PERIODICA POLYTECHNICA SER. CHEM. ENG. VOL. 44, NO. 2, PP. 123–132 (2000)

STRIPPING OF URANIUM FROM D2EHPA/TOPO SOLVENT BY AMMONIUM CARBONATE SOLUTIONS

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Received: Febr. 11, 2002

Abstract

Uranium is recovered from phosphoric acid by the D2EHPA/TOPO process. In this process uranium is stripped from the loaded D2EHPA /TOPO solvent in the second cycle by an ammonium carbonate solution.

This paper studied stripping of uranium from 0.3 mol/L D2EHPA / 0.075 mol/L TOPO in kerosene by different ammonium carbonate solutions. The ammonium carbonate solutions tested were either prepared locally from ammonia and carbon dioxide gases or commercial and laboratory grades available on the market. A comparison was made between these carbonate solutions in terms of purity, stripping efficiency and phase separation. Both stripping and phase separation were carried out under different conditions of phase ratios and concentrations.

The results obtained showed that ammonium carbonate prepared from direct reaction of ammonia and carbon dioxide gases had a high purity and gave the same stripping yield as the laboratory grade. The phase separation was also slightly improved using a pure synthesized ammonium carbonate solution. The phase separation was found to be the best at a concentration of 0.5 mol/L ammonium carbonate solution and at a phase ratio A/O of 1/1 and a temperature of 50 °C. It was possible to obtain $>$ 99% yield of uranium by operating 2 stripping stages counter-currently under these conditions.

Keywords: D2EHPA, stripping, TOPO, uranium.

1. Introduction

Uranium is recovered from wet phosphoric acid by extraction with D2EHPA/TOPO solvent in kerosene in two cycles. The first cycle consists of extracting uranium from phosphoric acid in four stages by mixing with D2EHPA/TOPO solvent in kerosene. The loaded solvent is then stripped from uranium by mixing with concentrated and reduced current of phosphoric acid. In the second cycle uranium is extracted from the concentrated acid by contacting it with D2EHPA/TOPO solvent in kerosene in other four stages. The loaded solvent is then stripped by an alkaline solution. Ammonium carbonate solutions in different concentrations and pHs are usually used at a temperature of 50 °C. EZAHR [1] mentioned that the solvent was first washed with water or dilute sulfuric acid to remove traces of P_2O_5. It was then stripped by an ammonium carbonate solution of 250 g/L concentration at A/O = 1/5 by volume phase ratio. BERRY [2] stated that the D2EHPA/TOPO solvent was first washed with water to remove dissolved phosphoric acid. It was then stripped by a dilute solution of ammonium carbonate solution to prevent precipitation of uranium.

The solution was then treated with sulfuric acid to reduce the pH and to remove CO_2. Uranium was then precipitated by addition of ammonia. SCHNEIDER [3] mentioned that stripping was achieved in two stages by counter-current contact of loaded organic solvent with a solution of ammonium carbonate keeping NH_3 and pH at specific values to precipitate uranium in the form of ammonium uranyl carbonate AUC. FATOVIC [4] found that stripping should be achieved at a constant pH of the order of 8–8.4 because the selectivity was not good at pH < 8, while at pH > 8.4, iron precipitated in the form of $Fe(OH)_3$ and polluted the yellow cake. SINGH [5] used sodium carbonate at 0.15 % w/v to obtain a salt containing more than 7 g/L U_3O_8. He used a phase ratio O/A $= 0.5/1$ to get a good phase separation. Uranium was then precipitated by sodium hydroxide solution. KHORFAN et al. [6] studied stripping of uranium from 0.1 mol/L D2EHPA in kerosene by different acids and alkalis. The results showed that stripping by alkaline solutions was always higher than by acidic solutions. Stripping by alkaline solutions decreased in the following order:

$$Na_2CO_3 > (NH_4)_2CO_3 > NH_4HCO_3.$$

Stripping also enhanced by an increase in the pH and concentration of the solution. An ammonium carbonate solution at 0.5 mol/L gave a yield > 99.8% at a temperature of 20 °C.

2. Materials and Methods

2.1. Preparation of Ammonium Carbonate

Fig. 1 is a schematic diagram of the reactor used to synthesize ammonium carbonate. The reactor was made of stainless steel SS904L and supplied with 4 baffles. The volume of the reactor was 40 liters and the diameter was 0.35 m. Ammonia gas with a purity of 99.92% vol was introduced via the top of the reactor from a gas cylinder under a pressure of 8–10 bar. Carbon dioxide as a gas with a 99.95% vol purity was also introduced at the top of the reactor from a gas cylinder with a pressure of 50–55 bar. The flow of both gases was accurately controlled. Water was introduced to the reactor and a mixer of 12 cm diameter was operated by a 0.75 kW motor. The product in the form of an ammonium carbonate solution was withdrawn at measured rates from the bottom of the reactor.

Samples were withdrawn at certain intervals and analyzed by a Metrohum E536 type potentiometer. The solution was titrated by 0.1 N HCl solution. The composition of the solution was determined from the resulting curves according to methods mentioned in the literature [7, 8].

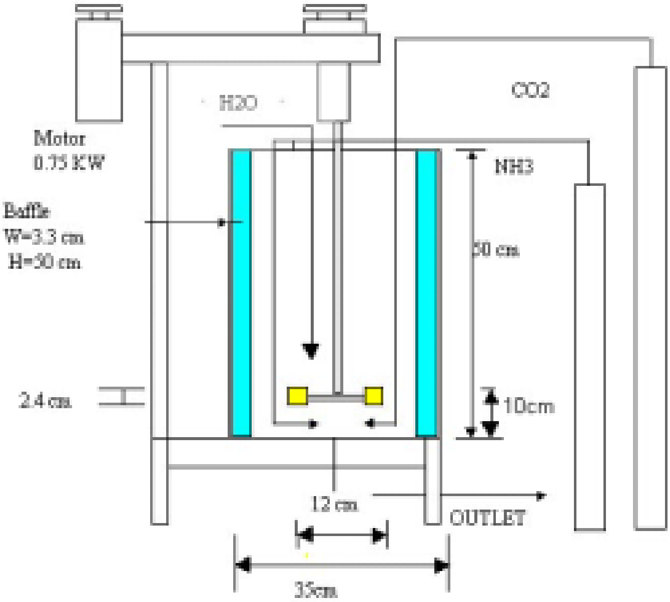

Fig. 1. Schematic diagram of the reactor for synthesis of ammonium carbonate from ammonia and carbon dioxide gases

2.2. *Stripping of Uranium*

Stripping of uranium from loaded 0.3 mol/L D2EHPA/0.075 mol/L TOPO in kerosene solvent containing 8 g/L of U was carried out using either prepared ammonium carbonate or a commercial bicarbonate with 85% purity or a laboratory grade carbonate from BDH Laboratory Supplies, England, with $> 95\%$ purity. The stripping was carried out at 50 °C. The time of mixing was fixed in 5 minutes and that for separation in 20 minutes. Phase ratios A/O 0f 1, 1.5 by volume were used. The concentrations of ammonium carbonate solution used were 1 mol/L and 0.5 mol/L. Uranium concentration in aqueous and organic phases was determined by a Gamma Spectrometer with an NaI crystal of the Canberra Industries Model 80 L type with a Multi Channel Analyzer MCA Series 35 Plus. The uranium concentration was calculated from the U^{235} peak at 186 Kev [9, 10]. The distribution ratio D for uranium between the aqueous and organic phases was calculated from this relationship:

$$D = [U]_A/[U]_O, \tag{1}$$

where:

$[U]_A$ concentration of uranium in the aqueous phase g/L.
$[U]_O$ concentration of uranium in the organic phase g/L.

2.3. Phase Separation

Experiments at the speed of phase separation were conducted on prepared ammonium carbonate and commercial ammonium carbonate solutions. The loaded solvent was mixed with the ammonium carbonate solution for 5 minutes at a temperature of 50 °C. The mixture was allowed to settle in a measuring cylinder with a volume of 100 c.c. and a height of 19 cm. The height of the interface was measured at certain time intervals. The experiment was carried out with 0.5 mol /L and 1 mol /L ammonium carbonate solutions at 0.5, 1, 1.5 and 2.0 O/A phase ratios.

3. Results and Discussion

3.1. Preparation of Ammonium Carbonate

Ammonium carbonate solution was prepared in the reactor shown in *Fig.* 1. The reaction reached the steady state after 60 minutes where a constant flow of approximately 2 mol/L of ammonia and 1 mol/L of carbon dioxide reacted to form 1 mol/L of ammonium carbonate solution according to the reaction:

$$2\,NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2\,CO_3. \qquad (2)$$

The results are represented in *Fig.* 2. The purity of ammonium carbonate was measured by the potentiometer and found to be $>$ 99% wt.

Decomposition of the ammonium carbonate solution was tested by analyzing samples over a period of 1 week. The results showed no appreciable change in the composition at a temperature of 25 °C over this period.

3.2. Stripping of Uranium

Results on stripping of uranium from the loaded solvent are shown in *Fig.*3 where concentration of uranium in the aqueous phase is plotted vs. concentration of uranium in the organic phase for the three different types of ammonium carbonate solutions. The results fit a function of the type:

$$Y = a \,\mathrm{Ln}\, X + b, \qquad (3)$$

where:

Y = concentration of uranium in the aqueous phase g/L.
X = concentration of uranium in the organic phase g/L.
a, b = constants, $a = 7.8104$, $b = 9.8304$.
The correlation factor $R = 0.9716$.
This curve is called the stripping curve or the isotherm at 50°C.

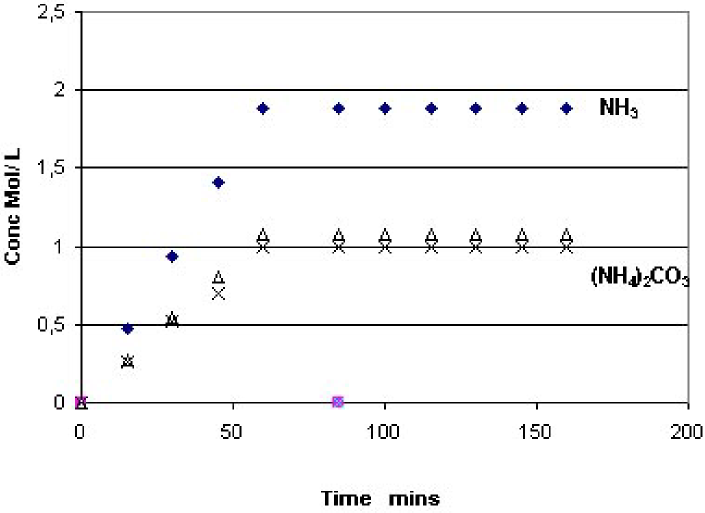

Fig. 2. Synthesis of ammonium carbonate from ammonia and carbon dioxide gases

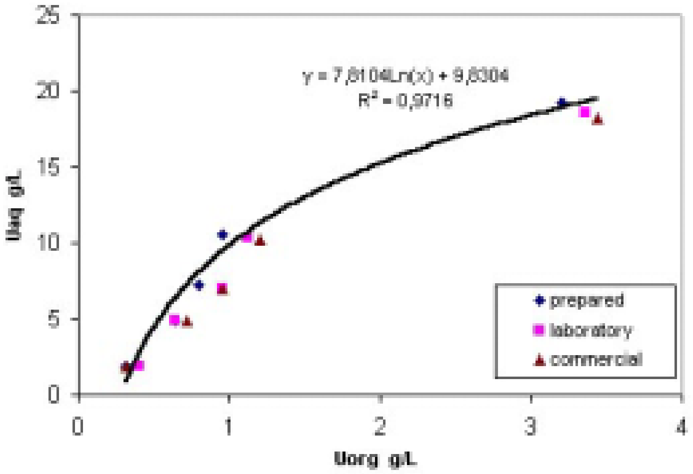

Fig. 3. Equilibrium curve for stripping of uranium from different ammonium carbonate solutions. ($T = 50$ °C, $[U]_O = 8$ g/L, $[(NH_4)_2CO_3] = 0.5$ mol/L)

The correlation could be simplified for concentrations of uranium in the aqueous phase in the range $0 - 8$ g /L which is the usual range encountered in practice. The new relationship was represented in the form of a straight line as:

$$Y = m \cdot X, \tag{4}$$

where:

$m = 10.763$.

The distribution ratio D as defined by *Eq.* (1) is:

$$D = m = 10.7. \tag{5}$$

The results show a very little difference as far as stripping is concerned between the three types of ammonium carbonate solutions. *Fig.* 4 shows the McCabe & Thiele diagram [11] for stripping 0.3 mol/L D2EHPA /0.075 mol/L TOPO in kerosene loaded with 8 g/L uranium by 1 mol/L ammonium carbonate solution at 1 and 1.5 O/A phase ratios. This method as illustrated in *Fig.* 4 shows that 2 counter-current stages are enough to give 99% stripping yield and to reduce the uranium content in the solvent to less than 200 ppm. This result is identical to the operation of a stripping unit in a commercial plant.

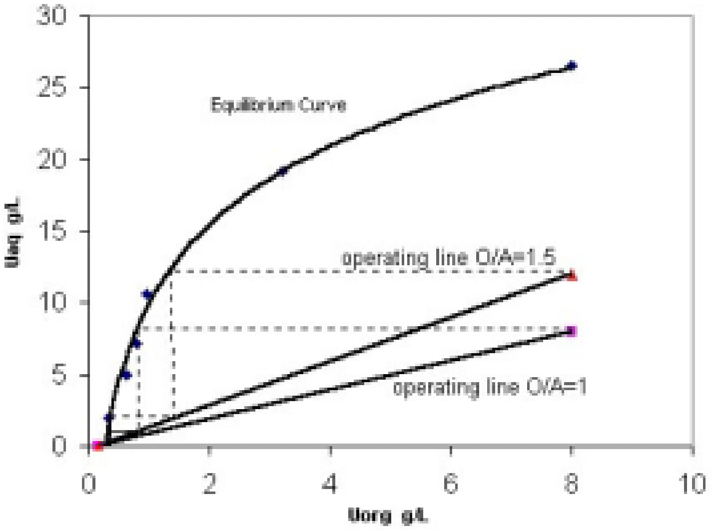

Fig. 4. Number of stages for stripping of uranium from ammonium carbonate solutions by McCabe & Thiele Method. ($T = 50$ °C, $[U]_O = 8$ g/L, $[(NH_4)_2CO_3] = 0.5$ mol/L.)

3.3. *Phase Separation*

In stripping it is not only important to have a high transfer of uranium from organic to aqueous phase, but it is essential to have a quick separation of phases with no

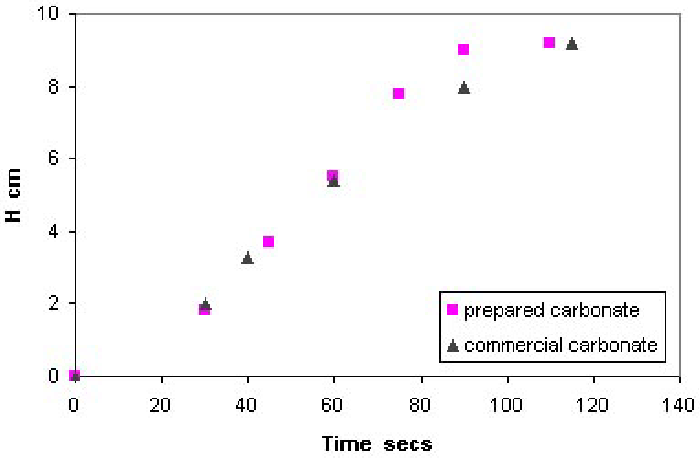

Fig. 5. Height of interface vs time for ammonium carbonate solutions ($[M] = 0.5$ mol/L , $T = 50$ °C, O/A = 1.0)

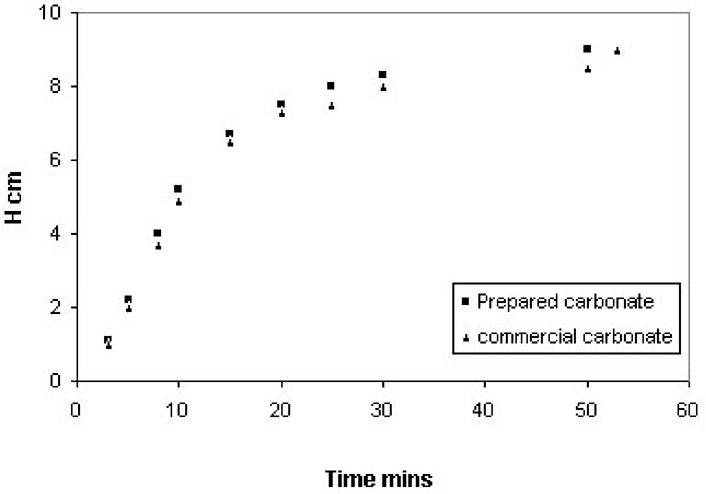

Fig. 6. Height of interface vs time for ammonium carbonate solutions ($[M] = 0.5$ mol/L, $T = 50$ °C, O/A = 1.5)

emulsions. Phase separation experiments were conducted at 50 °C and different ammonium carbonate concentrations and phase ratios for the prepared and the commercial carbonate. The results obtained show that phase separation is always quicker for the prepared carbonate. *Figs.* 5, 6, 7 and 8 indicate that phase ratios of

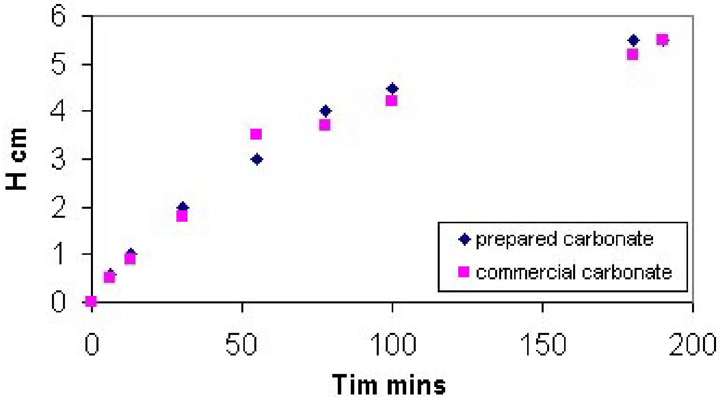

Fig. 7. Height of interface vs time for ammonium carbonate solutions ([M] = 0.5 mol/L, T = 50 °C, O/A = 2)

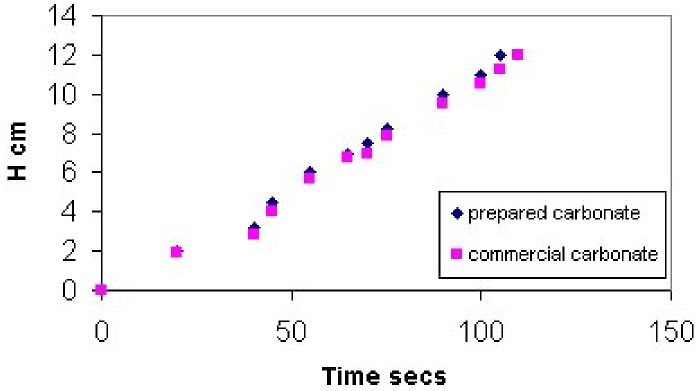

Fig. 8. Height of interface vs time for ammonium carbonate solutions ([M] = 0.5 mol/L, T = 50 °C, O/A = 0.5)

O/A = 1 and 0.5 are better for phase separation than O/A = 1.5 and 2 under the same temperature and carbonate concentration.

The effect of ammonium carbonate concentration on phase separation is illustrated by comparing *Figs.* 5 and 9 or 6 and 10. It is clear that at the same phase ratio and temperature, the phase separation is much quicker at 0.5 mol/L carbonate concentration than at 1 mol/L.

A height of 6 cm is reached after 1 minute for 0.5 mol/L compared with 15 minutes for the 1 mol/L concentration at O/A = 1. When phase ratio O/A is 1.5, the

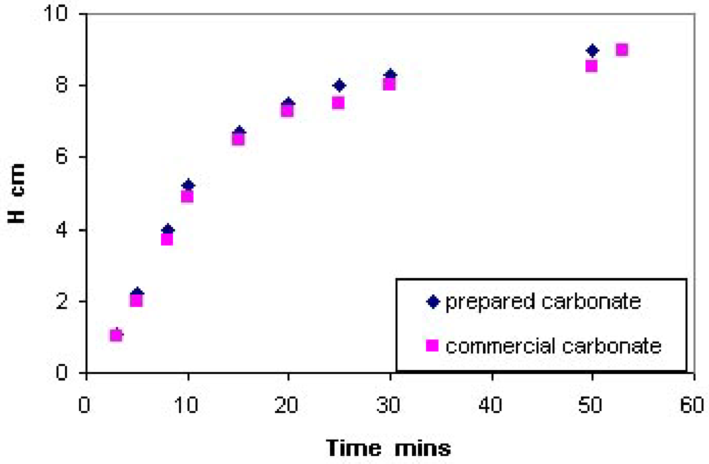

Fig. 9. Height of interface vs time for ammonium carbonate solutions ($[M] = 1.0$ mol/L, $T = 50$ °C, O/A = 1.0)

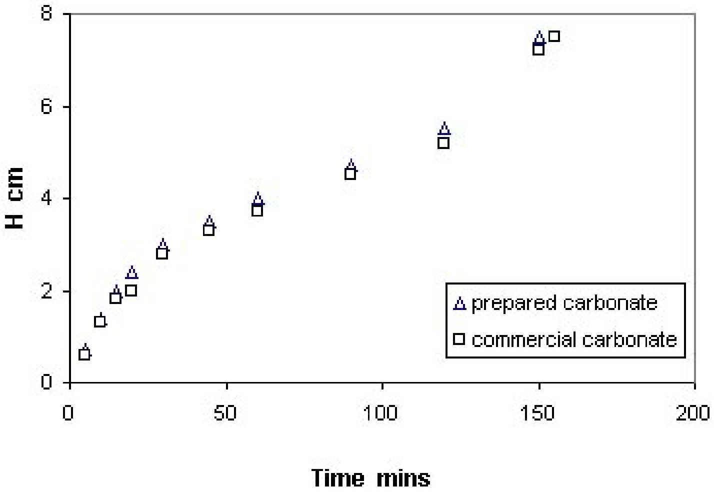

Fig. 10. Height of interface vs time for ammonium carbonate solutions ($[M] = 1.0$ mol/L, $T = 50$ °C, O/A = 1.5)

phase separation is even slower especially for ammonium carbonate concentration of 1 mol/L as shown in *Fig. 10*.

4. Conclusion

Ammonium carbonate solutions prepared by synthesis from ammonia and carbon dioxide pure gases are found to have higher purity than commercial or laboratory grade ammonium carbonates. This was proved to give a slightly better stripping and phase separation while the cost of the prepared ammonium carbonate was less than the laboratory grade by a factor of 17. Stripping yield was shown to be $> 99\%$ when carried out counter-currently in 2 stages at a temperature of 50 °C and 0.5 mol/L ammonium carbonate solution and a phase ratio $O/A = 1$. Phase separation was optimal for 0.5 mol/L ammonium carbonate concentration, $O/A = 1$ phase ratio, and a temperature of 50 °C. A height of 6 cm was reached after 1 minute compared with 140 minutes for 1 mol/L ammonium carbonate concentration and $O/A = 1.5$ phase ratio.

Acknowledgement

The authors would like to express their thanks to the General Director of Syrian Atomic Energy Commission Dr Ibrahim Othman for his help and encouragement and to Dr Hasan Kallawi for his useful remarks.

References

[1] EZAHR, I., IAEA, Recovery of Uranium from Phosphoric Acid, Nov. (1989) p. 87.
[2] BERRY, W. W., IMC/Prayon Uranium Recovery from Phosphoric Acid, *ISEC'80*, **3**, Lieja (1980) pp. 1–10.
[3] SCHNEIDER, B., The D/T Extraction Process and its Application to Phosphoric Acid, *IAEA-EC-DOC-533*, (1989).
[4] FATOVIC, I., *International Solvent Extraction Conference ISEC* (1986) p. 231.
[5] SINGH, H., *Int. Symp Uranium Tech.*, Bombay (1989).
[6] KHORFAN, S. – STAS, J. – KASSEM, M., *J. Radioanal. Nucl. Chem.*, **238**, (1998) p. 145.
[7] FRITZ, J. S. – SCHENK, G. M., *Quantitative Analytical Chemistry*, 3rd ed., USA (1974).
[8] BASSETT, J. – DENNEY, R. C. – JEFFERY, G. H. – MENDHAM, J., *Quantitative Inorganic Analysis*, Longman Limited, London and NewYork (1978) pp. 306–312.
[9] *Nuclear Data Sheets*, Academic Press (1988), Table VII, p. 288r.
[10] KNOLL, G. F., *Radiation Detection & Measurement*, John Wiley, New York (1979) p. 422.
[11] PERRY, Robert, H. – GREEN, Dun, *Perry's Chemical Engineers' Handbook*, McGraw-Hill Inc. New York (1984) p. 15-1.