

Stabilization of Hydrogen Peroxide used as Oxidizing Agent in the In-situ Leaching of Uranium from Arkosic Sandstone

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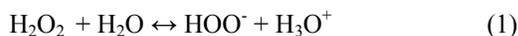
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Summary: H₂O₂ was used as oxidizing agent of the insoluble tetravalent uranium into the soluble hexavalent state along with NH₄HCO₃ as complexing agent in tap water solvent. The study was conducted to look at the possibility of commercial scale insitu leaching of uranium from an underground arkosic sandstone ore deposit. It was found that the peroxide was unstable in the basic tap water solvent as well as in the lixivants to be used for uranium leaching, especially, in the presence of Ca ions and NH₄HCO₃. The rate of dissipation of the oxidizing agent was studied in different media at room temperature for 192 hours with distilled water as a reference medium. The material was stabilized by complexing the different ions / metal catalysts in the lixiviant by EDTA. In the presence of EDTA the stability behaviour of the peroxide became almost identical in the distilled water and tap water lixivants.

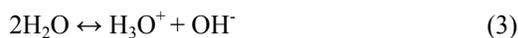
Introduction

Insitu leaching is the newest of the static bed leaching technologies which is used to extract uranium and some other metals from low grade underground ore bodies [1]. In the underground ores [2], a large part of uranium is in the insoluble tetravalent state [3] which requires oxidation to the soluble hexavalent state. Thus, a suitable oxidizing agent is essentially required in nearly all the insitu operations for uranium.

A laboratory simulation study was carried out to look at the possibility of large scale alkaline insitu leaching of uranium from an underground ore that was identified as arkosic sandstone. In this study, H₂O₂ was used as oxidizing agent [4] along with NH₄HCO₃ as complexing agent in tap water solvent. NH₄HCO₃ was used as a source of CO₃²⁻ / HCO₃⁻ ions for the formation of stable and soluble UO₂(CO₃)₃⁴⁻ complex in aqueous solution. The detail of the process is given elsewhere [5]. Distilled water was used as a reference solvent of NH₄HCO₃ and H₂O₂ for comparison. H₂O₂ is a weak acid and dissipates in two ways as follows;



The partner of the perhydroxyl anion (HOO⁻) *i.e.* H₃O⁺ is also in equilibrium with OH⁻ from the dissociation of water as;

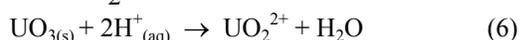
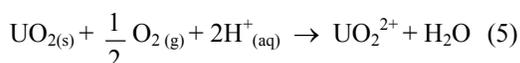


As reaction (3) shows, any increase in OH⁻ concentration will depress the level of H₃O⁺ in accordance with Le,Chatliers Principle and a corresponding dissociation of more H₂O₂ in reaction (1) to compensate this deficiency. Thus, with the increase in the alkalinity of the medium, more H₂O₂ will dissociate [6].

The decomposition reaction (2) is irreversible and is strongly catalyzed in basic medium by transition metals, especially, Cu, Mn and Fe ions [6]. The heavy metal Cr ions are also detrimental to the stability of peroxy compounds. Generally, metal (Mⁿ⁺) catalyzes the decomposition of H₂O₂ as [7];



Reaction (2) is important for the production of oxygen, required for the oxidation of uranium into the soluble hexavalent state. At higher pH values of the solution, reactions (1) and (2) are accelerated but still, (2) *i.e.* decomposition of H₂O₂ remains dominant even at pH values above 10 [8]. Hence, the preferred route of H₂O₂ dissipation is decomposition *i.e.* direct production of O₂, which is desirable. The overall oxidation of uranium is represented by either of reactions (5) and (6) where both oxidant and H⁺ are required.



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Reactions (5, 6) are equally applicable to acidic and alkaline leaching of uranium. In acidic leaching, the H^+ is provided by acid while in alkaline leaching, it is supplied by bicarbonate (HCO_3^-) which must be present for this purpose. In its hexavalent form (e.g. UO_2^{2+}), uranium goes directly into solution.

As H_2O_2 is known to be quite unstable in alkaline media but it was found that the instability was highly increased by the presence of Ca^{2+} and NH_4HCO_3 in solution. Insitu leaching is a lengthy process often continued for several years. Normally, the lixiviant (reagent solution used for the extraction of the target species) is prepared at a central place and distributed through pipelines to different injection points on the ore body. Depending upon the size of the ore body, the pipelines may attain a length of several hundred meters. If the reagents in the lixiviant are unstable and decompose prematurely before injection to the ore, the result will be a failure of the process. One solution to the problem may be that the lixiviant is prepared and injected on different individual points of the ore or the unstable reagent is added as close to the ore body as possible. But this becomes a laborious task and sometimes impracticable. Hence, another option was tried in the simulation study *i.e.* stabilization of the unstable component H_2O_2 in the lixiviant in such a manner as to have no adverse impact on the leaching of uranium [9, 10].

In the literature, various types of materials have been quoted to stabilize the peroxide. Among these, $MgSO_4 \cdot 7H_2O$ was tried first as it does not produce any hazardous residue [9] but no stabilization of peroxide was achieved. In another attempt, a different route was adopted and instead of tampering with the H_2O_2 molecule itself, the ions responsible for catalyzing the dissociation / decomposition of the peroxide were attacked through masking / complexation. For this purpose, the chelating agent (complexing agent) ethylenediaminetetra-acetic acid (disodium salt of EDTA) was employed to complex such type of ions in the lixiviant which may destabilize the H_2O_2 molecule prematurely. The reaction of EDTA with all the cations (e.g. M^{x+}) is in 1:1 ratio which is represented as;

$$M^{x+} + H_2Y^{2-} \leftrightarrow MY^{x-4} + 2H^+ \quad (7)$$

When EDTA was employed to complex the probable cationic catalysts in the dissipation process of H_2O_2 , the premature dissipation of the peroxide was successfully overcome in the presence of Ca ions

and NH_4HCO_3 . In this way, the stability behaviour of peroxide in the tap water lixiviant became almost identical to the distilled water lixiviant.

Few samples of the target ore were tested for uranium leaching with and without the complexing agent EDTA in the lixiviant of H_2O_2 and NH_4HCO_3 .

Results and Discussion

The dissolution behaviour of U was observed in alkaline media Insitu leaching from specific arkosic sandstone the composition of which with regard to heavy minerals is given in (Table-1). Uranium was found disseminated as urano-organic complexes among a large number of light minerals in the ore. Since the concentration of uranium (as U_3O_8) was only about 0.07 % in the ore so the concentration of H_2O_2 in the lixiviant was optimized to 0.7 % (purity of $H_2O_2 = 50$ %) for oxidizing the insoluble tetravalent uranium into the soluble hexavalent form. The concentration of NH_4HCO_3 (purity > 99 %) as complexing agent of U was optimized to 4 g/L in the same lixiviant with tap water as a solvent. Tap water was preferred over distilled water in the laboratory to economize the reagents for the commercial scale operation. H_2O_2 was found to be very unstable in the basic tap water alone and especially, in the presence of NH_4HCO_3 (Tables 2-4).

Table-1: Heavy Minerals Analysis of the Ore (Arkosic Sandstone).

Name of Mineral	Average (%)
Magnetite $Fe^{2+}Fe^{3+}_2O_4$	0.18
Hematite Fe_2O_3	0.03
Ilmenite $Fe^{2+}TiO_3$	0.16
Garnet $X_3Y_2(SiO_4)_3$	1.12
	$X = Ca^{2+}, Mg^{2+}, Fe^{2+}, Y = Al^{3+}, Fe^{3+}, Cr^{3+}$
Amphibole $Ca_2(Fe, Mg)_5Si_8O_{22}(OH)_2$	6.39
Epidote $Ca_2(Fe, Al)Al_3(SiO_4)(Si_2O_7)O(OH)$	4.06
Tourmaline $XY_3Z_6(T_6O_{18})(BO_3)_3V_3W$	0.03
	$X = Ca, Na, K, \text{vacancy}$ $Y = Li^+, Mg^{2+}, Fe^{2+}, Mn^{2+}, Zn^{2+}, Al^{3+}, Cr^{3+}, V^{3+}, Fe^{3+}, Ti^{4+}, \text{vacancy}$ $Z = Mg^{2+}, Al^{3+}, Fe^{3+}, Cr^{3+}, V^{3+}$ $T = Si, Al, B \quad B = B, \text{vacancy} \quad V = OH, O \quad W = OH, F, O$
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

Table-2: Dissipation of H_2O_2 (0.7 g/L, from 50 % pure H_2O_2) + NH_4HCO_3 (4 g/L) in Distilled Water.

Temperature = 25 ± 1 °C				
S.No	Time Lapse (Hrs)	H_2O_2 (g/L)	pH	% Dissociation / Decomp. of H_2O_2
1	0	0.359	8.43	0
2	24	0.265	8.25	26.18
3	48	0.18	8.42	49.86
4	72	0.1	8.72	72.14
5	96	0.076	8.82	78.83
6	120	0.06	8.98	83.29
7	144	0.048	8.84	86.63
8	168	0.0391	8.88	89.11
9	192	0.0317	8.96	91.17

Table-3: Dissipation of H₂O₂ (0.7 g/L, from 50 % pure H₂O₂) in Tap Water.

Temperature = 25 ± 1 °C				
S.No	Time Lapse (Hrs)	H ₂ O ₂ (g/L)	pH	% Dissociation / Decomp. of H ₂ O ₂
1	0	0.358	8.69	0
2	24	0.297	8.76	17.04
3	48	0.262	8.67	26.82
4	72	0.234	8.74	34.64
5	96	0.2199	8.84	38.58
6	120	0.192	8.87	46.37
7	144	0.164	8.74	54.19
8	168	0.139	8.73	61.17
9	192	0.114	8.75	68.16

Table-4: Dissipation of H₂O₂ (0.7 g/L, from 50 % pure H₂O₂) + NH₄HCO₃ (4 g/L) in Tap Water.

Temperature = 25 ± 1 °C				
S.No	Time Lapse (Hrs)	H ₂ O ₂ (g/L)	pH	% Dissociation / Decomp. of H ₂ O ₂
1	0	0.363	8.2	0
2	24	0.267	8.16	26.45
3	48	0.184	8.31	49.31
4	72	0.13	8.3	64.19
5	96	0.1006	8.42	72.29
6	120	0.077	8.54	78.79
7	144	0.06	8.54	83.47
8	168	0.048	8.62	86.78
9	192	0.039	8.69	89.26

The vulnerability of H₂O₂ to dissipation can be expected in alkaline media as it is a weak acid. However, when H₂O₂ was mixed with NH₄HCO₃ during the preparation of lixiviant, the pH of the resulting solution though, did not rise significantly but still the dissipation rate of peroxide accelerated (Tables 2-5). It means that in the presence of different ions in basic tap water (Table-6), some complex interaction between the added NH₄⁺ and HCO₃⁻ ions and H₂O₂ molecules results in faster decomposition of the peroxide.

Table-5: Dissipation of H₂O₂ (0.7 g/L, from 50 % pure H₂O₂) in Distilled Water.

Temperature = 25 ± 1 °C				
S.No	Time Lapse (Hrs)	H ₂ O ₂ (g/L)	pH	% Dissociation / Decomp. of H ₂ O ₂
1	0	0.367	7.03	0
2	24	0.362	7.43	1.36
3	48	0.357	7.72	2.72
4	72	0.35	7.07	4.63
5	96	0.3497	7.13	4.71
6	120	0.348	7.45	5.18
7	144	0.346	7.23	5.72
8	168	0.342	7.18	6.81
9	192	0.3399	7.2	7.38

Total % Dissipation of H₂O₂ = [Initial value (g/L) – Final value (g/L)] x 100 / Initial value
i.e. [0.367 - 0.3399] x 100 / 0.367 = 7.38

MgSO₄.7H₂O was employed as a source of Mg ions for the stabilization of H₂O₂. Aqueous solutions of different concentrations of MgSO₄.7H₂O were used. The highest concentration of Mg ions used was up to 0.3 % (0.125 M) but no significant stabilization of H₂O₂ could be achieved (Table-7).

This result was obvious as very little precipitation of Mg²⁺ as Mg(OH)₂ could be expected in the pH range of the study (pH value remains below 9 in all cases) while it is Mg(OH)₂ precipitate which forms at a pH~11 [10, 11] and probably traps superoxide anion radicals formed in the dissipation process of H₂O₂. Hence, the free radical chain reactions of the peroxide are interrupted resulting in the slow / retarded dissociation of the material [13].

Table-6: Tap Water Analysis, Used as Solvent in the Leaching Study at 25 °C.

S. No	Element / Radical etc.	Conc. (ppm)
1	Na ⁺	146
2	K ⁺	02
3	Ca ²⁺	18
4	Mg ²⁺	10
5	NH ₄ ⁺	Nil
6	SO ₄ ²⁻	231
7	Cl ⁻	162
8	CO ₃ ²⁻	11
9	HCO ₃ ⁻	218
10	Fe ^{2+/3+}	451 ppb
11	Mn ²⁺	626 ppb
12	Cu ²⁺	79 ppb
13	Zn ²⁺	70 ppb
14	V ^{3+/5+}	468 ppb
15	Mo ²⁺	<1 ppb
16	Cr ³⁺	01
17	Ti ²⁺	03
18	TDS	700
19	pH	8.35

Table-7: Dissipation of H₂O₂ (0.7 g/L, from 50 % pure H₂O₂) + 0.3% Mg (from MgSO₄.7H₂O) in Tap Water.

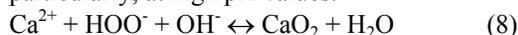
Temperature = 25 ± 1 °C				
S.No	Time Lapse (Hrs)	H ₂ O ₂ (g/L)	pH	% Dissociation / Decomp. of H ₂ O ₂
1	0	0.334	7.16	0
2	24	0.311	7.16	6.89
3	48	0.289	7.20	13.47
4	72	0.269	7.26	19.46
5	96	0.252	7.30	24.55
6	120	0.230	7.34	31.14
7	144	0.211	7.40	36.83
8	168	0.189	7.43	43.41
9	192	0.168	7.49	49.70

Since a variety of ions also catalyze the decomposition of H₂O₂ so a different route was adopted for its stabilization. This time, instead of tampering with the H₂O₂ molecules or its byproducts, attention was focused on the ions responsible for catalyzing the decomposition of the peroxide. Among the 17 ions analyzed in tap water (Table-6) three metals ions are known in the literature as catalysts for the decomposition of hydrogen peroxide. These are Fe²⁺, Mn²⁺ and Cu²⁺. Ca²⁺ is also suspected to have some sort of disrupting effect on the H₂O₂ molecule [14, 15]. To observe the effect of different ions on the stability of H₂O₂, the dissipation behaviour of the peroxide was observed in tap water (Table-3) and also in the lixiviant employing tap water as a solvent (Table-4) for 192 hours *i.e.* 09 days. For comparison,

the same procedure was repeated with distilled water (Table-5) and a lixiviant of distilled water (Table-1). Afterwards, different concentrations of complexing agent EDTA were added to all the mentioned systems of tap water and distilled water, prepared afresh, for trapping / masking the different ions and the dissipation behaviour of H₂O₂ was observed (Table-8).

The three known metal catalysts for H₂O₂ dissipation (Fe, Mn, Cu) are found in very low concentration in tap water (<01 ppm, as shown in Table-6). Na⁺ is found in a high concentration (146 ppm) but its complex with EDTA is very weak (formation constant $\beta = 10^{1.7}$ for Na⁺, Table-9) [15]. The concentration of K⁺ is also very low (~2 ppm) and its complex with EDTA is weaker ($\beta = 10^{0.8}$) than with Na⁺. Similarly, the other elements such as Zn, V and Mo are found in low concentrations in tap water. Cr and Ti ions are found in a comparatively reasonable concentrations (01 and 03 ppm respectively) but their complexes with EDTA may not be in appreciable amount in the pH range of this study (typically in the range of pH = 8 – 9). Cr³⁺ precipitates out as hydroxide around pH = 6 along with Zn²⁺ and Cu²⁺ [11, 12].

In the pH range of the study and the ions analyzed, only Ca and Mg ions are known for making stable complexes with EDTA (in the pH range 8-10, Table-3). No destabilizing effect of Mg is known over H₂O₂. But since, it forms a complex with EDTA, so it is a consumer of the mentioned complexing agent in the pH range of the study. Similarly, Ca forms a complex with EDTA and consumes the latter in the pH range 8-10. One reaction in the literature definitely shows that Ca⁺² might contribute to the instability of H₂O₂ [17] particularly, at high pH values.



The perhydroxyl anion (HOO⁻), which is a dissociation product of H₂O₂ (reaction-1), is thus consumed by Ca which will certainly result in the dissociation of more H₂O₂.

Keeping in view all the above factors, the total volume of EDTA (0.01 M) consumed by Ca and Mg in tap water was determined by titrimetry. This volume came out to be ~ 84 ml per 1000 ml tap water. Addition of 84 ml (0.01 M EDTA), made the system (tap water) ~ 312 ppm in EDTA. Since all the ions in tap water were not determined so an exact content of EDTA required for the complexation of all these ions could not be estimated in one step. Hence, different volumes of EDTA solutions (0.01 M) were added to 01 litre of tap water lixiviant (4 g/L NH₄HCO₃ + 0.7 g/L H₂O₂) and the concentration of H₂O₂ was monitored for the period of 192 hours (9 days). Readings for the concentration of H₂O₂ were taken after an interval of each 24 hours. The distilled water lixiviant was treated identically for comparison. When EDTA concentration, equivalent to the amount of Ca and Mg in tap water, was added to the tap water lixiviant (making the lixiviant ~ 312 ppm in EDTA), the rate of dissipation of the peroxide dropped from ~ 89 % to ~ 15 % (Table-9). The same was the effect on the distilled water lixiviant where the rate of dissipation of peroxide declined from ~ 91 % to ~ 15 % by the same concentration of EDTA. When an excess amount of EDTA was added to both types of lixiviants (employing tap water and distilled water as a solvent), above that required for complete complexation of Ca and Mg ions (*i.e.* making the system more concentrated than 312 ppm in EDTA), there was no significant improvement in the stability of H₂O₂. For example, when the lixiviants were made 450 ppm in EDTA, there was no substantial improvement towards the stability of the peroxide. It means that when Ca and Mg ions were complexed, the decomposition of H₂O₂ was successfully overcome in the presence of NH₄HCO₃.

Table-9: Dissipation Behaviour of H₂O₂ (0.7 g/L, from 50 % pure H₂O₂) in Various Media within a Time Lapse of 192 hrs (9 days).

Temperature = 25±1 °C											
S.No	Time Lapse of H ₂ O ₂ (Hrs)	% Diss. of H ₂ O ₂ (D.W)	% Diss. of H ₂ O ₂ (D.W.S)	% Diss. of H ₂ O ₂ (T.W)	% Diss. of H ₂ O ₂ (T.W.S)	% Diss. of H ₂ O ₂ (D.W.S + 100 ppm EDTA salt)	% Diss. of H ₂ O ₂ (T.W.S + 100 ppm EDTA salt)	% Diss. of H ₂ O ₂ (D.W.S + 312 ppm EDTA Salt)	% Diss. of H ₂ O ₂ (T.W.S + 312 ppm EDTA Salt)	% Diss. of H ₂ O ₂ (D.W.S + 450 ppm EDTA Salt)	% Diss. of H ₂ O ₂ (T.W.S + 450 ppm EDTA Salt)
1	0	0	0	0	0	0	0	0	0	0	0
2	24	1.36	26.18	17.04	26.45	8.74	2.02	5.71	4.86	5.87	5.16
3	48	2.72	49.86	26.82	49.31	9.08	2.59	7.98	6.15	7.56	7.43
4	72	4.63	72.14	34.64	64.19	9.31	5.17	10.03	7.85	8.31	8.02
5	96	4.71	78.83	38.58	72.29	12.37	9.77	11.55	9.55	9.08	9.09
6	120	5.18	83.29	46.37	78.79	12.64	12.29	12.89	10.31	9.86	10.52
7	144	5.72	86.63	54.19	83.47	12.94	17.7	13.77	11.54	11.02	13.12
8	168	6.81	89.11	61.17	86.78	13.24	24.12	14.45	12.74	11.82	13.32
9	192	7.38	91.17	68.16	89.26	14.12	32.11	15.01	14.93	15.09	13.46

D.W = H₂O₂ (0.7 g/L) in Distilled Water only
D.W.S = H₂O₂ (0.7 g/L) in Distilled Water + NH₄HCO₃ (4 g/L)
T.W = H₂O₂ (0.7 g/L) in Tap Water only
T.W.S = H₂O₂ (0.7 g/L) in Tap Water + NH₄HCO₃ (4 g/L)
Where EDTA is involved, the system has the conc. of EDTA (Na salt) in each case.

Table-9: Stability Constants (Formation Constants) of Some Metallic Ions with EDTA (25 °C).

S.No	Ion	Stability Constant	pH (EDTA Titration)	ppt as Hydroxide (pH)
1	Na ⁺	10 ^{1.66}	[0.1]*	-----
2	K ⁺	10 ^{0.8}	[0.1]	-----
3	Ca ²⁺	10 ^{10.8}	[0.1]	8-10
4	Mg ²⁺	10 ^{8.79}	[0.1]	8-10
5	Mn ²⁺	10 ^{13.78}	[0.1]	5.5
6	Fe ²⁺	10 ^{14.32}	[0.1]	5
7	Fe ³⁺	10 ²⁵	[0.1]	1
8	Cu ²⁺	10 ^{18.8}	[0.1]	3
9	Mo ⁵⁺	10 ^{6.4}	[0.1]	-----
10	Ti ³⁺	10 ^{21.3}	[0.1]	-----
11	V ²⁺	10 ^{12.7}	[0.1]	-----
12	V ³⁺	10 ²⁶	[0.1]	-----
13	Zn ²⁺	10 ^{16.5}	[0.1]	6
14	Cr ³⁺	10 ^{23.4}	[0.1]	6
15	U ⁴⁺	10 ^{25.7}	[0.1]	-----
16	UO ₂ ²⁺	10 ^{19.7}	[1.0]	-----

* Ionic Strength

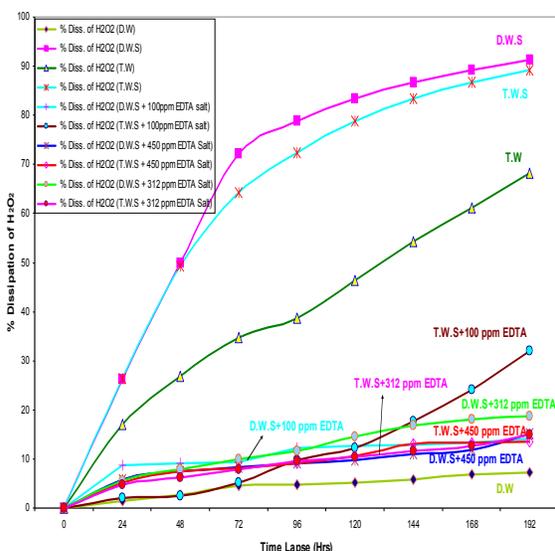


Fig. 1: Dissociation of H₂O₂ in Different Media. [All the media contain H₂O₂ (0.7 g/L) while the media with "S" contain NH₄HCO₃ (4 g/L)].

From the experimental work, it can be observed (Table-9, Fig. 1) that in case of distilled water lixiviant (having no Ca ions) about the same extent of stability to the peroxide was obtained by making the system 100 ppm and 312 ppm in EDTA (14 % - 15 % dissipation of H₂O₂). In contrast, in case of tap water lixiviant the stability of the peroxide was increased to a much lesser extent by 100 ppm EDTA solution (from 89 % to 32 % dissipation of H₂O₂) as compared to 312 ppm EDTA in the lixiviant (from 89 % to ~ 15 %). It means that the instability impact of NH₄HCO₃ on the peroxide is suppressed by a smaller concentration of EDTA (100 ppm) while in the presence of Ca ions a larger concentration of EDTA is required to subside the same amount of

instability. In fact, all the Ca in the tap water lixiviant requires to be masked by EDTA to attain the same amount of stability as in distilled water lixiviant (*i.e.* ~ 14 % dissipation of H₂O₂ after 192 hours). It is therefore, concluded that at a concentration of 312 ppm EDTA, the dissipation behaviour of the peroxide becomes almost identical in both types of lixiviant *i.e.* employing distilled water and tap water as solvents.

When it was established that the premature dissipation of H₂O₂ can be overcome by EDTA, the next step was to see the impact of the presence of EDTA in the lixiviant on the leaching of uranium. The ore body is a heterogeneous system differing in the content of various substances from point to point. But the same spot of the ore body has similar content of different substances. Keeping in view this property of the ore body, two samples (length = 30.48 cm, diameter = 8.5 cm) were taken from the same spot of the ore using a special tool and fixed in a column as shown in Fig. 2. From the top of each sample, few grams were taken and analyzed to determine the oxidized content (U⁺⁶) of uranium. For both of the samples, the oxidized content of uranium was found to be about 12 %. The total uranium content of the two samples differed slightly from each other in the same size of the sample showing the heterogeneity of the ore body. A lixiviant of tap water without EDTA (Table-10) and containing EDTA (Table-11) were passed through each of the samples (see experimental for detail).

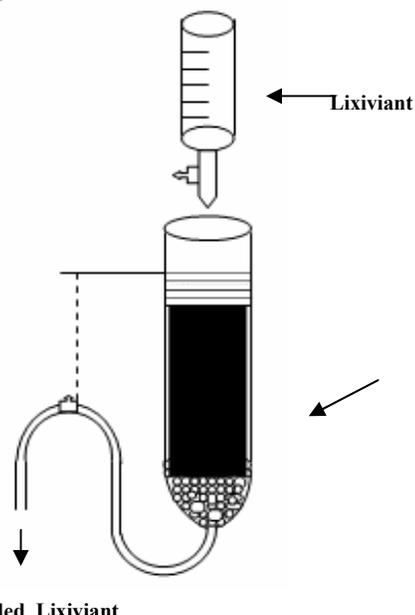


Fig. 2: Leaching / Extraction Column for Uranium Ore.

In the presence of H₂O₂ in the lixiviant, the leaching of uranium was significantly increased and more than 75 % of the total uranium was leached in the absence as well as in the presence of EDTA (Tables 11, 12). As only 12 % of uranium was originally present in oxidized form (soluble form) so the rest was oxidized by H₂O₂ and brought into solution. The presence of EDTA in the lixiviant did not adversely affect the leaching of uranium.

Therefore, it is concluded that in the lixiviant of tap water, the oxidizing agent H₂O₂ can be stabilized in the presence of Ca and NH₄HCO₃ by making the system 312 ppm in EDTA. It is also proved that the presence of EDTA in the lixiviant does not adversely affect the leaching of uranium from the ore.

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

S.No	Vol. collected (mL)	U ₃ O ₈ (ppm)*	U ₃ O ₈ (gm) Leached	U ₃ O ₈ Leaching (%)
1	910	19	0.017	2.039
2	990	64	0.063	7.554
3	980	95	0.093	11.152
4	995	85	0.085	10.193
5	995	69	0.069	8.274
6	995	54	0.054	6.475
7	1000	39	0.039	4.677
8	-do-	30	0.030	3.597
9	-do-	39	0.039	4.677
10	-do-	53	0.053	6.355
11	-do-	33	0.033	3.957
12	-do-	10	0.010	1.199
13	-do-	10	0.010	1.199
14	-do-	16	0.016	1.919
15	-do-	08	0.008	0.959
16	-do-	05	0.005	0.600
17	-do-	06	0.006	0.719
18	-do-	04	0.004	0.480
19	-do-	04	0.004	0.480
20	-do-	04	0.004	0.480
Total Leached (U ₃ O ₈)			0.642 gm	76.98 %
Residue (U ₃ O ₈) = 121 ppm				

* The leached uranium is U⁶⁺ (in the form of UO₂(CO₃)₃⁴⁻, a water soluble uranyl tricarbonate complex). Conventionally, U content is quoted as U₃O₈ as the latter is the most stable oxide of uranium.

**Lixiviant Composition: {NH₄HCO₃ (g/L) = 4.0, H₂O₂ (g/L) = 0.7} in Tap Water Total Uranium Content of the Ore Sample (U₃O₈) = 0.8339451 gm Oxidized Uranium Content of the Ore Sample (U₃O₈) = 12 % Volume of Lixiviant used in One Irrigation = 01 Lit. Contact Time of Lixiviant & Ore Sample = 01 Hr

Experimental

50 % pure H₂O₂ obtained from Sitara Chemicals Faisal Abad was used in the study. The solutions, 0.7 g/L in H₂O₂ in all cases and 4 g/L in NH₄HCO₃ wherever applicable, were prepared in 01 liter volumetric glass flasks at room temperature. The concentration of H₂O₂ was noted volumetrically against standard KMnO₄ solution [18] at intervals of 24 hours for 192 hours (09 days) using 10 ml aliquot. Except H₂O₂, all the other chemicals used in the study were of Merck, RDH and BDH origin. The

transition metals Ti, V, Cr, Mn, Fe, Cu, Zn and Mo were analyzed in tap water by atomic absorption spectrometry, using Perkin Elmer AA-700 instrument. U, Cl and SO₄²⁻ were determined spectrophotometrically (λ_{max} = 410 nm) using standard procedures on Shimadzu-1201 spectrophotometer. Ca²⁺, Mg²⁺, CO₃²⁻ and HCO₃⁻ were analyzed by titrimetry while Na⁺ and K⁺ by flame photometry using PFP-7 (Jenway) flame photometer. To know the quality of tap water being used as a solvent, measurement of total dissolved solids (TDS) was carried out by portable TDS meter (Hanna Instruments).

Table-11: Extraction of Uranium from the Selected Ore Samples (T = 25 ± 1 °C)*

S.No	Vol. collected (mL)	U ₃ O ₈ (ppm)	U ₃ O ₈ (gm) Leached	U ₃ O ₈ Leaching (%)
1	905	21	0.019	2.315
2	970	71	0.069	8.406
3	980	95	0.093	11.330
4	995	80	0.080	9.746
5	995	65	0.065	7.919
6	1000	61	0.061	7.431
7	-do-	45	0.045	5.482
8	-do-	34	0.034	4.142
9	-do-	39	0.039	4.751
10	-do-	39	0.039	4.751
11	-do-	38	0.038	4.629
12	-do-	11	0.011	1.340
13	-do-	12	0.012	1.462
14	-do-	11	0.011	1.340
15	-do-	10	0.010	1.218
16	-do-	06	0.006	0.731
17	-do-	06	0.006	0.731
18	-do-	04	0.004	0.487
19	-do-	03	0.003	0.365
20	-do-	03	0.003	0.365
Total Leached (U ₃ O ₈)			0.648 gm	78.94 %
Residue (U ₃ O ₈) = 111 ppm				

*Lixiviant Composition: {NH₄HCO₃ (g/L) = 4.0, H₂O₂ (g/L) = 0.7, EDTA (ppm) = 312} in Tap Water

Total Uranium Content of the Ore Sample (U₃O₈) = 0.820835 gm

Oxidized Uranium Content of the Ore Sample (U₃O₈) = 12 %

Volume of Lixiviant used in One Irrigation = 01 Lit.

Contact Time of Lixiviant & Ore Sample = 01 Hr

To conduct the uranium leaching / extraction, samples were recovered from the underground ore body. The length of the samples was one foot (30.48 cm) with a fixed diameter of 8.5 cm. The samples after recovery 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 content and other changeable properties of the ore.

Specially designed columns of fibreglass of 50 cm length and 10 cm diameter were employed to hold the ore samples in the leaching experiment (Fig. 2). The waxed samples were given a transverse section at both ends so to give way to the lixiviant

(leaching solution) during the experiment. These samples were then fitted vertically in the columns above pebble stones bed of few centimeters height. The pebble stones not only support the samples but would also filter out any sandy material coming out of the samples. Hence, 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 in it at the top of the sample. Thus, whole of the lixiviant was forced to pass through the sample only and not at its sides. The selected lixiviants were added from graduated glass devices of 01 litre capacity. Twenty litre lixiviant was passed through each sample, one litre at a time. One hour contact time was given to each litre of lixiviant to react with the ore sample. During this period, the drain tap of the column was kept closed. After one hour, the drain tap was opened to collect the U loaded lixiviant coming out of the sample in glass flasks and the uranium content was measured spectrophotometrically, using dibenzoyl methane as chromogenic / coloring agent [19]. The residue of the ore samples were recovered from the column and the remaining uranium content was determined. The leached uranium was added to the uranium in the residue and so total uranium in each sample was calculated.

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