-2} in the Lixiviant of NH_4HCO_3 and H_2O_2 in Tap Water.

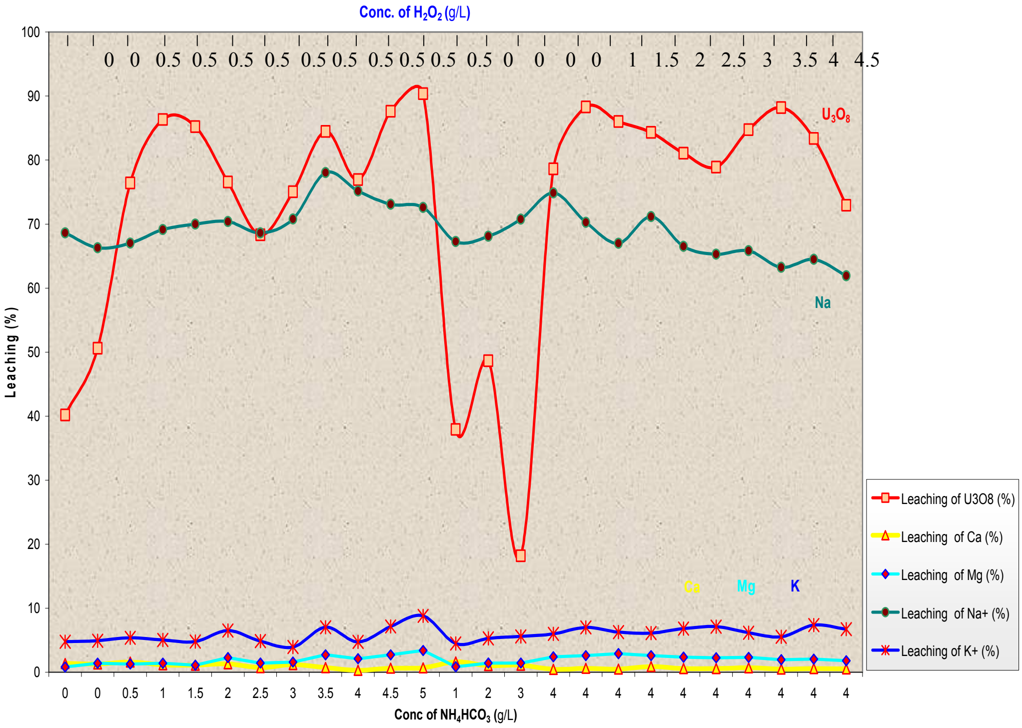

Fig-4: Comparison of the Leaching of Uranium with Na, K, Ca and Mg in the Lixiviant of NH_4HCO_3 and H_2O_2 in Tap Water.

From Fig. 3 and 4 along with Tables [9, 10] it can be observed that in the media, comprising hydrogen peroxide (H_2O_2) and ammonium bicarbonate (NH_4HCO_3) in the range 0-5 g/L and changing their concentrations with respect to each other, the solubility criteria of the species followed the pattern $Cl^- > SO_4^{-2} > U > Na^+ > K^+ > Mg^{+2} > Ca^{+2} > CO_3^{-2}$. Thus "$CO_3^{-2}$", followed by "Ca" is the least soluble in these media while "Cl" followed by "SO_4^{-2}" is the most soluble one. The other elements among the non-transition metals have intermediate solubilities. The dissolution of Ca is potentially very much important as it can precipitate as $CaCO_3$ or $CaSO_4$, resulting in partial or complete blockage of the channels within the ore and lines controlling the fluid (fresh and loaded lixiviant) flow. The literature has reported <0.1 % Ca dissolution in carbonate leaching [12] but in the present study, values of 0.32 % - 1.63 % has been obtained.

While in case of acidic leaching, almost complete solubility of these elements and radicals would be expected but in the present case of non-acidic /carbonate leaching; only a part of most of the involved species is soluble. Thus, purest uranium product is obtained proving the economical effectiveness as well as the environment friendly nature of the technique. It may be noted that the tap water being used as solvent (Table-4) also contains these metals and non-metals in varying amounts. Being unavoidable, these were considered as background or blank concentrations.

By looking at the Tables 9 and 10, it can be seen that the values of oxidation-reduction potential (ORP) are somewhat abnormal and are not proportional to the amount of H_2O_2 added. The values of ORP are a measure of the oxygen content in the medium. Suitably high values of ORP are essentially required for the leaching / extraction of uranium in both acidic and alkaline leaching. Unfortunately, redox potential (ORP) in nature cannot be determined simply and unambiguously. The reason for the abnormal or unexpected values of ORP has been cited in the literature [24] which explains that most redox potential measurements in nature give us only qualitative or semi-quantitative information, particularly in cases where oxygen is involved as in the present work. The matter has been complicated further by the presence of the oxidant H_2O_2 (source of O_2) which is highly unstable in alkaline media like ours.

Table-10: Extraction of Uranium from the Selected Ore Samples (T = 25 ±1 C°)*.

S.No	Vol. collected (ml)	U_3O_8 (ppm)	U_3O_8 (gm)	U_3O_8 Leaching (%)	Ca^{+2} (ppm)	Mg^{+2} (ppm)	Cl^- (ppm)	SO_4^{-2} (ppm)	Na^+ (ppm)	K^+ (ppm)	CO_3^{-2} (ppm)	pH 7.72[a]	ORP (mV) 157.2	Cond. µS/cm 13300
1	960	02	0.00192	0.3212	20	12	166	145	147	05	N.D	7.99	134.0	11200
2	990	04	0.00396	0.6624	17	15	163	169	167	05	N.D	7.87	158.3	13300
3	993	10	0.00993	1.6611	25	21	121	242	159	08	N.D	7.87	164.4	16100
4	993	07	0.00695	1.1628	24	25	132	248	155	11	N.D	7.83	152.3	14000
5	1000	06	0.006	1.0037	23	26	159	209	146	11	N.D	7.82	150.9	13600
6	------	06	0.006	1.0037	22	24	129	214	146	11	N.D	7.84	146.2	13000
7	------	07	0.007	1.1709	19	22	147	190	141	10	N.D	7.87	138.9	13100
8	------	12	0.012	0.0073	17	21	126	194	141	08	N.D	7.89	148.7	15900
9	------	11	0.011	1.8401	13	18	134	213	150	06	N.D	7.88	135.6	10500
10	------	05	0.005	0.8364	14	16	143	228	150	06	N.D	7.89	162.7	10300
11	------	03	0.003	0.5018	13	15	148	215	141	03	N.D	7.95	126.2	11400
12	------	04	0.004	0.6691	12	13	157	209	141	04	N.D	7.89	139.1	11500
13	------	03	0.004	0.5018	11	15	148	197	141	04	N.D	7.92	133.5	11000
14	------	04	0.004	0.6691	12	12	127	216	141	03	N.D	7.89	167.8	10700
15	------	04	0.004	0.6691	11	11	128	255	136	04	N.D	7.96	122.5	12200
16	------	04	0.004	0.6691	10	11	146	172	136	04	N.D	7.92	159.4	12000
17	------	04	0.004	0.6691	10	13	146	198	141	03	N.D	7.93	150.3	12600
18	------	04	0.004	0.6691	12	10	134	227	141	03	N.D	7.89	156.8	12500
19	------	04	0.004	0.6691	12	11	156	232	136	03	N.D	7.91	151.3	11700
20	------	05	0.005	0.8364	12	10	141	210	136	03	N.D	7.92	141.2	11600
Leached (U_3O_8)			0.10876 gm	18.19 %	1.09 %	1.45 %	97.71%	92.72 %	70.75 %	5.59 %				
Residue (U_3O_8)		311 ppm	% Leaching		1.72 %	1.29 %	37 ppm	226 ppm	713 ppm	1284 ppm	5. 34 %			

***Conditions**: Lixiviant Composition {NH_4HCO_3 (g/L) = 3.0, H_2O_2 (g/L) = 0} in Tap Water
Total Uranium Content of the Ore Sample (U_3O_8) = 0.5978053 gm
Volume of Lixiviant used in One Irrigation = 01 Lit.
Contact Time of Lixiviant and Ore Sample = 01 Hr
a: Values of Physical Parameters for the Fresh Lixiviant

Table-11: Relationship of Contact Time of the Ore and Lixiviant with Leaching of Uranium.

S. No	Sample No	Contact Time (hr)	Pregnant Lixiviant U_3O_8 (ppm)	% Leaching	Rate Constant K (hr^{-1})
1	B-42-10	1	55.84	81.95	2.2475
2	B-42-11	2	59.56	87.67	1.5385
3	B-42-12	3	62.44	89.50	------

The conductivity values were also measured for all the lixiviant systems and each individual irrigation during the course of the experiment. These values did not give a flat profile and widely differed from one irrigation to the other. This fact is obvious as numerous ions were involved and their extraction from the heterogeneous ore body varied in different irrigations.

Leaching of Transition Metals along with Uranium from the Ore

The content as well as the leaching behaviour of eight transition metals was observed in the laboratory simulation study of the target ore. These transition metals are Fe, Mn, Cu, Zn, V, Mo, Cr and Ti. Their leaching behaviour is shown in Fig. 5. Except Fe, which is >1% of the ore, the other transition metals are ~0.02 % or less in concentration. Knowledge of the ore content of the metals as well as study of their leaching behaviour is of prime importance as not only these contaminate the final product but some of these, particularly, Mo and V pose a serious problem during purification of uranium where these metals also load along with uranium on a cation exchange resin. Mo is also environmentally deleterious [25]. Small amounts of vanadium in solution are particularly difficult to separate from uranium during subsequent processing and often cause contamination of the final "yellow cake" product unless special purification steps are included in the process [26]. The transition metals, particularly Fe, Mn and Cu also catalyze the undesirable decomposition of the oxidant H_2O_2. The heavy metal Cr is known for its detrimental effects on the peroxy compounds [27].

Among the transition metals studied in the present work, Fe has the highest concentration, varying in the range ~ 8000 ppm -16000 ppm. But fortunately, leaching of Fe has been very low, typically in the range of 0.04 – 0.2 % except the last sample. The low leaching behaviour of Fe in the relatively mild alkaline solutions of this study is understandable as in neutral or basic solutions, it often occurs in the form of divalent compounds, easily precipitating out from aqueous solutions. On the contrary, in acidic solutions Fe appears as trivalent compounds which can be easily removed from the solid phase [28-30].

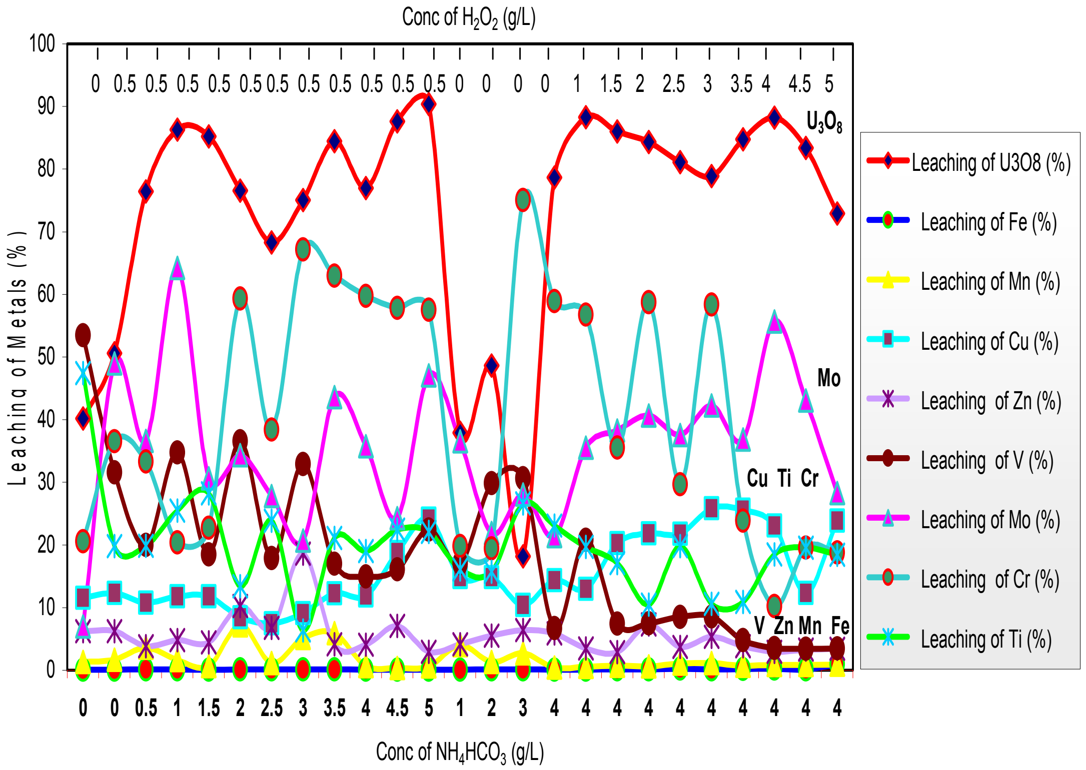

Fig. 5: Comparison of the Leaching of Uranium with Transition Metals, Fe, Mn, Cu, Zn, V, Mo, Cr and Ti in the Lixiviant of NH_4HCO_3 and H_2O_2 in Tap Water.

In all the samples analyzed, the concentration of Mn is around 200 ppm and its leaching remained up to 7 % only. The reason of the low leaching of this metal may be that firstly, Mn is mostly found in the target ore in tourmaline (14 number silicate minerals group, Table-1) which is in small concentration (0.03 %) and secondly and more importantly, carbonate leaching of silicate type of uranium minerals is accomplished with difficulty [2]. Similarly, the metals Cu, Zn and Cr are found in very low concentration in the ore i.e. up to 10, 33 and 34 ppm respectively. The leaching of Cu remained low, reaching up to 26 % and showing an upward trend for dissolution when the concentration of oxidizing agent was increased in the lixiviant. The case of Zn is similar to that of Cu showing low leaching of up to ~ 10 % in all but one case. However, the difference between the two metals is that unlike Cu, their has been no change in the leaching trend of Zn with the increasing concentration of oxidizing agent H_2O_2 in the lixiviant. Zn is also found mostly in silicate minerals along with Cu which are not effectively attacked by carbonate lixiviant. Another important reason of the low leaching of the two metals Cu and Zn may be the fact that the hydroxide of both are precipitated out of the solution at around pH = 6, while the pH values of the lixiviants used have been well above this value i.e. ~ 8 or more [31-32]. Thus these two factors i.e. mineralogical inertness of silicates and precipitation of the hydroxides at low pH values resulted in the poor leaching of Cu and Zn from the ore. In case of Cr, leaching of the metal is somewhat abnormal attaining a highest value of 75 %. This value is in the absence of any added oxidant and at relatively high value (4 gm/L) of the complexing agent NH_4HCO_3. This can be explained on the ground that the added HCO_3^- is a consumer of any OH^- in the medium by the reaction;

$$HCO_3^- + OH^- \rightarrow H_2O + CO_3^{--} \qquad (6)$$

Thus, the possibility of the reaction which can precipitate any Cr^{+3} (dominant valence state), is reduced as;

$$Cr^{+3} + 3OH^- \rightarrow Cr(OH)_{3\,(ppt)} \qquad (7)$$

Hence, more Cr is available for leaching. In the presence of H_2O_2 in the lixiviant, in most of the cases, reasonably high values of leaching have been recorded (~ 67 %) but in other cases, the presence of H_2O_2 (> 3 g/L) does not improve leaching of the metal. This may be due to the fact that at high concentrations, the rate of decomposition of H_2O_2 is reduced [33] and consequently, the revelation of its oxidizing power requires more time and the one hour contact time may be inadequate for this purpose.

Ti appeared to be soluble up to ~ 47 % in tap water but as the complexing agent was added to the lixiviant, the leaching rate of the metal sharply declined. This type of leaching behaviour has been cited in the literature which states that compounds of Ti are nearly insoluble in carbonate solution [2] and the releases of the metal from ore are independent of the bicarbonate concentration at pH 8 [14].

Uranium is often found associated with vanadium [25]. Vanadium in the more common silicate and oxide minerals is not solubilized to any great extent in carbonate leaching. However, in carnotite mineral, both uranium and vanadium are readily soluble [2]. The concentration of V in the present ore varied in the range 11 – 41 ppm. The leaching remained below 40 % in all the samples except one case where more than this amount has been leached out in tap water solvent. In this regard, V has behaved similarly to Ti where maximum leaching has been obtained in case of tap water and in the absence of any complexing and oxidizing agent. Thus, in the presence of H_2O_2 and NH_4HCO_3 some complex interaction might have taken place which resulted in a desired lower leaching of both these unwanted metals. It means that carbonate leaching, as claimed, has been proved to be selective for uranium leaching [2, 25]. The tap water used as solvent contains less than 1 ppm V (Table-4) so it has not contributed much to the amount of the leached metal.

Molybdenum (Mo) is often found as a contaminant of the uranium-bearing ores. At least a portion of Mo content of the ore is dissolved during alkaline leaching of uranium and is present in the resulting leach solution [34]. Fortunately, in the ore under study, the concentration of Mo has been found to be quite low (> 01 ppm) in all the samples except one sample where more than this amount has been noted (2.35 ppm). Most of the lixiviant systems employed have leached less than 40 % of Mo from the ore.

Fig. 5 shows that the lixiviant systems used have accomplished the leaching of transition metals in the order; U > Cr > Mo > V > Ti > Cu > Zn > Mn > Fe.

Thus the leaching of uranium lies at the top of all the targeted transition metals. Hence, the use of NH_4HCO_3 – H_2O_2 lixiviant system for leaching of uranium from the ore under study is selective for uranium.

Influence of Contact Time on the Leaching of Uranium and Calculation of First Order Rate Constant K

First order rate constant was calculated for the leaching of uranium from the ore by the lixiviant composition which gave the maximum recovery of the metal. Samples from the same spot on the ore body were taken as these have close values of different parameters such as porosity and permeability etc. as compared to the samples from different spots of the ore body [35]. The lixiviant was allowed to react with these separate samples for 1 hour, 2 hours and 3 hours to determine the influence of contact time of the ore and lixiviant on the leaching of uranium. The pregnant lixiviant obtained was analyzed spectrophotometrically for uranium content. The uranium, expressed as octoxide (U_3O_8), leached by the 02 hour and 03 hour contact time was compared to the amount leached by one hour contact time. The data is shown in Table-11. The first order rate constant (K) was calculated in accordance with the equation;

$$K= \frac{2.303}{t} \log \frac{Cf}{Cf - Ct} \quad (8)$$

where Ct = Concentration of uranium in the pregnant lixiviant obtained by 01 hour or 02 hour contact time (taken as incomplete leaching at time t).

Cf = Concentration of uranium in the pregnant lixiviant obtained by 03 hour contact time i.e. total uranium obtained from the sample after complete leaching.

t = Time lapse between the initial irrigation (01 hr contact time) and any other of the 02 and 03 hrs contact time.

The K values in Table-11 show that in the initial stages, the leaching of uranium is fast as the ore body ejects rather smoothly its soluble content of the metal but later on, the leaching slows down as the lixiviant is faced with the less soluble material that may need oxidation as well as some part of uranium may be entrapped in the rather refractory ore grains which are attacked by the mild carbonate lixiviant with difficulty.

Experimental

Acquisition of Samples from the Underground Ore Body

Samples were recovered for laboratory simulation study from the underground ore body. These samples, having a diameter of 8.5 cm, were of 30.48 cm (1 foot) length. After recovery, the samples were immediately wrapped in a cloth and molten wax was applied to them so to preserve the original (in-situ) oxidation states of the elements therein, the moisture and other changeable properties of the ore.

Identification of the Ore Body

The petrographic study (description and classification of rocks) of the samples was carried out. The grain size ranged from very coarse to very fine (1.07 – 0.05 mm), with well defined boundaries. The main detrital (loose mass of stones, silt etc. worn away from rocks) constituents of the samples were found to be quartz, feldspar and rock fragments. The rock formation of the ore was Sandstone and since the feldspar content was found to be greater > 25 % so it was classified as "Arkosic type of sandstone" [1]. The mineral was identified as uraninite (radioactive, uranium rich mineral) the overall chemical composition of which is represented as UO_2. After extensive sampling, the ore grade was found to be ~ 0.07 % U_3O_8.

Heavy Minerals Analysis of the Ore Body

Bromoform is an organic liquid commonly used for the separation of heavy minerals from the light minerals. Its specific gravity is = 2.98. The minerals which sink in this liquid are classified as "sink" while those which do not sink are called "float". This was the process performed with the ore samples under study. The "sink" portion was recovered from bromoform, dried in the oven and magnetite was removed with the help of hand magnet. After removal of magnetite the remaining sink was fed into the "Isodynamic Separator". The minerals were thus separated on the basis of their magnetic susceptibility. All the fractions were analyzed for uranium. The average percentage of the "sink" is given in Table-1.

Light Minerals Analysis of the Ore Samples

Since the "sink" contained no uranium so the remaining portion i.e. "float" was dried at room temperature and ground with fingers. No hammering was performed so to preserve the actual grain size of the ore. Samples were then passed through mesh no. 60. Sample fractions retained by mesh no.60 "i.e. + 60 mesh" was crushed / ground again with fingers so most of the sample passed through mesh no.60. Following set of sieves were used in "Sieve Analysis" of the ore.

(i) Mesh no.60 (ii) Mesh no.100 (iii) Mesh no.150 (iv) Mesh no.200 (v) Mesh no.250

The results of the chemical analysis of the different "floats" of the two ore samples (A and B) for uranium are given in Table-2. The uranium was analyzed spectrophotometrically.

Leaching / Extraction of Uranium

For the laboratory simulation of the ore for uranium leaching and some other metals and non-metals, the waxed samples were cut into 15 – 20 cm length. Specially designed columns of fiberglass of 50 cm length and 10 cm diameter were employed to hold the ore samples in the leaching / extraction experiments (Fig. 1). A set of six columns was used. The samples were fitted vertically in the columns above pebble stones bed of few centimeters height. The pebble stones would filter out any sandy material coming out of the samples so that clear filtrate could be obtained. The space between the sample and the column wall was plugged with glass wool and molten wax was applied to the entire sample at the top end. When the wax cooled down and hardened to some extent, a hole was bored through it at the top of the sample. This arrangement would force the entire lixiviant to pass through the sample only and not through its sides. The selected lixiviants were added from graduated glass devices of 01 litre capacity. 20 litres of each type of lixiviant was passed through one sample, one litre at a time. The drop-wise addition of lixiviant to the sample column was started, keeping the drain tap of the column fully closed. The addition of lixiviant was continued until it stood up at about 3 cm at the top of the sample. At this stage, further addition of the lixiviant was held on for 01 hour. When the contact time of 01 hour between the lixiviant and the sample lapsed, the drain tap, as shown in Fig. 1, was fully opened. The lixiviant addition was resumed and its in-flow rate was adjusted in such a way that the out-flow of the pregnant lixiviant (lixiviant passed through the sample) through the drain tap at the bottom was equal to the in-flow of the fresh lixiviant at the top. Hence, the level of lixiviant at the top of the sample was maintained at Δh up to a time when all the lixiviant was added to the column. Δh, called the "hydraulic head" was kept the same for all the samples i.e. 17.5 cm. Hydraulic head is the length of liquid column from its level at the top up to the exit point. This parameter is used in the Darcey's equation (Eqs-10, 11) for calculating the parameter "Permeability". At this stage, the pregnant lixiviant coming out of the sample was collected in a small graduated cylinder for about 4 – 5 minutes. Collection time of the pregnant lixiviant was noted with the help of a stop watch. Flow rate (ml / minute) of the loaded lixiviant from each sample was calculated. The uranium and the other metals and non-metals under study were analyzed in both the pregnant lixiviant and in the sample residue for each lixiviant system. Different analytical techniques were used for this purpose. U, Cl^- and SO_4^{-2} were analyzed spectrophotometrically, using UV-Visible (Shimadzu-1201) instrument. Na and K were determined by flame photometry employing PFP-7 (Jenway) flame photometer. Ca, Mg and CO_3^{-2} were analyzed by titrimetry. The transition metals Ti, V, Cr, Mn, Fe, Cu, Zn and Mo were determined by atomic absorption spectrometry. The instrument used was Perkin Elmer AA-700. The chemicals used were of Merck, Fluka and BDH origin.

Porosity and Permeability Measurement of the Ore

As mentioned above, 20 litre lixiviant was passed through each sample, in succession of 01 litre. The out-coming lixiviant (filtrate) from each sample was collected and measured in a graduated cylinder. The collected volume was obviously less than the volume of lixiviant passed. The balance volume was supposed to be trapped in the void spaces within the sample. The original moisture content of each sample was known that was determined before setting the sample to the column. For this purpose, suitable weight was taken from a cut off part of each individual sample and dried in the oven at 105 °C for 04 hrs. This moisture content was added to the volume of lixiviant trapped in the sample. Hence, the total volume of moisture, trapped in the sample was determined which was taken as the void space in the sample. The total volume of each sample was known that was determined for all the cylindrical samples before starting the leaching experiment. This was done by using the formula $[(\pi.d^2/4).L)]$, where "d" is the diameter of the sample and "L" is its length. The total volume of moisture in the sample was compared to the total volume of the sample (including both voids and solid) and so the percentage porosity (η) was calculated by the equation,

$$\eta = (Vv \times 100) / V \qquad (9)$$

Where Vv = Void volume or space in a unit volume of earth material.

V = Unit volume of earth material, including both voids and solids.

For permeability calculation, the flow rate of lixiviant (*Q*) from each sample was put in equation-10 or 11. The length (L) and cross sectional area (A) of the transverse section of each sample were known while the value of the "hydraulic head" Δh was also known. These values were put in the Darcy's equation (Eq-10 or 11), and the coefficient of permeability (*K*) values were calculated for all the samples as given in Table-7.

$$K = (Q \times L) / (\Delta h \times A) \quad \text{cm/ min} \qquad (10)$$

or

$$K = (Q \times L \times 14.4) / (\Delta h \times A) \quad \text{m/ day} \qquad (11)$$

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