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Geochemical Characteristics and Uranium Neutral Leaching through a CO₂ + O₂ System—An Example from Uranium Ore of the ELZPA Ore Deposit in Pakistan

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Abstract: Geochemical characterization studies and batch leaching experiments were conducted to explore the effects of a CO₂ + O₂ leaching system on uranium (U) recovery from ores obtained from an eastern limb of Zinda Pir Anticline ore deposit in Pakistan. The mineralogy of the ore was identified by Electron Probe Micro-analyzer (EPMA) and Scanning Electron Microscope-Energy Dispersive Spectrometer (SEM-EDS), showing that pitchblende is the main ore mineral. XRD was also used along with EPMA and SEM characterization data. Experimental results indicate that U mobility was readily facilitated in the CO₂ + O₂ system with Eh 284 mV and pH 6.24, and an 86% recovery rate of U₃O₈ was obtained. U speciation analysis implied the formation of UO₂ (CO₃)₂^{2−} in the pregnant solution. The plausible mechanism may be attributed to the dissolved CO₂ gas that forms carbonate/bicarbonate ion releasing oxidized U from the ore mineral. However, U recovery in the liquid phase was shown to decrease by higher U(VI) initial concentration, which may be due to the saturation of Fe adsorption capacity, as suggested by an increase in Fe concentration with increasing initial U(VI) concentration in the solid phase. However, further studies are needed to reveal the influencing mechanism of U(VI) initial concentration on U recovery in the solid phase. This study provides new insights on the feasibility and validity of the site application of U neutral in situ leaching.

Keywords: geochemical characteristics; pitchblende; U neutral leaching; ELZPA ore deposit in Pakistan

1. Introduction

Uranium (U) ore deposits are important to society as a primary material for the generation of nuclear power [1–3]. Interest in in situ leach (ISL) mining has grown considerably over the last 30 years [4] because of its significant advantages over conventional methods for mining, especially low-grade sandstone-type ore deposits. Research on U mobilization has focused on its migration and mineralization under natural conditions, as well as its impact on the environment [5–17]. The incorporation or release of U to or from mineral structures is determined primarily by its redox state and mineral solubility [18]. The change in oxidation state from U(IV) to U(VI) usually occurs in nature under oxidizing conditions at the geosphere/atmosphere interface or within the lithosphere from contact

with oxygenated groundwater [19]. Generally, sulfuric acid/iron sulfate and carbonate/bicarbonate are common leachants in acidic and alkaline leaching systems, respectively [20,21].

A number of leaching tests have been reported to study the U leaching mechanism from porous media under different leaching conditions [22–27]. The impact of parameters including pH, Eh, and alkalinity on U recovery parameter was investigated. Combining a modeling approach, U chemical leaching and adsorption tests were performed by Briganti et al. [28], showing that pH and alkalinity were main factors regulating geochemical behavior of U during ignimbrite-water interaction. However, their study lacks the consideration of Eh and suggests that the greatest leaching of U occurs at 50 °C, which seems irrational in field trials [29,30]. Furthermore, U leaching efficiency was shown to be complicated by factors including chemicals' initial concentrations and Fe and other metals' adsorption, of which the influential mechanisms are not sufficiently studied.

The influential ISL parameters of U recovery can be classified into two different categories. One concerns technological factors and the other concerns natural factors where U ores are leached mostly under oxidizing conditions in order to convert U contained into minerals from a relatively insoluble tetravalent form (U(IV)) into water-soluble hexavalent U (U(VI)) [31]. Under the CO₂ + O₂ leaching condition, their partial pressure was kept constant for U dissolution. The constant pressure parameter may produce in situ conditions during laboratory experiments. Indeed, the dissolution of U minerals is promoted by increasing the partial pressure of O₂ or CO₂, which is covered in a later discussion. Hence, it is essential to describe redox conditions and solution chemistry in the natural prevalent environments in order to better understand the geochemical behavior of the U species.

The presence of the U species in a water-rock interaction system is attributed to the evolution of redox conditions. Although acidic and alkaline leaching of U from limestone and sandstone media has been practiced extensively in the past, the shortcomings presented the opportunity to investigate the use of neutral leaching of U to understand its leaching mechanism, considering that limited research has been published on U neutral leaching. The novelty of this work is to unravel the mechanism of U mobilization during the neutral leaching process from U ore of an eastern limb of Zinda Pir Anticline (ELZPA) ore deposit. Therefore, the objectives of this study were the following: (i) identify the deposit mineralogy and geochemical behavior of the U species and (ii) determine the effects of leaching parameters on the release of U from U-bearing sandstone.

2. Materials and Methods

2.1. Geological and Hydrological Setting of the Study Deposit

The study deposit is located within the eastern ward extension of the Sulaiman Range, Dera Ghazi Khan, Pakistan, known as the eastern limb of Zinda Pir Anticline (ELZPA) ore deposit. It is a typical sandstone-type U deposit. The exposed rocks in the Sulaiman Fold Belt range were deposited from the Triassic to Tertiary periods with an estimated thickness of more than 7000 m [32–36].

The ore body is mainly found at a burial depth of 70–120 m in the Neogene molasses sequence, commonly known as Siwalik, that was uplifted and deformed to form the Zinda Pir Anticline range. The strata dip steeply to the east with angles of between 75° and 80°. The layers above and below the mineral-bearing strata are impermeable and retain confined pore water at varying water table depths. The water has a pH between 7 and 8, and consists mainly of SO₄^{2−}, HCO₃[−], Na⁺, Ca²⁺, and Mg²⁺ ions, as shown in Table 1.

The ELZPA deposit is divided into four zones (locally), i.e., Lal-Ashab uraniferous horizon (Z-I), Fowl creek uraniferous horizon (Z-II), Zamdani uraniferous horizon (Z-III), and Ghazzi uraniferous horizon (Z-IV). All the zones except Z-I are bounded by lower and upper shales, and a volcanic ash layer deposited parallel to zone IV. The ore body (Z-I) is tabular upward and exhibits a slanting shape along the down dip. The host sandstone is overlain by 7 to 10 m thick brownish grey shale, running parallel to the strike of the host sandstone. The shale below the ore-bearing strata is however not continuously developed. The three predominant formations that form the major subdivision

of the Siwalik series are the Vihowa, Litra, and Chaudhwan Formations. The deposit is located in the middle part of the Litra Formation (Middle Siwalik). The hosted sandstone is grey to dirty grey, fine- to medium-grained and loosely to moderately cemented. Sometimes it is cross-bedded and contains limonitic and hematitic alternation bands. The sandstones in the lower part are moderately cemented, thus forming high peaks, whereas those in the upper part are less cemented and fragile, thereby forming a flatter topographic scenario. The average permeability coefficient and porosity of the rock aquifer are 0.61 m/d and 22%, respectively. The climate in the area is semi-arid to arid. The maximum and the minimum annual temperatures are 50 and 5 °C (average temperature is 30 °C). A frost period rarely occurs except for some seasonal snowfall on high peaks of the Sulaiman Range. The precipitation is about 200 mm, which falls mostly during the period of July to September and winter [37,38].

Table 1. Chemical composition of ground water (ppm).

Sample	pH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ [−]	SO ₄ ^{2−}
Z2TW1	7.35	144	57	200	6	195	619
Z2TW2	7.11	145	101	175	5	176	1122
Z2E-148	7.46	130	102	300	5	171	978
T1WNE2	7.46	64	46	163	4	152	293
FR1T-826C	7.88	51	33	75	4	190	321
Z2TW28/88	7.80	139	21	202	9	156	118
Z2TW26/77	7.68	152	71	220	10	166	1163
Z2TW23/68	7.80	166	123	312	9	156	1274
E-312	7.90	81	68	168	7	207	651
Z1W2230	7.80	90	43	176	7	171	665
Z1W2247	6.75	80	40	245	12	249	574
E-324	8.17	211	113	180	9	130	1302
Z2TW27/42	7.70	142	91	225	12	192	1206

2.2. Sample Collection

The material was sourced from the sandstone-type U deposit that existed in the ELZPA, Sulaiman Range, Dera Ghazi Khan, Pakistan. At each sampling location, three replicate samples were collected and the unrepresentative materials were removed. The depth of the investigated boreholes spanned from 90 to 165 m. Samples were coated with wax during the core recovery process to avoid contact with atmospheric oxygen. All samples were transported to the laboratory for further treatment (discussed below).

2.3. Sample Preparation

Representative (in composite) ore samples were prepared before being analyzed and for laboratory leaching experiments. Briefly, the natural grain size of the crushed ore sample was used for the leaching batch test. For this study, natural grain size means that the ore sample was first gently loosened without reducing the sand grain size. The corresponding particle size distribution ranges were <0.5 mm, 0.5 mm to 1.00 mm, and >1.00 mm. A total of 36 samples were dried, homogenized, and sieved. All the ore samples were grouped as mixed, high, medium, and low grade on the basis of % U₃O₈ concentration, as shown in Table 2. The coning and quartering method was used to prepare representative samples. A portion of the homogenized ore material was then milled to 200 mesh size for the determination of % U₃O₈ in each sample group.

2.4. Reagents

All chemicals used in this work were of analytical reagent grade and used without further purification. The solutions and dilutions used for calibration were prepared using deionized water. Lixiviant solutions used for batch leaching experiments were prepared with laboratory tap water

(LTW), of which the composition is shown in Table 3. The representative ore sample was first grounded into a final 200 mesh size and pulverized before being analyzed (discussed below).

Table 2. Sample grouping.

Sample	Group Name	% U ₃ O ₈ Range
TCS-04	Mixed	0.01 to all
TCS-03	High	0.051 and above
TCS-02	Medium	0.036 to 0.050
TCS-01	Low	0.01 to 0.035

Table 3. Chemical composition of laboratory tap water (g/L).

U ₃ O ₈	HCO ₃ [−]	CO ₃ ^{2−}	Ca ²⁺	Mg ²⁺	SO ₄ ^{2−}	Cl [−]	Na ⁺	Fe ²⁺	Fe(T)
BDL	0.18	0.02	BDL	BDL	0.03	0.01	0.11	BDL	BDL

BDL—Beyond Detection Limit.

2.5. Batch Leaching Process

Batch extraction tests typically involve mixing a sample with a specific amount of leaching solution without renewal of the leaching solution [39]. Leaching experiments were carried out in batches with a liquid-to-solid (L/S) ratio of 2 in the autoclave reactor [40]. A Karl Kolb Scientific Technical Supplies autoclave (25 bar, BTR temperature of 300 °C, volume of 0.5 L, Dreieich, Germany) was used. An amount of 150 g of ore sample (TCS-04) was mixed in the prepared 300 mL of lixiviant (liquid) of varying conditions (variable bicarbonate solution concentration), while the ore samples (TCS-03 and TCS-02) were processed under only the best result of HCO₃[−] concentration. Experiments were performed to investigate the long-term release of the recalcitrant uranium from the ore under varying lixiviant solution conditions (variable bicarbonate solution concentration), and replicate tests were conducted under the same conditions. The leached solution was sampled at regular time intervals, i.e., from 0.5, 2.5, 7.5, 17.5, 41.5 h to days, and so on, until the equilibrium condition was acquired (i.e., no further change in U₃O₈ recovery in the leached solution). Leaching tests performed by the researchers indicated that the L/S ratio and grain size were important factors for determining the metal release; however, 24 h was not sufficient for a thorough assessment of leaching [41]. The leaching process was kept free from mechanical agitation at room temperature. The batch sampling process consisted of removing 10 mL of leached solution and filtering it through a 0.45 µm filter (Millipore, Merck, Germany). The pH and Eh were monitored throughout the batch process. The filtered sample was analyzed for U₃O₈ and HCO₃[−] concentration. Immediately after sampling, the sample was kept in a refrigerator until analysis. The HCO₃[−] concentration was controlled by adding ammonium bicarbonate (NH₄HCO₃) in the lixiviant solution. The pH of the leaching regulation system was set in the range of 6 to 6.6. The industrial oxygen gas (O₂) was injected as oxidant to oxidize U(IV) into U(VI). The ratio of CO₂ and O₂ was fixed at 1:10 with a constant injection pressure of 2 bar throughout the batch process. At the end of each test, solid and liquid phase separation was accomplished by centrifugation. For centrifugation, 15 mL of the batch were transferred to 50 mL polycarbonate centrifuge tubes and centrifuged at 4000 rpm for 15 min. The volume of leachate recovered was measured and recorded. The pH and Eh were monitored with a Hanna Instruments HI 98121 device (Hanna, Hungary). The Hanna meter was calibrated for pH function with 4.0 and 7.0 buffers. The Eh calibration was performed using a Zobell solution.

2.6. Characterization Techniques

Alkalinity of the leachate was measured by titration with HCl. The endpoint of the titration was determined by a color change. Briefly, methyl orange and phenolphthalein were used to detect the bicarbonates and carbonates, respectively. The liquid phase was analyzed for U₃O₈ through fluorimetry

and spectrophotometrically using dibenzoyl methan as coloring agent, depending on the concentration of U_3O_8 in the leached solution. The cations Ca^{2+} , Mg^{2+} , Fe^{2+} , Fe^{3+} , Na^+ , and K^+ were measured by acid-base titration and flame photometry, respectively. The anions (SO_4^{2-} , Cl^-) were analyzed spectrophotometrically. All liquid samples were filtered using a syringe. The elemental composition and SiO_2 were analyzed through atomic absorption spectrometer and spectrophotometrically, respectively, while the whole rock was analyzed through XRF. For solid material, U assays were carried out by taking 5 g of pulverized sample of the finely milled to 200 mesh size. The 5 g sample was moistened with (1.00 N) HNO_3 for the removal of carbonates with effervescence, then 2 mL $HClO_4$ and 10 mL HF were added; the sample was then heated to dry in a microwave oven-digester. Again, 10 mL HNO_3 and 10 mL HF were added and the sample was heated to dry again. Followed by addition of 50 mL of (1.00 N) HNO_3 , and the mixture was leached for one hour, and finally it was diluted to a volume of 100 mL. Inorganic carbon was analyzed through acidification of the finely grounded sample using concentrated HCl followed by back titration with NaOH. Organic carbon (C org.) was analyzed by oxidizing the sample with a $K_2Cr_2O_7$ and H_2SO_4 mixture followed by back titration using freshly prepared ferrous ammonium sulphates. Total carbons were analyzed in this manner and cross-checked using a sulfur analyzer (CS-800 Eltra, Germany).

XRD patterns of the U ore sample were recorded using a diffractometer (Bruker D8 ADVANCE, Karlsruhe, Germany) with $CuK\alpha$ radiation (40 kV, 40 mA) in a continuous scanning mode, and the 2θ scanning ranged from 3° to 80° . EVA software (V4.2.1, developed by Bruker Corporation) was used to analyze the mineral composition with XRD data using the default crystallography open database COD 2013. An EPMA (JXA-8230) was used to identify the U ore mineral. A small sample (<0.5 g) of material was drawn from the fraction that was expected to be enriched with U mineral. The feed ore and leached residue sediment samples were characterized using a scanning electron microscope (SEM) (NovaNano 450, Fei Czech, Co., Ltd.), while the distribution of elements was detected by energy-dispersive X-ray spectrometry (EDS) (Oxford X-Max^N).

3. Results and Discussion

3.1. Mineral Association and Geochemical Characteristics

Mineral association in the U ore shown by sample TCS-04 is listed in Table 4 and the XRD pattern is shown in Figure 1. It shows that quartz and mica are the predominant phases with percentages accounting for 30.40% and 20.30%, respectively. The percentages of albite and labradorite are 14.40% and 10.80%, respectively. The quartz is angular with a 0.05 to 0.4 cm size suggesting a nearby source. The oligoclase and pyroxene have percentages of 8.0% and 7.7%, respectively, along with orthoclase accounting for 3.40%. Mostly weathered oligoclase shows polycrystalline orthoclase aggregates. The distribution of calcite is very uneven and it can be localized as calcareous cemented masses or calcareous cemented thin layers. The content of calcium carbonate in the non-calcareous uncemented core samples is about 1.50%.

Table 4. Mineral analysis (%) of uranium ore by XRD.

Sample	Hematite	Magnetite	Zircon	Epidote	Staurolite	Kyanite	Amphibole	Calcite
TCS-04	0.1	0.4	0.1	0.1	0.1	0.1	0.7	1.5
Sample	Mica	Orthoclase	Pyroxene	Oligoclase	Labradorite	Albite	Quartz	
TCS-04	22.3	3.4	7.7	8	10.8	14.4	30.4	

The minor minerals including amphibole, kyanite, staurolite, epidote, zircon, magnetite, and hematite possess percentages below unity. The content of magnetite and hematite is 0.4% and 0.10%, respectively.

Figure 1. XRD pattern of uranium ore.

The geochemical composition for the four groups' ore samples is shown in Table 5. SiO_2 is the major composition with a percentage range accounting for 57.36–68.87%, followed by Al_2O_3 , CaO , and CO_2 with percentage ranges of 10.09–14.89%, 4.75–11.85%, and 4.10–10.35%, respectively. The percentages of oxides of Na, K, Mg and Fe are in the range of 1.00–2.00%, and TiO_2 is less than unity.

Table 5. Geochemical composition of uranium ore samples (wt.%).

Sample	U_3O_8	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	CaO	MgO	Na_2O	K_2O	P_2O_5	CO_2
TCS-04	0.0363	64.58	0.32	10.09	1.34	1.36	0.08	7.35	1.66	1.63	1.06	0.09	5.93
TCS-03	0.0540	68.87	0.28	12.78	1.19	1.43	0.05	4.76	4.46	1.82	1.26	0.08	4.31
TCS-02	0.0447	65.78	0.35	14.89	1.77	1.70	0.08	5.88	1.96	1.60	1.01	0.09	4.10
TCS-01	0.0150	57.36	0.21	11.15	0.92	1.26	0.10	11.85	2.72	1.72	0.89	0.08	10.35

The U mineral in the investigated sample (TCS-04) of ore is mainly silica-bearing pitchblende and its composition analysis through EPMA is listed in Table 6. An electronic photograph is shown in Figure 2.

Table 6. Composition of pitchblende (%) analyzed by EPMA.

Sample	EPMA Point	FeO	K_2O	CaO	TiO_2	Al_2O_3	SiO_2	La_2O_3	Ce_2O_3	PbO	Sm_2O_3	Dy_2O_3
TCS-04	3-001	1.30	-	1.98	0.01	7.10	30.93	0.03	0.30	-	-	-
TCS-04	3-003	0.53	-	1.61	0.04	1.06	14.76	-	0.40	0.08	0.06	0.02
TCS-04	3-006	1.29	-	2.18	0.07	2.83	23.78	-	0.46	-	0.04	0.14
TCS-04	3-007	1.12	-	2.20	-	2.52	21.38	0.04	0.44	-	-	0.33
TCS-04	3-008	0.82	-	2.03	0.20	2.41	36.33	0.02	0.15	0.03	0.08	0.06
TCS-04	3-009	1.58	0.09	1.75	-	5.35	26.87	-	0.18	0.02	-	0.04
Sample	EPMA Point	Ho_2O_3	Yb_2O_3	Y_2O_3	MoO_3	Gd_2O_3	UO_2	Na_2O	MgO	P_2O_5	Pr_2O_5	Nd_2O_3
TCS-04	3-001	-	-	0.07	0.05	0.01	46.35	0.98	1.38	0.86	0.86	0.03
TCS-04	3-003	0.03	-	0.19	0.06	-	63.83	2.64	0.17	0.79	0.79	0.216
TCS-04	3-006	0.04	-	0.29	-	0.11	62.64	1.10	0.59	0.91	0.04	0.27
TCS-04	3-007	0.07	0.08	0.81	-	0.18	34.32	0.94	0.48	1.16	0.05	0.33
TCS-04	3-008	-	-	0.05	-	-	45.74	0.54	0.20	0.92	0.03	-
TCS-04	3-009	-	-	-	-	0.07	56.26	1.59	0.83	0.82	-	0.02

Figure 2. The backscattered electronic photograph of the uranium ore sample. Qz: quartz; Pit: pitchblende.

The U oxide content results of the examined mixed ore sample (TCS-04) and of the ore samples (TCS-03, TCS-02, and TCS-01) with three different grades (high, medium, and low) are shown in Table 7. The geochemical information about sample TCS-04 reflects an overview of the ore deposit with respect to presence of special element characteristics. This sample has an average of 363 ppm of U_3O_8 with a U(IV)/U(VI) ratio of 21 (Table 7) and shows the mobility of U in terms of the U oxidation state. This sample analysis shows that 4.55% of U_3O_8 in the ore deposit may exist in the oxidized form (UO_2^{2+}). The oxidized form may be leachable without injecting an oxidant during the leaching process. However, 95.19% of U_3O_8 in the ore deposit exists in the reduced form (U(IV)), and might be made leachable by injecting an oxidant during the leaching process. A similar composition was observed in the other three groups (TCS-03, TCS-02, and TCS-01), where the oxidized form of U accounted for 12.23%, 9.50%, and 7.08%, respectively. The presence of the U species in ore samples was attributed to the evolution of redox conditions. This is indicated by the Fe species (Fe^{2+} and/or Fe^{3+}) being positively correlated to U(VI), as shown in Figure 3. The general reactivity of Fe significantly influences U geochemistry, and Fe (Fe^{2+} and/or Fe^{3+}) forms mostly oxide, oxyhydroxide, and S-mineral compounds with its substitution in U-minerals commonly [42]. Moreover, there is no well-defined correlation between the U species and organic carbon. It probably suggests that the oxidized U associated with inorganically dominated carbon as compared to organics. Recently, a similar study was documented from the eastern Suliman range of Dear Ghazi Khan, Pakistan [37,38] showing that U ore was mostly associated with organic matter (probably petroleum) as well as other phases of the ore (e.g., biotite). Consequently, the geochemistry of U-containing minerals indicates a relatively pre-complexed environment of the investigated ore deposit, where the occurrence of U(IV) was favored as compared to U(VI). It in turn indicates that the injection of oxidant was needed for the mobilization of the reduced form of U during in situ leaching. A similar case has been reviewed and reported by Shamim Akhtar [43], showing that U deposits in Pakistan were formed in a reduced environment. Various studies have reported that U solubility is affected by its speciation and aqueous chemistry including organic matter (OM) concentrations [44–46]. Low OM concentration was shown to promote U solubility, whereas high OM concentration may immobilize U [47]. Of all the inorganic ligands, carbonates are more active ones to complex U, as compared to others such as SiO_2^{4-} and PO_4^{3-} [48,49].

3.2. Neutral Leaching

Different leaching methods including neutral, acidic, and alkaline have been reported in U mining sites [50–55]. The present study investigated the processing of neutral leaching with the pH value being monitored in the experimental scope. These operational conditions were suggested to favor the application of the neutral leaching since it avoids excessive consumption of reagents (discussed below).

Table 7. Special characteristics of uranium ore.

Sample	U ₃ O ₈ (ppm)	U _{Total} (ppm)	U(VI) (ppm)	U(IV) (ppm)	U(IV) (%)	U(VI) (%)	U(IV)/ U(VI)	C _{org.} (%)	C _{inorg.} (%)	Fe ³⁺ (%)	Fe ²⁺ (%)	SO ₃ (%)
TCS-04	363	308	14	293	95.19	4.55	21	0.08	1.62	0.94	1.06	1.06
TCS-03	540	458	56	401	87.57	12.23	7	0.05	1.18	1.28	1.32	1.11
TCS-02	447	379	36	342	90.23	9.50	10	0.06	1.12	1.26	1.32	1.32
TCS-01	150	127	9	117	91.98	7.08	13	0.10	2.82	0.64	0.98	0.98

Figure 3. Trend of U(VI) and Fe(III) with organic carbon (C org.) in uranium ore.

3.2.1. Effect of Bicarbonate Concentration and Chemical Dynamics during Leaching

Concentrations of HCO_3^- are shown as a function of time in Figure 4. Overall, two trends were observed during the course of experiments. In the first test, where 0.60 g/L of HCO_3^- concentration was used for the preparation of the lixiviant solution, the U_3O_8 was determined to be 157 mg/L after equilibrium was obtained, while its initial concentration was of 12 mg/L before starting the batch processing (Figure S1). For the two tests (#2 and #3), 0.80 g/L and 1.00 g/L of HCO_3^- concentrations were used, respectively, and the U_3O_8 was determined to be 25 mg/L and 64 mg/L, with an initial concentration of 12 and 5 mg/L before starting the batch processing, respectively. Similarly, in the fourth test (#4), 1.20 g/L of HCO_3^- concentration was used, and the final concentration of U_3O_8 was determined to be 124 mg/L, with its initial concentration of 3 mg/L. The highest U recovery (86%) was found using a 0.60 g/L of HCO_3^- concentration. The U recovery with a concentration of 1.00 g/L of HCO_3^- was 45%, followed by a 0.8 g/L batch where recovery was 13%. The U recovery with 1.20 g/L of HCO_3^- was 68%. The changes in uranium recovery for the tests are shown in Figure 5.

Consequently, the dissolution of the U was favored more easily with 0.6 g/L of HCO_3^- , and only 8.70 days was needed to achieve high recovery leaching time. The lower limit of HCO_3^- concentrations in the aforementioned tests shows a slightly gentle process fluctuation as compared to those on the higher side, and a general improvement in the recovery was observed as the HCO_3^- concentrations increased from 0.8 to 1.2 g/L during the process. The effect of varying concentrations of the leaching agent (HCO_3^-) on U recovery was studied by Elizângela and Ana [56]. Results obtained from the authors showed that 1.00 mol/L of HCO_3^- was the best concentration, under which >95% recovery was obtained in 24 h via alkaline leaching, while a general improvement in the recovery was observed as the HCO_3^- concentrations increased. However, the highest recovery of 86%, as a special result, was obtained from test #1 with 0.6 g/L of HCO_3^- . The lowest recovery of the 0.8 g/L HCO_3^- test may be due to lower bicarbonates and the constantly stable concentration of HCO_3^- as U recovery may highly correlated with it [57]. The geochemical analysis results of ore and residuals are shown in Table 8.

It can be seen that the CaO concentration in all test residues was decreased significantly. This may be due to the injection of CO₂ gas causing the dissolution of calcite (Figure 6), as shown by Equation (1):

Figure 4. Change in HCO₃⁻ concentration in the leaching solution.

Figure 5. Change in uranium recovery in the leaching solution.

The maximum dissolution of calcium with a concentration of 0.80 g/L of HCO₃⁻ was 2.33%, followed by the 1.0 g/L batch where the dissolution was 1.56%, while U recoveries were 13% and 45%, respectively. In contrast, the calcium dissolution with 0.60 g/L of HCO₃⁻ was 1.14%, and in the 1.20 g/L batch, 0.56% calcite was dissolved, with U recoveries being 86% and 68%, respectively. The relationship between U recovery and calcite dissolution is not totally positively correlated. However, 0.60 g/L concentrations of HCO₃⁻ test have comparatively higher U₃O₈ recovery than that of 1.20 g/L HCO₃⁻ test with a calcite dissolution range accounting for 1.14% and 0.56%, respectively.

Table 8. Geochemical analysis of ore and residues.

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	CO ₂
TCS-04	%										
Before leaching	64.58	10.09	1.34	1.36	0.08	7.35	1.66	1.63	1.06	0.09	5.93
After leaching (Test #1)	62.16	9.69	1.23	1.67	0.08	6.21	1.34	1.66	1.40	0.08	5.99
After leaching (Test #2)	62.81	10.17	1.10	1.45	0.06	5.02	1.31	1.73	1.28	0.06	5.97
After leaching (Test #3)	64.83	9.84	1.26	1.60	0.08	5.79	1.48	1.83	1.26	0.09	6.21
After leaching (Test #4)	62.42	10.02	1.19	1.65	0.06	6.79	1.34	1.67	1.23	0.08	5.99

Figure 6. Concentration of oxides before and after leaching.

3.2.2. Effect of pH

The pH decreases quickly and then it remains stable (Figure 7); in addition, its relationship to Eh shows regular patterns (Figure 8). Different patterns of leaching as a function of pH were also observed (Figure 9). The leaching recovery of U increased with changing pH in the early stages of the process and then there was no further change in U recovery. For example, in the test using 0.6 g/L of HCO₃⁻, high U recovery was found, while the pH value reduced from 8 to 6.57. Mean and final values recorded for pH for each of the leaching protocols are shown in Table 9. Probably, the plausible mechanism may be due to the injection of CO₂ gas. CO₂ dissolved in water results in reducing pH of the system. The carbonate/bicarbonate ion in turn promotes the release of adsorbed U(VI) from

the U-bearing mineral. The released U(VI) dissolved into the liquid phase depends upon contact time and mineral charge density. In addition, increasing H^+ results in the dissolution of gangue minerals like calcite (Figure 6). It can be seen (Figure 9) that the lowest pH value and highest Eh value (most oxidizing conditions) were observed for the best addition of HCO_3^- (0.6 g/L). It should also be noted that pH showed almost a negative correlation with recovery (Figure 9a), i.e., more recovery resulted towards the lower pH of the neutral range, resulting in the formation of more H^+ in the solution. Briganti et al. [28] conducted a study using chemical leaching and adsorption tests with a simple modeling using PHREEQC. They found that the geochemical behavior of U during ignimbrite-water interaction was controlled mainly by temperature, pH, and solution chemistry (especially alkalinity). The main results of their work indicated that U was more easily mobilized by a slightly basic solution (pH 7.5). However, the results obtained from the research revealed that U was more easily mobilized by a slightly acidic solution (pH range 6 to 6.6) during nearly neutral leaching conditions. In many respects, leaching behavior as reflected by pH leaching tests and related characterization provide a better means of assessing environmental impact than an analysis of total composition, such as how the solubility changes if in situ pH changes occur. The pH is one of the key parameters that determines heavy metal mobility depending upon soil and sediment properties.

Figure 7. Change in pH measurements in the leaching solution.

The aqueous U(VI) carbonate system has been thoroughly studied by many researchers [58–64]. It is well accepted that the three monomeric complexes of general formula $UO_2(CO_3)$, $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$ present under the appropriate conditions [65].

In neutral to carbonate media, U is converted into a series of carbonate complexes (UO_2CO_3 (maximum fraction at pH 5), $UO_2(CO_3)_2^{2-}$ (maximum fraction at pH 6.5), and $UO_2(CO_3)_3^{4-}$ (maximum fraction at pH 10 to 11)) when the pH of the solution is increased.

Nevertheless, in all the tests performed, the concentration of CO_3^{2-} was not detected in the leached solution during analysis because of the pH range condition was 6 to 6.6 (which indicates that $UO_2(CO_3)_2^{2-}$ is the main carbonate complex in the condition studied in this work). In such cases, the recovery of U from a nearly neutral medium is possibly due to the formation of stable U carbonate complex-like $UO_2(CO_3)_2^{2-}$ [66] via Equation (2):

Figure 8. Trend of Eh and pH in leaching solution with different HCO_3^- concentrations: (a) 0.60 g/L; (b) 0.80 g/L; (c) 1.00 g/L; (d) 1.20 g/L.

Figure 9. Trend of U_3O_8 recovery and pH in leaching solution with different HCO_3^- concentrations: (a) 0.60 g/L; (b) 0.80 g/L; (c) 1.00 g/L; (d) 1.20 g/L.

Table 9. pH, Eh, and recovery changes against each of the leaching protocols investigated.

Sample	HCO ₃ [−]	Leachate pH		Leachate Eh (mV)		U ₃ O ₈ Recovery
	g/L	Mean	Final	Mean	Final	%
TCS-04	0.60	6.60	6.24	228	284	86
do	0.80	6.7	6.61	201	211	13
do	1.00	6.84	6.58	228	250	45
do	1.20	6.85	6.45	192	260	68
TCS-03	0.6	6.65	6.92	209	265	65
TCS-02	do	6.86	6.48	185	225	68

This is a stable U compound in the determined pH range. Many researchers have reported that when pH > 6, U(VI) is dominant in the presence of more complexes such as uranyl hydroxyl complexes and polynuclear uranyl hydroxyl complexes, and the reactivity of Fe inhibits U(VI) [67,68]. It may be the advantage of relatively less Fe (Table 4) in the investigated ores in terms of the experimental scope (pH 6 to 6.6). Under near-neutral conditions, U forms soluble complexes with carbonate and phosphates. Ma et al. [31] conducted an adsorption study of the U species and reported that these species are also influenced by the charge of the mineral surface, depending on the pH of the sorbate solution. Recently, Zhou et al. [46] reported from ISL research from mining sites that, as the pH value decreases, the adsorbed UO₂²⁺ can be replaced by protons and U concentration increases significantly in the leached solution.

3.2.3. Effect of U(VI) Initial Concentration

The effect of different U(VI) initial concentrations (in the solid phase) on U₃O₈ recovery was investigated. The results are listed in Table 10 and shown in Figure 10, showing that recovery was 86% at the lower initial U(VI) concentration (sample TCS-04). A higher U(VI) initial concentration in the solid phase leads to a lower recovery of U₃O₈ (Figure 10). This may be due to the saturation of Fe²⁺ + Fe³⁺ adsorption capacity as its concentration increases with increasing initial U(VI) concentration in the solid phase (Table 10). As the concentration of U(VI) increases in the liquid phase, UO₂²⁺ ions compete for adsorption sites or available functional groups [69]. It is reported that adsorption capacity continues to increase with the rise of initial U(VI) concentration, which may be due to the presence of more U(VI) ions around Fe [70]. Laboratory experiments focusing on U chemical species have been previously done as well for the purpose of researching in situ leaching of U ore, and have reported that the recovery of leaching U is decided jointly by both U content and its activity, according to Ma et al. [31]. Probably, it seems that another mechanism may be due to the presence of different U(VI) initial concentrations in the solid phase, as it is negatively correlated with U₃O₈ recovery (Figure 10).

Table 10. Initial U⁶⁺ concentration in rock samples and uranium recovery in nearly neutral media.

Sample	Initial Conc. of U ⁶⁺ (ppm)	Fe ²⁺ + Fe ³⁺ (%)	U ₃ O ₈ Recovery (%)
TCS-04	14	2.00	86.00
TCS-02	36	2.56	69.00
TCS-03	56	2.60	66.00

A similar nature of correlation between U(VI) initial concentration (in the solid phase) and leaching recovery was examined under alkaline leaching. A total of five samples with varying U(VI) initial concentrations were tested. These were the five ore samples (FR1T-860C-28, FR1T-859C-24, FR1T-860C-26, FR1T-860C-20, and FR1T-860C-24, Table 11) out of a total of 36 collected ore samples, which were used in the neutral experimental study after sample grouping. The objective was to confirm the effect of this special influential parameter on leaching recovery comparison as a trial through other

leaching media. The results are listed in Table 11 and shown in Figure 10, showing that recovery was 58% at the lower initial U(VI) concentration, while the recovery decreased by increasing U(VI) initial concentration in the solid phase. The parallel leaching experimental study showed a similar negative correlation of U(VI) initial concentration with U_3O_8 recovery in the leached solution.

Figure 10. Trend of uranium recovery (in leaching solution) with initial U^{6+} concentration (conc.) in rock samples.

Table 11. Initial U^{6+} concentration in rock samples and uranium recovery in alkaline media.

Sample	U_3O_8 (ppm)	U^{6+} (ppm)	U^{4+} (ppm)	NH_4HCO_3 (g/L)	H_2O_2 (g/L)	pH (Mean/Final)		U_3O_8 Recovery (%)
FR1T-860C-28	390	35	356	2.00	1.00	8.27	8.09	58
FR1T-859C-24	460	38	425	2.00	1.00	8.47	8.08	48
FR1T-860C-26	408	40	305	2.00	0.50	8.38	8.28	31
FR1T-860C-20	500	51	372	2.00	1.00	8.32	8.78	30
FR1T-860C-24	442	79	295	3.00	0.50	8.18	7.79	26

3.2.4. Effect of Redox Conditions

Trends of redox potential (Eh) values are shown as a function of time (Figure 11). Different patterns of oxidation as a function of Eh were observed. The test with 0.6 g/L of HCO_3^- has a high leaching rate, and the Eh value was enhanced more than three times (from 90 to 284 mV), while the test with 1.2 g/L of HCO_3^- enhanced the Eh value less than three times and a similar Eh increment was observed in the tests with 0.80 and 1.0 g/L of HCO_3^- concentrations, as shown in Figure 12. For the most part, the leaching of U increased with increasing Eh, although there was then no further change in U recovery at slightly increased Eh. Mean and final values recorded for Eh for each of the leaching protocols are shown in Table 9. It should also be noted that Eh showed almost a positive correlation with recovery, i.e., a higher recovery rate in higher oxidizing conditions at the later stage of the process (Figure 12), in the test with 0.6 g/L of HCO_3^- . The slope of the figure from different curves was 0.409, 0.050, 0.204, and 0.410 against HCO_3^- concentrations of 0.6, 0.8, 1.0, and 1.2 g/L, respectively. The Eh was almost directly affecting U mobilization. It is well accepted that Eh of the solution is the key factor affecting the dissolution of tetravalent uranium during the leaching of U, which is related to the composition and content of the variable valence ions in the solution. Zhou et al. [46] reported that change in the uranium concentration in the leached solution is time-lagged and its peak occurred synchronously with that of high Eh.

Figure 11. Change in Eh measurements in the leaching solution with different HCO_3^- concentrations.

Figure 12. Uranium recovery and Eh variations in leaching solution with different HCO_3^- concentrations: (a) 0.60 g/L; (b) 0.80 g/L; (c) 1.00 g/L; (d) 1.20 g/L.

4. Conclusions

This investigation included a geochemical characterization study and nearly neutral (pH: 6–6.6) leaching mechanisms of uranium (U) ore from the ELZPA deposit. The ore mineral was determined to be dominated by pitchblende, as revealed by EPMA and SEM-EDS analytical results. Leaching experiments with a $\text{CO}_2 + \text{O}_2$ system were performed to investigate U mobility and transformation. Parameters of pH, Eh, alkalinity, and major ion(s) were shown to influence U mobilization. U_3O_8 recovery was achieved to a high level (86%), mainly in the form of a stable $\text{UO}_2(\text{CO}_3)_2^{2-}$ complex in the leached solution. The plausible U migration mechanism may be due to the oxidizing conditions, and the

dissolved CO₂ gas via a formation of protons releasing oxidized U from the uranium-bearing minerals. However, the injection of CO₂ may cause a dissolution of gangue minerals (i.e., calcite). Comparatively, the overall uranium recovery in different ore group tests was significantly negatively correlated with prevalent organic complexed oxidized U in the solid phase under nearly neutral and alkaline leaching environments. Therefore, further studies are needed to explore such influential parameters within the research scope.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-4701/10/12/1616/s1>, Figure S1: Change in uranium concentration in the leaching solution.

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