

Recovery of Uranium from Philippine Wet Phosphoric Acid Using D2EHPA-TOPO Solvent Extraction

Botvinnik L. Palattao*, Jennyvi D. Ramirez, Estrellita U. Tabora,
Editha A. Marcelo, Edmundo P. Vargas, Socorro P. Intoy,
Reymar R. Diwa, and Rolando Y. Reyes

Philippine Nuclear Research Institute - Department of Science and Technology
Quezon City, Manila 1101 Philippines

Recovery of uranium from Philippine wet phosphoric acid was studied using a synergistic mixture of 0.5 M D2EHPA - 0.125 M TOPO diluted in kerosene. Results from characterization of materials in phosphate processing revealed the presence of valuable elements such as uranium and rare earths in both raw materials and fertilizer products. Variation of operating parameters on extraction such as P_2O_5 content and optical density was found to be inversely proportional with the extraction efficiency. The reaction was found to establish rapid equilibrium and is exothermic in nature. Distribution coefficient for the extraction of uranium from 27% P_2O_5 phosphoric acid was determined to be at 10.71 at about 25°C. Analysis of the equilibrium data and McCabe-Thiele plot based on batch testing indicates a 92.59% recovery rate could be achieved in three-ideal extraction stages at an aqueous to organic phase volume ratio of 4:1.

Key words: D2EHPA-TOPO, Philippines, phosphate fertilizer, phosphoric acid, uranium extraction

INTRODUCTION

Phosphate rocks contain a wide variety of useful elements apart from phosphorus used in making fertilizers. Among these elements that are of value contained in the mineral are uranium, thorium, radium, and rare earths elements (REE) (Preston et al. 1996; Kouraim et al. 2014; Emsbo et al. 2015; Ramos et al. 2016). In the wet processing of phosphate rock, the mineral is broken down by sulfuric acid, which then produces two intermediate products, namely phosphoric acid and phosphogypsum precipitate. During this process, trace elements like REE and naturally occurring radionuclides uranium, thorium, and radium contained in mineral distributes into these intermediate products. Majority of the uranium and thorium content in the rocks are reported to redistribute itself into the acid phase (Hodge & Popovici 1994; Rutherford et al. 1994;

Singh et al. 2009; Haneklaus et al. 2017) while most of the rare earths, and along with radium, precipitates with the phosphogypsum (USEPA 1992; Sahu et al. 2014; Kulczycka et al. 2015). The phosphoric acid is then further converted into fertilizers and, in the process, transfers all valuable elements into the product that is then consequently lost during land application. These valuable elements, if left in fertilizers, are considered as heavy metal contaminants and may pose negative environmental impacts. However, if recovered from phosphoric acid prior to fertilizer production, it presents a huge opportunity to utilizing these strategic metals in technological applications and/or marketable way. Recovery of these valuable elements thus, is not only a means of maximizing the mineral potential but also a means of environmental stewardship.

With the global increase in energy demand accentuated by a growing population, targeted gross domestic product (GDP), and environmental challenges (cutting

*Corresponding author: nikpalattao@gmail.com

carbon emissions), nuclear technology may play a very important part in ensuring reliable and secure energy supply (STC 2003; Brook et al. 2014). Thus, there is a need to develop capability to produce nuclear fuel from available resources in respective countries. For countries with limited uranium ore deposits, steps have been made to recover it from unconventional sources such as phosphates, black shales, lignite, and even sea water, with uranium in phosphates representing the largest reserve second only to seawater (WNA 2016). In the Philippines, there are about four fertilizer manufacturing plants, where three (3) of these plants produce phosphatic-based fertilizers and the other one manufactures sulphate of potash (Cruz 1997). Among the manufacturing plants, the largest and only plant that derives phosphoric acid production from mineral phosphates is the Philippine Phosphate Fertilizer Corporation (PhilPhos). PhilPhos processes around 1.97 million tons of phosphates rocks per year (Haneklaus et al. 2015). These phosphate rocks are imported from different countries such as Morocco, Egypt, Jordan, Peru, etc. The concentrations of uranium in these phosphate rocks vary from one reserve to another, ranging 50-200 ppm (Khleifia et al. 2013). Based on the capacity of PhilPhos, an estimate of 44.97 metric tons of uranium is being lost in the fertilizer processing (Haneklaus et al. 2015). This excludes loss from the other two phosphate fertilizer manufacturing plants and other imports of phosphoric acid and/or phosphatic fertilizers. There are several established methods for recovering uranium from wet phosphoric acid: 1) solvent extraction with octylpyrophosphoric acid (OPPA) and octyl phenyl acid phosphate (OPAP); 2) synergistic mixture of di-2-ethylhexyl phosphoric acid (D2EHPA) and trioctyl phosphine oxide (TOPO); and 3) ion exchange, precipitation, liquid membrane process, and froth flotation (Hurst et al. 1972; Beltrami et al. 2014). Among these extraction methods, the use of the synergistic mixture D2EHPA-TOPO has been proven to be the most useful and adapted method due to its selectivity and stability in different phosphoric acid systems (Khleifia et al. 2013; Beltrami et al. 2014). The D2EHPA-TOPO method though widely adapted method, recovery so far were conducted on single-sourced phosphoric acid and no plant were operated on mixed or varying phosphoric acid system. This has been the case since the extractability of uranium differs from each phosphoric acid system due to the variation of the type and quantity of dissolved cations and anions in the acid (Beltz et al. 1983; Dartiguelongue et al. 2015).

Study on uranium recovery from Philippine phosphoric acid using D2EHPA-TOPO was initiated in 1987 by Petrache and co-authors, where an initial extraction reached a 65- 75% recovery rate. In light of developing capabilities to recover uranium from indigenous resources, the DEHPA-TOPO process will be explored and tested along with other methods of recovery. This

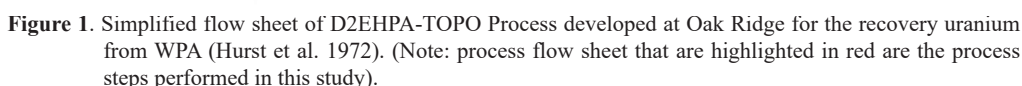
paper presents a study to better understand the effects of varying operating parameters affecting uranium recovery from Philippine wet phosphoric acid (WPA) using D2EHPA-TOPO extraction method. This study covers the characterization of raw materials, pre-treatment of phosphoric acid, uranium extraction at varying optical density, contact time, phosphoric acid content (given in terms of phosphorus pentoxide (P_2O_5) content), and temperature, as well as the development of the first cycle uranium extraction isotherm based on batch testing.

MATERIALS AND METHODS

In order to economically recover uranium from wet phosphoric acid, the extraction process was investigated in detail. An overview of the process for the D2EHPA-TOPO solvent extraction of uranium from wet phosphoric acid is shown in Figure 1. Experimental work on a laboratory scale was carried out on two of the most important steps, the phosphoric acid pretreatment and the first-cycle extraction. These steps determine the overall recovery rate and performance of the uranium extraction process. The pretreatment and extraction parameters (optical density, contact time, P_2O_5 concentration, and temperature) and extraction efficiency were studied. Feed material, process streams, and fertilizer product were characterized to determine uranium, REE, and other trace metals content.

Characterization of Raw Materials

Solid samples (phosphate rocks, phosphogypsum, and fertilizer products) provided by PhilPhos were dried and homogenized. A 0.5 g of dried and homogenized sample was digested with 5 mL mixture of 85%(v/v) nitric acid and 15%(v/v) hydrochloric acid. Meanwhile, an aliquot of aged (year-old) 27% P_2O_5 content phosphoric acid samples were treated with activated carbon, filtered, and then diluted with distilled water before analysis. Trace metal contents of the samples were measured using Flame Atomic Absorption Spectrometry (FAAS) (Varian AA240). Uranium content was measured using a uranium analyzer (ATS 300 GM Fluorometer) following the method of Smith and Lynch (IAEA 1992), where an aliquot of sample digest were pipetted into platinum dish, heated to dull red to remove organic compounds, cooled, and added with a high carbonate flux. The samples were then fused at 605°C to obtain fused bead required by the uranium analyzer. For the determination of rare earth element content, samples were submitted to Florida Industrial and Phosphate Research Institute (FIPR) in Florida, USA for Inductively-Coupled Mass Spectrometric (ICP-MS) analysis.



Pre-treatment of phosphoric acid involves the removal of suspended solids, dissolved organic material, and adjustment of the oxidation-reduction potential (ORP) of the acid. The raw phosphoric acid (27% P_2O_5) was treated with varying amounts of activated carbon (5 g/L, 10 g/L, 15 g/L, and 20 g/L), mixed for 10 min, and then filtered. The optical density (OD) of the acid was measured using a UV-Vis Spectrometer (ThermoScientific™ Evolution 201) at 408 nm wavelength. All acids were oxidized to >650 mV ORP by dropwise addition of 30% hydrogen peroxide (AR grade). Oxidation of the acid converts uranium into its extractable state which is hexavalent uranium (U(VI)).

First cycle extraction was studied by monitoring the uranium content and efficiency at each contact. Equal volumes of treated phosphoric acid and 0.5 M D2EHPA - 0.125 M TOPO were placed into contact in a beaker with automatic stirrer, mixed, allowed to settle, and then separated. After contact, the resulting phosphoric acid is now called as the first contact raffinate and the organic solvent as the first contact loaded solvent. The first loaded solvent was then placed into contact with another fresh

where: $U_{(org)}$ – concentration of uranium in the organic phase DEHPA-TOPO extractant at equilibrium
 $U_{(aq)}$ – concentration of uranium in the aqueous phosphoric acid phase at equilibrium

The extraction efficiency (E) can be defined as the percentage of uranium extracted or transferred into the organic phase given by the equation below:

$$E, \% = \frac{U_{(org)}}{U_{0(aq)}} \times 100\% \quad (3)$$

where: $U_{0(aq)}$ – initial concentration of uranium in the aqueous phosphoric acid phase

Alternatively, extraction efficiency, E, can be calculated using the value of the distribution coefficient given in equation (2):

$$E, \% = \left(\frac{K_d}{K_d + 1} \right) \times 100\% \quad (4)$$

Effect of Varying Extraction Parameters to Uranium Extraction

Experiments were carried out at different contact times (1, 5, 10, and 15 min) to determine the optimum time at which equilibrium is achieved. The effect of varying optical density on extraction efficiency was tested by varying the amount of activated carbon (5 g/L, 10 g/L, 15 g/L, and 20 g/L) added during the phosphoric acid pretreatment. The effect of varying phosphoric acid content, expressed as P_2O_5 concentration, was conducted by dilution of pretreated WPA with distilled water and/or by mixing with laboratory grade phosphoric acid of higher concentration to produce acid concentration ranging 20-53% P_2O_5 content. The effect of temperature (varied from 30°C to 60°C at 10°C increment) on uranium extraction was conducted by equilibrating aqueous and organic phase in covered test tubes in a water bath maintained at the target temperature for 15 min with mixing at every 3-min interval.

First Cycle Extraction Isotherm and Construction of McCabe-Thiele Diagram

The first cycle extraction isotherm was generated by plotting the concentration of uranium in the organic phase (y-axis) against uranium in the aqueous phase (x-axis) at each contact. Utilizing the extraction isotherm, a McCabe-Thiele plot was constructed to determine the theoretical number of stages needed to extract uranium from phosphoric acid and the aqueous to organic phase volume ratio.

RESULTS AND DISCUSSION

Characterization of Raw Materials

The trace element composition (Table 1) of the fertilizer products and phosphate rocks does not vary significantly. In some cases, fertilizer products have higher trace element concentration than in phosphate rocks. This explains why phosphate fertilizer plants always check the quality of phosphate rocks as these impurities (i.e., magnesium, zinc, nickel, manganese, chromium) are transferred to the fertilizer products and may result to grade problems (Dillard et al. 1982). Heavy metals associated to phosphoric acid like chromium, cadmium, and uranium (Beltrami et al. 2014) were found to have increasing concentrations along with increasing phosphate content in NPK fertilizers (Table 1). Studies on long term application of phosphate fertilizer in agricultural lands showed that impurities contained in the phosphates accumulate in the top/surface layer of the soil. These impurities included uranium, REE, and other heavy metals (Rothbaum et al. 1979; Özyaytekin & Uyanöz 2012). These strategic metals, if recovered, could add value to the mineral processing as well as eliminate the potential risk of heavy metal contamination in soils.

Effect of P_2O_5 Concentration on Extraction Efficiency

Difficulty in extracting uranium from phosphoric acid arises due to the high complexing factor of phosphates (PO_4^{3-}) with uranium. In a simple experiment to test the effect of phosphate content in the extraction of uranium, results clearly showed that as phosphate concentration increased, uranium transfer decreased (Figure 2). This suggests that recovery of uranium from phosphoric acid is best when recovered from acids with low P_2O_5 concentration.

Effect of Varying Optical Density on Extraction Efficiency

Optical density (OD) is an indication of the amount of dissolved organic matter and the presence of fine suspended solids in phosphoric acid. These dissolved organic materials affect the process of solvent extraction due to contamination of solvent mix and thus reduce the transfer of uranium from phosphoric acid to D2EHPA-TOPO during solvent extraction. Results of extraction experiments with different optical density showed a negative trend, wherein increasing the optical density resulted to decreasing extraction efficiency (Figure 3). Another important observation noted was that at high OD (2 to 3), there was a formation of stable emulsions or crud at the interface of aqueous and organic phase (Figure 3). This makes effective separation of the two

Table 1. Uranium, thorium, REE and other trace elemental content of phosphate rocks, fertilizers, phosphogypsum, and phosphoric acid.

SAMPLES	ELEMENTS (ppm)												
	Ag ^a	Cu ^a	Pb ^a	Zn ^a	Ni ^a	Co ^a	Mn ^a	Fe ^a	Cr ^a	Cd ^a	U ^b	Th ^c	Total REE, ^c
Zin Rock	5.42	22.99	38.83	218.95	33.27	12.60	43.40	1819.06	48.28	22.47	145.24	ND*	108.34
Egypt Rock	4.83	11.24	36.58	199.71	29.40	15.15	493.83	10735.73	79.41	11.47	66.87	1.02	196.59
Morocco Rock	6.66	31.41	39.49	216.81	43.42	13.19	45.99	1545.83	149.24	18.47	135.50	4.95	622.92
Togo Rock	5.26	41.65	39.42	269.96	43.96	22.09	253.97	10599.25	100.28	50.53	71.41	20.49	1085.53
Raw Phosphogypsum	2.91	4.45	61.24	36.05	9.67	8.91	24.00	1227.04	11.29	2.97	3.48	ND*	113.19
Treated Phosphogypsum**	3.86	4.88	41.37	13.24	11.21	10.97	23.35	766.38	11.90	3.61	12.00	1.25	210.64
MOP White (0-0-60)	3.11	3.10	33.79	13.54	10.19	9.46	7.41	79.95	1.94	1.53	0.38	ND*	ND*
MOP Red (0-0-60)	3.28	3.55	32.22	25.59	10.95	9.17	10.18	548.98	3.17	1.50	0.32	ND*	ND*
Urea (46-0-0)	0.09	0.18	3.34	1.90	0.20	0.56	1.34	134.39	6.22	ND*	0.64	ND*	0.12
21-0-0 (NPK Fertilizer)	0.22	0.29	14.29	2.91	3.07	2.84	1.61	137.94	4.63	0.73	26.42	ND*	ND*
14-14-14 (NPK Fertilizer)	1.08	10.39	23.48	78.15	13.66	5.60	58.15	1631.12	40.71	4.78	55.05	0.73	9.54
16-16-8 (NPK Fertilizer)	1.09	13.04	22.25	147.95	21.78	5.55	43.20	2473.01	50.87	8.58	81.66	0.24	22.32
16-20-0 (NPK Fertilizer)	1.09	19.72	19.93	120.30	20.83	5.00	11.93	1112.12	72.60	10.08	119.87	0.81	65.55
18-46-0 (NPK Fertilizer)	1.38	28.50	22.88	445.18	51.18	6.00	36.28	10164.24	131.35	17.70	228.08	0.69	18.86
Treated PA 27%	0.79	14.58	9.90	27.98	32.60	2.99	18.67	4328.75	72.02	15.70	108.67	ND*	2.74

*ND – not detectable.

**Treated phosphogypsum is raw phosphogypsum added with lime.

a – analyzed using FAAS by PNRI.

b – analyzed using fluorimetry by PNRI.

c – analyzed using ICP-MS by FIPR.

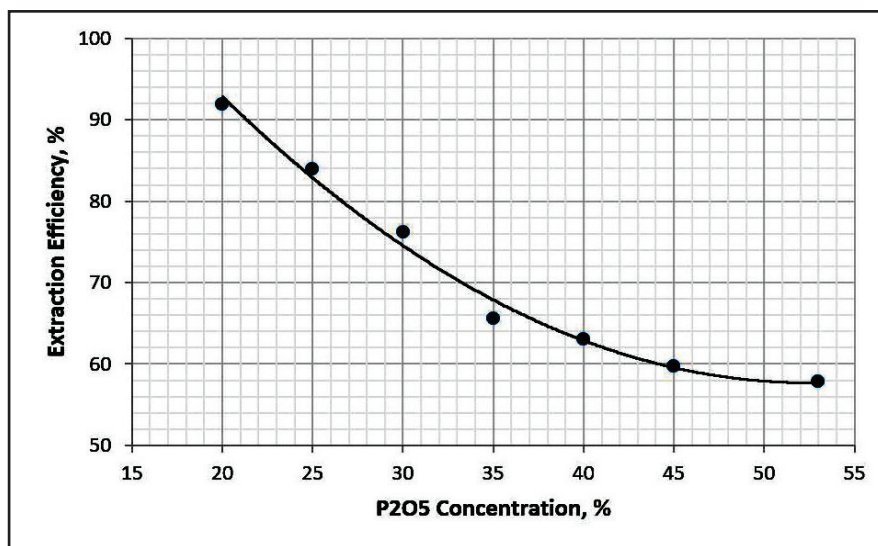


Figure 2. Effect of the variation of phosphoric acid content (P₂O₅) on the uranium extraction efficiency.

interphases difficult and could lead to the loss of expensive organic extractant. Some of the extractant may go along with the aqueous phase during separation and could damage the rubber linings in the storage tanks. To achieve higher uranium recovery and to prevent formation of emulsions and crud, the importance of the phosphoric acid pretreatment step must be emphasized and adopted

in uranium recovery plants by treating and purifying raw phosphoric acid to an OD of 0.2 to 0.3 (Hodge & Popovici 1994). Though this pretreatment process entails additional cost, it is justified by the rapid and effective mass transfer of uranium and reduction of solvent loss due to crud formation (IAEA 1987; Stas 2010).

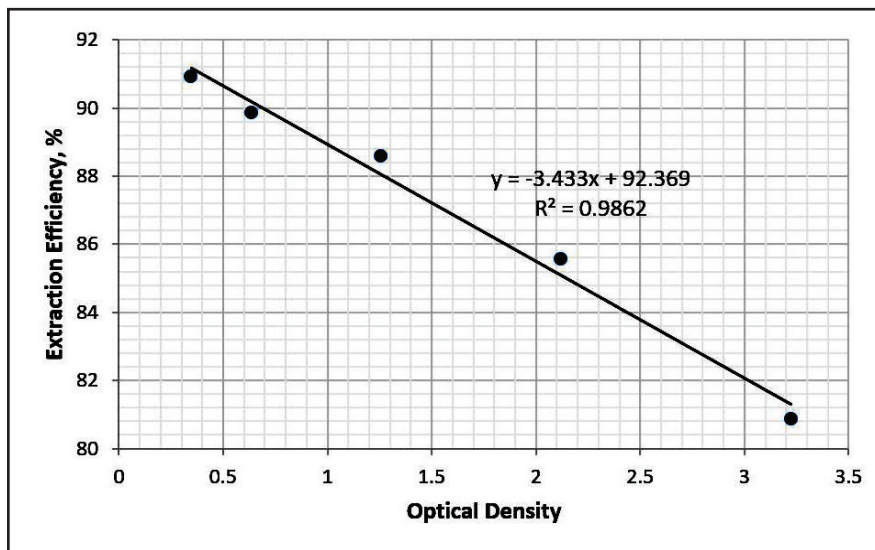


Figure 3. Effect of the variation of optical density on the uranium extraction efficiency.

Effect of Varying Contact Time on Extraction Efficiency

Experiment on the effect of contact time showed rapid complete uranium extraction equilibrium during the first minute of the reaction (Table 2). The obtained uranium extraction efficiency at 1-min contact time ($E = 91.66\%$) had no significant difference with the efficiencies at longer contact times ($E = 90.95\text{--}92.62\%$). In a commercial scale set-up, a shorter processing time would allow the use of small mixers and will thus reduce processing cost (IAEA 1987).

Effect of Varying Temperature on Uranium Extraction

The effect of temperature on uranium extraction from Philippine phosphoric acid was investigated. Reaction was carried out at varying temperatures ranging $30\text{--}60^\circ\text{C}$. The temperature had an inversely proportional effect on uranium extraction (Figure 4), indicating an exothermic nature.

In order to quantify the effect of temperature on uranium extraction, the enthalpy of reaction (ΔH) has to be calculated. A similar calculation was carried out based on the works of Khleifia and co-authors (2013), wherein the distribution coefficient was used in place of the equilibrium constant in the Van't Hoff Equation resulting to the following:

Table 2. Uranium extraction efficiency at varying contact time.

Contact Time, min	E, %
1	91.66
5	92.62
10	91.66
15	90.95

$$\ln(Kd) = -\frac{\Delta H}{RT} + c \quad (5)$$

The plot of $\ln(Kd)$ against $1/RT$ will thus yield a line with the slope equal to the negative of enthalpy of reaction ($-\Delta H$). As shown in Figure 5, the enthalpy of reaction of -70.59 kJ/mol was obtained at the given temperature range and showed great linearity, which clearly indicated an exothermic process. The importance of characterizing the nature of reaction in the development of an extraction process is crucial in deciding whether heating or cooling the system will increase or decrease the recovery rate. Phosphoric acid coming from the fertilizer plant has temperatures of $68\text{--}78^\circ\text{C}$ (IAEA 1987). In the conduct of uranium extraction, which was determined to be an exothermic process, the phosphoric will have to be cooled to some degree to increase extraction efficiency while keeping in mind the cost of cooling.

First Cycle Extraction Isotherm and Construction of McCabe-Thiele Diagram

Optimal parameters such as optical density (<0.3) and contact time (5 min) were applied in the investigation of extraction efficiency of D2EHPA-TOPO at nine (9) contacts with treated $27\% \text{ P}_2\text{O}_5$ content phosphoric acid. Results on the extraction of uranium from phosphoric acid at each contact had an average extraction efficiency of $\sim 91\%$ (Table 3). Close inspection of the efficiency shows large increments from 1st to 5th contact, indicating the approximate number of stages the solvent could be used economically to extract uranium in continuous industrial-scale extraction similar in the works of Hurst and co-authors (1972). From the 6th contact onwards, it was observed that the extraction efficiency lowered significantly ranging only from 20% to 50%.

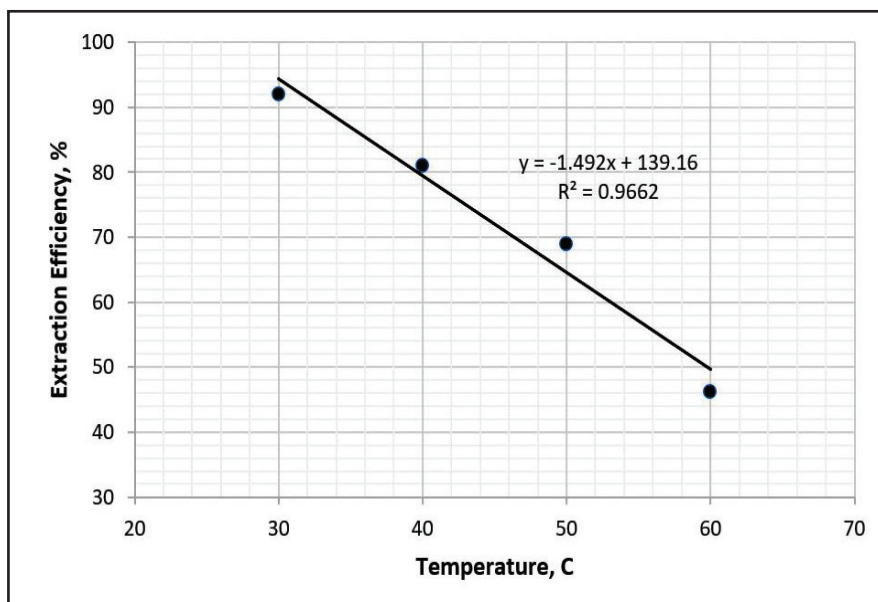


Figure 4. Effect of the variation of temperature on the uranium extraction efficiency.

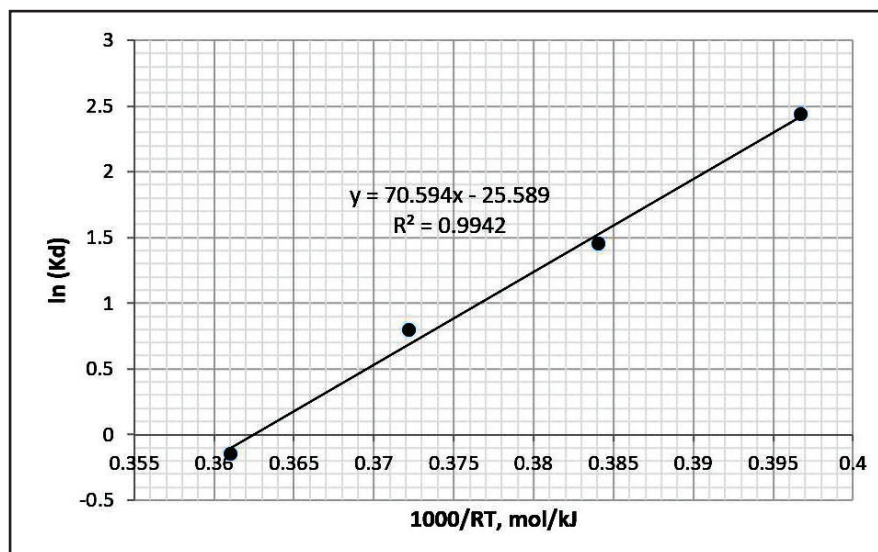


Figure 5. Van't Hoff Plot of uranium extraction from wet phosphoric acid.

Utilizing data from Table 2 and Table 3 (first contact), the average distribution coefficient (K_d) was calculated to be 10.71 (or $E = 91.46\%$). A high distribution coefficient would allow high aqueous to organic phase (A/O) ratio during extraction. An established full scale D2EHPA-TOPO extraction plant in Taiwan had similar conditions, where phosphoric acid solution contains 75 ppm uranium and had a 13.9 (or $E = 93.29\%$) distribution coefficient (Gupta & Singh 2003). The plant operates on a high phase ratio ($A/O = 1/4$) and extracts in five stages having an overall recovery rate of 97.27% for the first-cycle extraction. For this work, to estimate the number of stages

and uranium recovery, a McCabe-Thiele plot was made utilizing the equilibrium data obtained from batch testing. The operating line was constructed at different aqueous to organic phase volume ratio ($A/O = 1$ to 4), with the uranium in feed acid set at 108 ppm (equal to the initial uranium content in the acid). Among the operating lines constructed, the operating line with A/O ratio equal to 4 was deemed appropriate since uranium in the organic phase could be enriched higher at this volume ratio and at the same time, less of the expensive solvent is used. The McCabe-Thiele plot (Figure 6) indicates that a 92.59% uranium recovery could be achieved in three-ideal

Table 3. Extraction efficiency of D2EHPA-TOPO solvent at nth contact with treated 27% P₂O₅ phosphoric acid.

nth Contact	Run 1					Run 2					Run 3				
	U _{initial} ^b		U _{extracted} ^b	E, %	U in DEHPA- TOPO, ppm	U _{initial} ^b		U _{extracted} ^b	E, %	U in DEHPA- TOPO, ppm	U _{initial} ^b		U _{extracted} ^b	E, %	U in DEHPA- TOPO, ppm
	ppm	U _{final} ^b , ppm	ppm			ppm	ppm	U _{final} ^b , ppm			ppm				
1	108.67	8.30	100.37	92.36	100.37	108.67	10.72	97.95	90.14	97.95	108.67	10.72	97.95	90.14	97.95
2	108.67	21.40	87.27	80.31	187.64	108.67	20.45	88.23	81.19	186.18	108.67	21.93	86.74	79.82	184.70
3	108.67	30.98	77.69	71.49	265.33	108.67	34.20	74.47	68.53	260.65	108.67	33.69	74.98	69.00	259.68
4	108.67	38.18	70.49	64.86	335.82	108.67	37.76	70.91	65.25	331.57	108.67	39.65	69.02	63.51	328.69
5	108.67	47.92	60.75	55.90	396.56	108.67	43.24	65.43	60.21	396.99	108.67	50.69	57.98	53.35	386.67
6	108.67	57.43	51.24	47.15	447.81	108.67	52.68	55.99	51.53	452.99	108.67	63.54	45.13	41.53	431.80
7	108.67	61.09	47.58	43.78	495.38	108.67	61.57	47.10	43.35	500.09	108.67	67.38	41.29	38.00	473.10
8	108.67	62.55	46.12	42.44	541.50	108.67	63.55	45.13	41.52	545.21	108.67	77.98	30.69	28.24	503.79
9	108.67	69.22	39.45	36.31	580.96	108.67	68.77	39.91	36.72	585.12	108.67	72.82	35.85	32.99	539.63

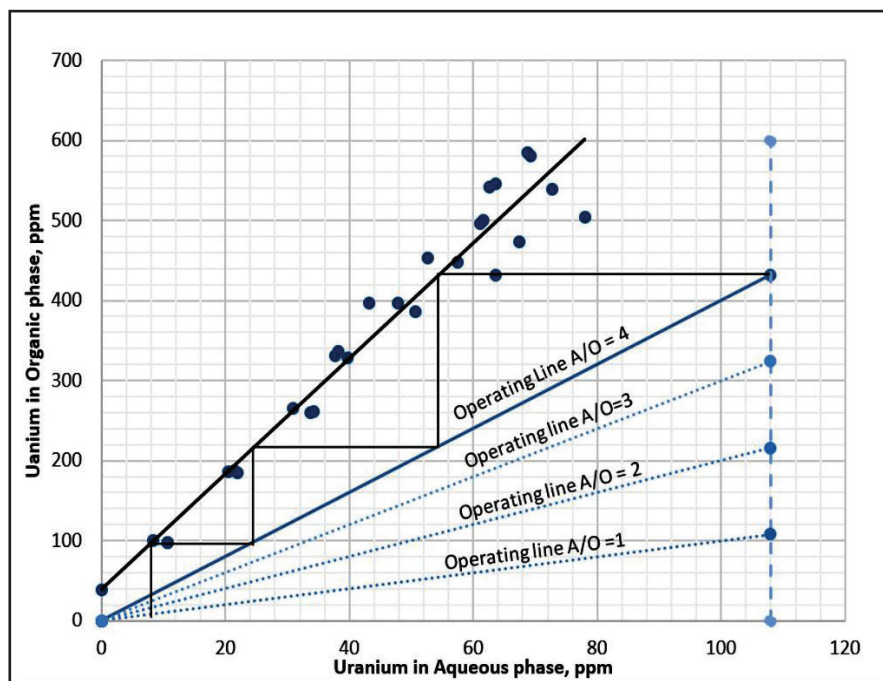


Figure 6. McCabe-Thiele Plot of the extraction of uranium from phosphoric acid using 0.5 M DEHPA - 0.125 M TOPO.

extraction stages at an A/O volume ratio of 4:1. In practice, a higher recovery rate could be achieved by addition of extraction stage.

CONCLUSION

Uranium extraction from Philippine phosphoric acid using the synergistic mixture solvent of D2EHPA – TOPO showed promising results with 91% recovery

rate. The study provided reliable data on the effect of different extraction parameters and on the determination of uranium extraction isotherm. However, it should be noted that results from this study were performed in batch testing and in laboratory conditions, thus data on uranium extraction isotherm will be slightly different compared to a continuous extraction setup where industrial conditions may be better simulated. The results from this study provides good tool for further investigation of the process, related recovery methods, and especially in the conduct

of up-scaled continuous uranium extraction systems. Fully developing the technology will contribute to the sustainable production of uranium, rare earth elements, and other valuable associated elements from phosphates in the Philippines, which will lead to: 1) minimal environmental impacts and protection of human health by producing cleaner fertilizers with greatly reduced uranium content; 2) zero waste and maximized resource utilization; and 3) opportunity to utilize uranium in nuclear fuel cycle if the Philippines will go into nuclear as power generation option or an additional revenue in the phosphate processing industry.

The experiment showed how the major parameters (optical density, contact time, P_2O_5 concentration, and temperature) affect the uranium recovery in the first cycle extraction. Based on experimental results, the recommended parameters for the first cycle extraction necessary to obtain to optimal uranium recovery are the following:

- 1) feed acid has 27% P_2O_5 content wet phosphoric acid;
- 2) OD of pretreated acid is <0.3 ;
- 3) extraction contact time ranges 2-5 min;
- 4) extraction temperature set at $30-40^\circ\text{C}$;
- 5) A/O ratio is equal to 4;
- 6) four extraction stages.

ACKNOWLEDGMENT

This study forms part of the International Atomic Energy Agency technically assisted project entitled "Enhancing National Capacity for Extraction of Uranium, Rare Earth Elements and Other Useful Commodities from Phosphoric Acid" and was also partially funded by the Department of Science and Technology - National Research Council of the Philippines under the project entitled "Comprehensive Extraction of Uranium, Rare Earth Elements and Other Valuable Resources from Wet Phosphoric Acid". Furthermore, the authors thank PhilPhos for their kind support and materials that they have provided, as well as the Florida Industrial and Phosphate Research Institute (FIPRI) for their assistance with the laboratory work conducted.

REFERENCES

BELTRAMI D, COTE G, MOKHTARIH, COURTAUD B, MOYER BA, CHAGNES A. 2014. Recovery of uranium from wet phosphoric acid by solvent extraction processes. *Journal of American Chemical Society* 114(24): 12002-23.

BELTZ K, FRANKENFELD K, LEHMANN R, ZINTL I. 1983. US Patent No. US4383978 A. USA: United States Patent. Retrieved from <https://www.google.com/patents/US4383978> on 20 Sep 2017.

BROOK BW, ALONZO A, MENELEY DA, MISAK J, BLEES T, VAN ERP JB. 2014. Why nuclear energy is sustainable and has to be part of the energy mix. In: *Sustainable Materials and Technologies*. Retrieved from <https://doi.org/10.1016/j.susmat.2014.11.001>.

CRUZ PS. 1997. Aquaculture feed and fertilizer resource atlas of the Philippines. Retrieved from <http://www.fao.org/3/a-w6928e.HTM> on 2016.

DILLARD EF, FRAZIER AW, WOODIS TC. 1982. Precipitated impurities in 18-46-0 fertilizers prepared from wet-process phosphoric acid. *Journal of Agricultural Food Chemistry* 30: 382-388.

DARTIGUELONGUE A, CHAGNES A, PROVOST E, FURST W, COTE G. 2015. Modelling of uranium (VI) extraction by D2EHPA/TOPO from phosphoric acid within a wide range of concentrations. *Hydrometallurgy*, doi:10.1016/j.hydromet.2015.11.007.

EMSBO P, MCLAUGHLIN PI, BREIT GN, DU BRAY EA, KOENIG AE. 2014. Rare earth elements in sedimentary phosphate deposits: Solution to the global REE crisis? *Gondwana Research* 27(2015): 776-85. Retrieved from doi:10.1016/j.gr.2014.10.008.

GUPTA C, SINGH H. 2003. Uranium resource processing: secondary resources. Germany: Springer. p. 309-345.

HANEKLAUS N, REYES RY, LIM WG, TABORA EU, PALATTAO BL, PETRACHE C, VARGAS EP, KUNITOMI K, OHASHI H, SAKABA N, SATO H, GOTO M, YAN X, NISHIHARA T, TULSIDASH, REITSMA F, TARJAN S, SATHRUGNAN K, JACIMOVIC R, AL KHALEDI N, BIRKY BK, SCHNUG E. 2015. Energy neutral phosphate fertilizer production using high temperature reactors - a Philippine case study. *Philippine Journal of Science* 44(1): 69-79.

HANEKLAUS N, SUN Y, BOL R, LOTTERMOSER B, SCHNUG E. 2017. To extract, or not to extract uranium from phosphate rock, that is the question. *Environmental Science and Technology* 51: 753-754. Retrieved from <http://pubs.acs.org/doi/pdfplus/10.1021/acs.est.6b05506>.

HODGE CA, POPOVICI N. ed. 1994. Pollution control in fertilizer production. ed. NY: Marcel Dekker Incorporated. p. 237-250.

HURST FJ, CROUSE DJ, BROWN KB. 1972. Recovery of uranium from wet phosphoric acid. *Industrial and Engineering Chemistry Process Design and*

- Development 11(1): 122-128.
- IAEA. 1987. IAEA-TECDOC-533. Recovery of uranium from phosphoric acid. Vienna, Austria: International Atomic Energy Agency. Retrieved from http://www-pub.iaea.org/MTCD/publications/PDF/te_0533.pdf on 11 Feb 2016.
- IAEA. 1992. Analytical techniques in uranium exploration and ore processing (Technical Report Series 341). Vienna, Austria: International Atomic Energy Agency. p. 65-72. Retrieved from http://www-pub.iaea.org/MTCD/Publications/PDF/trs341_web.pdf on 15 Sep 2017.
- KHLEIFIAN N, HANNACHI A, ABBES N. 2013. Studies of uranium recovery from Tunisian wet process phosphoric acid. *International Journal of Innovation and Applied Studies* 3(4): 1066-71.
- KOURAIM MN, FAWZY MM, HELALY OS. 2014. Leaching of lanthanides from phosphogypsum waste using nonyl phenol ethoxylate associated with HNO₃ and HCl. *International Journal of Sciences: Basic and Applied Research* 16(2): 31-44.
- KULCZYCKA J, KOWALSKI Z, SMOL M, WIRTH H. 2015. Evaluation of the recovery of Rare Earth Elements (REE) from phosphogypsum waste – case study of the WIZÓW Chemical Plant (Poland). *Journal of Cleaner Production*. Retrieved from doi: 10.1016/j.jclepro.2015.11.039.
- ÖZAYTEKIN H, UYANÖZ R. 2012. Trace and Rare Earth Element (REE) status of ÇarsambaFan soils in the ancient Konya lake region, Turkey. *African Journal of Agricultural Research* 7(7): 1110-17.
- PETRACHE C, MARCELO EA, SANTOS JR G. 1987. Notes on the extraction of uranium from phosphoric acid. *Philippine Technology Journal* 12(4): 95-99.
- PRESTON JS, COLE PM, CRAIG WM, FEATHER AM. 1996. The recovery of rare earth oxides from a phosphoric acid by-product. Part 1: Leaching of rare earth values and recovery of a mixed rare earth oxide by solvent extraction. *Hydrometallurgy* 41: 1-19.
- RAMOS SJ, DINALI GS, DE CARVALHO TS, CHAVES LC, SIQUEIRA LC, GUILHERME LRG. 2016. Rare earth elements in raw materials and products of the phosphate fertilizer industry in South America: Content, signature, and crystalline phases. *Journal of Geochemical Exploration* 168: 177-186.
- ROTHBAUM HP, MCGAVESTON DA, WALL T, JOHNSTON AE. 1979. Uranium accumulation in soils from long-continued applications of superphosphate. *European Journal of Soil Science* 30: 147-153.
- RUTHERFORD PM, DUDAS MJ, SAMEK RA. 1994. Environmental impacts of phosphogypsum. *Science of the Total Environment* 149(1-2): 1-38.
- SAHU SK, AJMAL PY, BHANGARE RC, TIWARI M, PANDIT GG. 2014. Natural radioactivity assessment of a phosphate fertilizer plant area. *Journal of Radiation Research and Applied Sciences* 7(1): 123-128. Retrieved from <https://doi.org/10.1016/j.jrras.2014.01.001>.
- STAS J, OTHMAN I, ABBAS M, SHLEWIT H. 2010. Uranium extraction from Syrian phosphate: A case study. *Journal of Economics and Environmental Geology* 1(2): 30-34.
- SINGH SK, DHAMI PS, TRIPATHI SC, DAKSHINAMOORTY A. 2009. Studies on the recovery of uranium from phosphoric acid medium using synergistic mixture of (2-ethyl hexyl) phosphonic acid, mono(2-ethyl hexyl ester (PC**A) and tri-n-butyl phosphate (TBP). *Hydrometallurgy* 95: 170-174.
- [STC] Scientific and Technical Committee Euratom. 2003. The energy challenge of the 21st century: The role of nuclear energy. Belgium: European Communities. p. 2-9. Retrieved from http://cordis.europa.eu/pub/fp6/docs/euratom_challenge_21stcentury.pdf on 20 Dec 2017.
- [USEPA] United States Environmental Protection Agency. 1992. Potential uses of phosphogypsum and associated risks. Retrieved from <https://www.epa.gov/sites/production/files/2015-07/documents/0000055v.pdf> on 9 Sept 2017.
- [WNA] World Nuclear Association. 2016. Supply of uranium. Retrieved from <http://www.world-nuclear.org/information-library/nuclear-fuel-cycle/uranium-resources/supply-of-uranium.aspx> on 20 Dec 2016.