

## Reduction of $\text{UO}_2^{2+}$ by $\text{H}_2$

Ella Ekeröth<sup>a,\*</sup>, Mats Jonsson<sup>a</sup>, Trygve E. Eriksen<sup>a</sup>, Kristina Ljungqvist<sup>a</sup>,  
Sándor Kovács<sup>b</sup>, Ignasi Puigdomenech<sup>b,1</sup>

<sup>a</sup> Department of Chemistry, Nuclear Chemistry, Royal Institute of Technology, SE-100 44 Stockholm, Sweden

<sup>b</sup> Department of Chemistry, Inorganic Chemistry, Royal Institute of Technology, SE-100 44 Stockholm, Sweden

Received 17 December 2003; accepted 23 April 2004

### Abstract

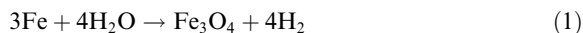
The reactivity of  $\text{H}_2$  towards  $\text{UO}_2^{2+}$  has been studied experimentally using a PEEK coated autoclave where the  $\text{UO}_2^{2+}$  concentration in aqueous solution containing 2 mM carbonate was measured as a function of time at  $p_{\text{H}_2} \sim 40$  bar. The experiments were performed in the temperature interval 74–100 °C. In addition, the suggested catalytic activity of  $\text{UO}_2$  on the reduction of  $\text{UO}_2^{2+}$  by  $\text{H}_2$  was investigated. The results clearly show that  $\text{H}_2$  is capable of reducing  $\text{UO}_2^{2+}$  to  $\text{UO}_2$  without the presence of a catalyst. The reaction is of first order with respect to  $\text{UO}_2^{2+}$ . The activation energy for the process is  $130 \pm 24$  kJ mol<sup>-1</sup> and the rate constant is  $k_{298\text{K}} = 3.6 \times 10^{-9}$  l mol<sup>-1</sup> s<sup>-1</sup>. The activation enthalpy and entropy for the process was determined to 126 kJ mol<sup>-1</sup> and 16.5 J mol<sup>-1</sup> K<sup>-1</sup>, respectively. Traces of oxygen were shown to inhibit the reduction process. Hence, the suggested catalytic activity of freshly precipitated  $\text{UO}_2$  on the reduction of  $\text{UO}_2^{2+}$  by  $\text{H}_2$  could not be confirmed.

© 2004 Elsevier B.V. All rights reserved.

### 1. Introduction

One of the key issues for the safety assessment of a spent nuclear fuel repository according to the KBS-3 concept [1] is dissolution of the  $\text{UO}_2$ -matrix accompanied by release of actinides and fission products. As has been shown in numerous studies [2–5], this process is enhanced by oxidizing radiolysis products ( $\text{OH}^\bullet$ ,  $\text{H}_2\text{O}_2$ ,  $\text{HO}_2^\bullet$  and  $\text{O}_2$ ) formed in the otherwise reducing groundwater. However, radiolysis of water also results in production of reductants, i.e.,  $\text{e}_{\text{aq}}^-$ ,  $\text{H}^\bullet$  and  $\text{H}_2$  that could act as inhibitors for oxidative dissolution. In addition, when the shielding copper canister fail (this being a prerequisite for radiolysis of water to occur in the first place), anoxic ground water will come in contact with the innermost cast iron. Anaerobic corrosion of the

cast iron canisters will produce large amounts of  $\text{H}_2$  resulting in an overall reducing environment according to reaction (1) [4]:



The possible inhibiting effect of  $\text{H}_2$  on dissolution of spent nuclear fuel has so far not been studied explicitly. One obvious effect of increased levels of  $\text{H}_2$  is the reaction with  $\text{OH}^\bullet$ , which inevitably will suppress the production of radiolytical oxidants, reaction (2):



$$k_{298\text{K}} = 4 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1} \text{ (pH} = 5) \text{ [6].}$$

Another plausible effect is reduction of dissolved  $\text{UO}_2^{2+}$  to  $\text{UO}_2(\text{s})$ . This reaction is thermodynamically feasible ( $\Delta G^\circ = -86.3$  kJ mol<sup>-1</sup>), however, the activation barrier and thereby the rate constant for the uncatalyzed process has not been established previously. The reduction of  $\text{UO}_2^{2+}$  was first studied in the 1950's as a step in the production of nuclear fuel. Carbonate solutions were

\* Corresponding author. Tel.: +46-8 790 9279; fax: +46-8 790 8772.

E-mail address: [ella@nuchem.kth.se](mailto:ella@nuchem.kth.se) (E. Ekeröth).

<sup>1</sup> Present address: SKB, SE-10240 Stockholm, Sweden.

used for leaching U(VI) from ores. These solutions were treated with H<sub>2</sub> ( $p_{\text{H}_2} = 6\text{--}20$  bar) at 100–200 °C in the presence of a catalyst. Cobalt, platinum and nickel were used as catalysts. Later it was suggested that the product UO<sub>2</sub> was itself catalyzing the reaction [7].

Consequently, there are at least two ways by which H<sub>2</sub> can affect the concentration of uranium in solution: (1) Dissolution of spent nuclear fuel (UO<sub>2</sub>) can be inhibited by reactions between oxidants and H<sub>2</sub> in a protecting step. (2) Reduction of already dissolved UO<sub>2</sub><sup>2+</sup> or U(VI) on the spent nuclear fuel surface to UO<sub>2</sub>. It should be noted that the reduction of UO<sub>2</sub><sup>2+</sup> by H<sub>2</sub> in solution is not expected to affect the release of fission products and actinides significantly. The aim of this work is to study the kinetics (at  $p_{\text{H}_2} \sim 40$  bar) of the possible reaction between H<sub>2</sub> and UO<sub>2</sub><sup>2+</sup> in aqueous solution.

## 2. Experimental

All chemicals of the purest grade available were used as supplied. Millipore water was used for all solutions. Uranyl solutions were prepared using UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O (Merck, PA). The gases used in the experiments were H<sub>2</sub> (Hydrogen+, AGA), Ar (Argon instrument, AGA) and Ar containing 5% O<sub>2</sub> (AGA). The UO<sub>2</sub>-powder was supplied from Westinghouse Atom Co. The UO<sub>2</sub>-powder has a surface area of 5.85 m<sup>2</sup> g<sup>-1</sup> (Micromeritics Flow Sorb II 2300; He/N<sub>2</sub>:70/30, BET-method: single point surface area measurement), O/U is 2.12 according to the supplier. The powder was washed with concentrated carbonate solution, distilled water and ethanol prior to use. The reaction vessel used was specially manufactured for these experiments (Métro Mesures). The vessel consists of a thermostated stainless steel autoclave with an internal vessel made of polyether ether ketone (PEEK). PEEK is used for all details and surfaces in direct contact with the solution in order to minimize catalytic effects of the vessel itself. The volume of the PEEK vessel is 2 dm<sup>3</sup>. The vessel is also equipped with a stirrer and inlet and outlet tubes for pressurizing and sampling.

All experiments were carried out at a gas pressure of approximately 40 bar and the temperature was in the range 74–100 °C. The solutions were heated to the desired temperature and purged with Ar for a period of 24 h before the experiment started unless otherwise stated. The initial concentration of UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> was ~10 μM and the carbonate concentration was 2 mM (Swedish groundwater contains ~2 mM carbonate [8]). The uranyl concentration of the solutions was measured using a Scintrex UA-3 Uranium Analyser [9].

## 3. Results and discussion

In Fig. 1, the uranyl concentration is plotted as a function of reaction time at four different temperatures.

Under the experimental conditions defined above the predominating U(VI)-species is UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>4-</sup> [10]. In contrast to the conclusions of earlier studies [11], H<sub>2</sub> appears to reduce the UO<sub>2</sub><sup>2+</sup> concentration also in the absence of a catalyst. The reactivity of uranyl follows first order kinetics, which is most obvious at the highest temperature, Fig. 1.

When opening the reaction vessel after the experiment a black precipitate was observed. The visual appearance of the precipitate strongly resembled that of UO<sub>2</sub>-powder. To identify the black solid product we performed an experiment using a solution containing about 1 mM uranyl and 20 mM NaHCO<sub>3</sub>. The black solid product found when the experiment was terminated was isolated, dried and analyzed by X-ray powder diffraction (Rigaku). The diffraction pattern is presented in Fig. 2. Clearly, the diffraction pattern of the product matches the lines for UO<sub>2</sub>. However, the high background follows a radial distribution function, RDF, which is characteristic for non-crystalline material. Thus, a significant part of the UO<sub>2</sub> produced in the reduction of uranyl by H<sub>2</sub> appears to be amorphous.

The first order rate constant at each temperature is divided by the H<sub>2</sub> concentration<sup>2</sup> to obtain the second order rate constant, Table 1. The logarithm of the second order rate constant is plotted against the inverted temperature according to the Arrhenius equation (3):

$$k = A e^{-E_a/RT} \quad (3)$$

The activation energy for H<sub>2</sub> reduction of UO<sub>2</sub><sup>2+</sup> is calculated to be 130 ± 24 kJ mol<sup>-1</sup>, and the rate constant is  $k_{298\text{K}} = 3.6 \times 10^{-9}$  1 mol<sup>-1</sup> s<sup>-1</sup>, Fig. 3. By using the Eyring equation (4),

$$k = \frac{k_B T}{h} \times e^{\Delta S^\ddagger/R} \times e^{-\Delta H^\ddagger/RT} = \frac{k_B T}{h} \times e^{-\Delta G^\ddagger/RT}, \quad (4)$$

the activation enthalpy ( $\Delta H^\ddagger$ ) and the activation entropy ( $\Delta S^\ddagger$ ) can be determined. For the present reaction,  $\Delta H^\ddagger = 126$  kJ mol<sup>-1</sup> and  $\Delta S^\ddagger = 16.5$  J mol<sup>-1</sup> K<sup>-1</sup>.

The activation energy for H<sub>2</sub> reduction of UO<sub>2</sub><sup>2+</sup> catalyzed by nickel is 41 kJ mol<sup>-1</sup> [11]. The uranyl and carbonate concentrations used by Forward and Halpern were 100 and 1000 times higher than in this work. The UO<sub>2</sub> precipitation was studied under  $p_{\text{H}_2} = 27$  atm and a temperature interval 121–177 °C. The reaction time needed for complete reduction of UO<sub>2</sub><sup>2+</sup> was less than

<sup>2</sup> At  $p_{\text{H}_2} = 39$  bar, and  $T = 373.15$  K the mol fraction of dissolved H<sub>2</sub> in water is determined to be 0.000595 [12]. Since the temperature interval is relatively small (348–373 K), the mol fraction is set to be constant, which should not affect the calculations considerably [13]. The hydrogen pressure in the experiments is fluctuating between 39 and 42 bar. Assuming that the amount dissolved hydrogen is small compared to the mol fraction dissolved water:  $[\text{H}_2]_{\text{aq}} = 0.033$  M.

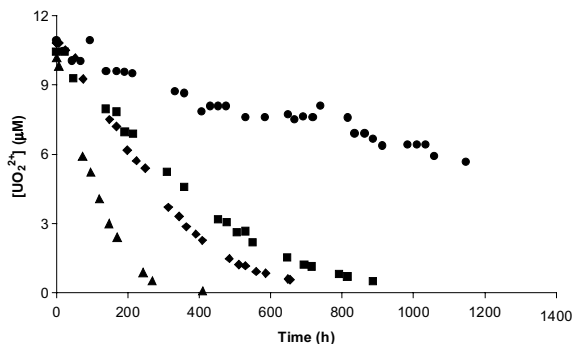


Fig. 1. The concentration of  $\text{UO}_2^{2+}$  as a function of time at  $p_{\text{H}_2} \sim 40$  bar. (●):  $T = 74$  °C, (■):  $T = 83$  °C, (◆):  $T = 89$  °C, (▲):  $T = 100$  °C.

1 h. The considerable difference between the two activation energies shows how effective the Ni-catalyst is. Forward and Halpern showed that without a catalyst, no reduction would occur. The time scale for their experiment was less than 4 h. Given our experimental

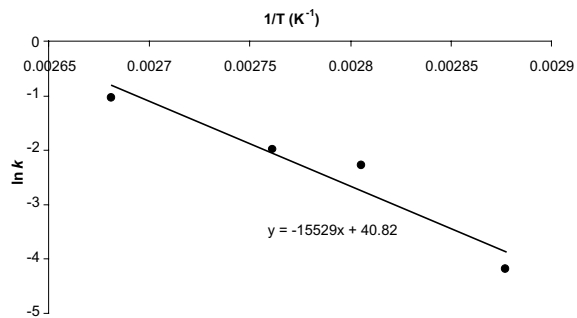


Fig. 3. Arrhenius plot for the reaction between  $\text{H}_2$  and  $\text{UO}_2^{2+}$ .

results presented above, this time window is far too small to observe a significant decrease in  $\text{UO}_2^{2+}$  concentration. Since the time horizon for storage of spent nuclear fuel exceeds the experimental time scales by several orders of magnitude, slow processes such as the uncatalyzed reduction of  $\text{UO}_2^{2+}$  must also be accounted for. It should be noted that Bunji and Zogovic [14] concluded that freshly precipitated  $\text{UO}_2$  worked very

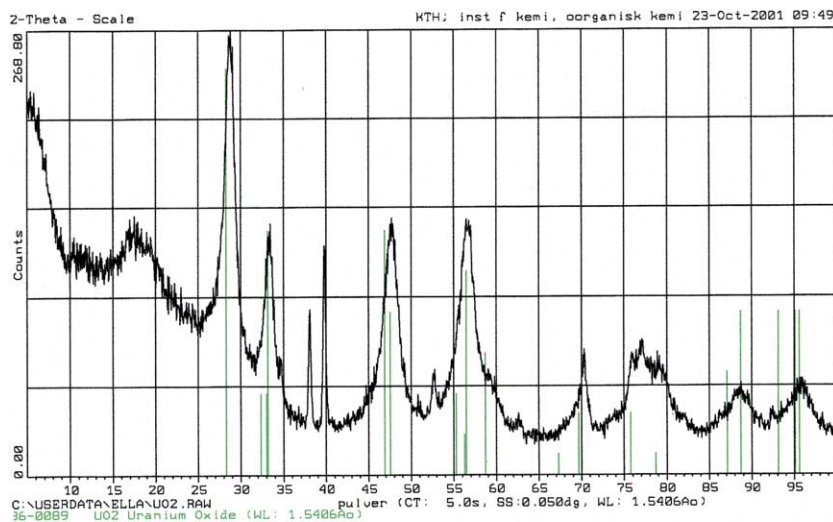


Fig. 2. X-ray powder diffraction pattern for the black product formed upon reduction of uranyl by  $\text{H}_2$  compared to the expected lines for  $\text{UO}_2$ .

Table 1

Measured first order rate constants and calculated second order rate constants,  $k$ , for the reaction between  $\text{H}_2$  and  $\text{UO}_2^{2+}$  at different temperatures

$k_{[\text{uranyl}]}$ ( $\text{h}^{-1}$ )	$k_{[\text{uranyl}]} / [\text{H}_2]$ ( $\text{l mol}^{-1} \text{h}^{-1}$ )	$\ln k$	$1/T$ ( $\text{K}^{-1}$ )
$5.01 \times 10^{-4}$	$1.52 \times 10^{-2}$	-4.19	$2.88 \times 10^{-3}$
$3.40 \times 10^{-3}$	$1.03 \times 10^{-2}$	-2.27	$2.81 \times 10^{-3}$
$4.55 \times 10^{-3}$	$1.38 \times 10^{-1}$	-1.98	$2.76 \times 10^{-3}$
$1.17 \times 10^{-2}$	$3.55 \times 10^{-1}$	-1.03	$2.68 \times 10^{-3}$

well as a catalyst for the reaction. However, dried precipitated  $\text{UO}_2$  did not show any catalytic effect. The catalytic reactions were found to be of first order with respect to catalyst surface and hydrogen pressure and zero order with respect to  $\text{UO}_2^{2+}$  concentration. Forward and Halpern believed that the reason why the precipitation rate was independent of the concentration of  $\text{UO}_2^{2+}$  was that the catalyst surface became saturated with adsorbed uranium under the experimental conditions used. However, the experimental results presented in Fig. 1 do not display any autocatalytic behavior. Hence, the  $\text{UO}_2$  produced in the uncatalyzed  $\text{H}_2$  reduction of  $\text{UO}_2^{2+}$  does not show any significant catalytic activity. To further study the suggested catalytic effect of  $\text{UO}_2$  we conducted experiments where  $\text{UO}_2^{2+}$  was added to the solution after consumption of the initially added  $\text{UO}_2^{2+}$ , i.e., two consecutive experiments where performed in the same solution. The freshly precipitated  $\text{UO}_2$  produced in the first part of the experiment was thereby never dried nor exposed to air. In another experiment commercial  $\text{UO}_2$  powder was added to the solution prior to the experiment. None of these experiments showed any increased reactivity due to the presence of  $\text{UO}_2$ . Long-term experiments where commercial  $\text{UO}_2$  was added to the reaction vessel pressurized with Ar instead of  $\text{H}_2$  displayed a slow decrease in  $\text{UO}_2^{2+}$  concentration. This can probably be attributed to sorption of  $\text{UO}_2^{2+}$  onto  $\text{UO}_2$ . Experiments performed in the absence of solid  $\text{UO}_2$  using Ar to pressurize the vessel showed no significant decrease in  $\text{UO}_2^{2+}$  concentration over a period of 1000 h.

To assess the possible (although improbable) catalytic capacity of the reaction vessel material, PEEK, we performed an experiment in the presence of PEEK powder. In this experiment the PEEK surface exposed to the solution was 20 times higher than the vessel itself. The rate of  $\text{UO}_2^{2+}$  reduction was not significantly affected by the increased PEEK surface. Hence, we can conclude that PEEK has no catalytic activity on this process.

In some of the initial experiments performed at the lowest temperature the dynamics of the process was far from obvious (Fig. 4).

During the first 100–150 h the  $\text{UO}_2^{2+}$  concentration did not change significantly. This period was followed by a short period during which the process accelerated until reaching a rate similar to that given in Fig. 1. This behavior was first erroneously interpreted as the process being autocatalyzed as suggested in the literature. However, it soon became apparent that the initial lag-phase could depend on traces of oxygen not being removed during the Ar-purging. To test this hypothesis we conducted an experiment where the solution was purged with Ar containing 5%  $\text{O}_2$  prior to pressurizing the vessel with  $\text{H}_2$ . The result of this experiment is shown in Fig. 5.

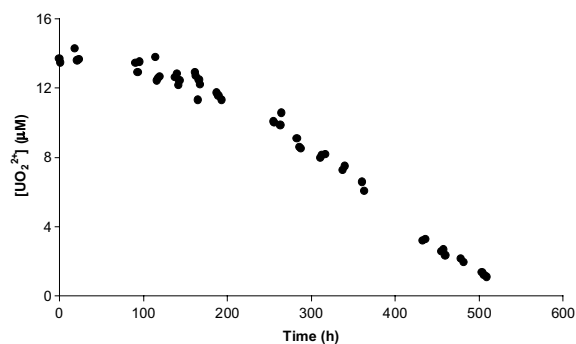


Fig. 4. The concentration of  $\text{UO}_2^{2+}$  as a function of time at  $p_{\text{H}_2} \sim 40$  bar and  $T = 74$  °C.

As can be seen, the  $\text{UO}_2^{2+}$  concentration does not decrease significantly over a period of 1000 h. Hence, the presence of  $\text{O}_2$  clearly inhibits the reduction of  $\text{UO}_2^{2+}$  by  $\text{H}_2$ . When initially adding  $\text{UO}_2$  powder to the experiments performed the lag-phase was considerably shortened. This was also initially mistaken as a proof for the catalytic activity of  $\text{UO}_2$ . To further elucidate the effect of  $\text{UO}_2$  we added a portion to a solution purged with Ar containing 5%  $\text{O}_2$  and thereafter pressurized the vessel with  $\text{H}_2$ . The result is shown in Fig. 6.

In this case the  $\text{UO}_2^{2+}$  concentration decreases after a considerable lag-phase. The lag-phase in this system is 50–100 times longer than the lag-phase observed in the experiments using  $\text{UO}_2$  containing solutions purged with pure Ar prior to pressurizing with  $\text{H}_2$ . This difference can be attributed to the  $\text{O}_2$  concentration being much higher in the experiment presented in Fig. 6. The obvious conclusion to be drawn from these experiments is that  $\text{UO}_2$  either consumes (reduces) the oxygen present in the solution or catalyzes the reaction between  $\text{H}_2$  and  $\text{O}_2$  and thus reduces the oxygen dependent lag-phase.

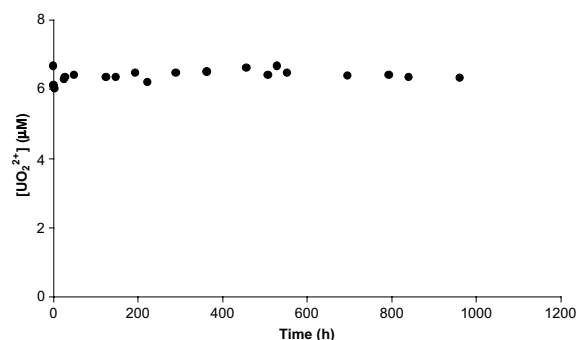


Fig. 5. The concentration of  $\text{UO}_2^{2+}$  as a function of time at  $p_{\text{H}_2} \sim 40$  bar and  $T = 74$  °C. The solution was purged with 5%  $\text{O}_2$  in Ar prior to pressurizing with  $\text{H}_2$ .

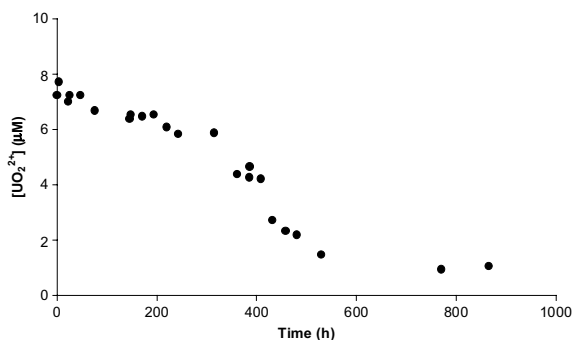


Fig. 6. The concentration of  $\text{UO}_2^{2+}$  as a function of time at  $p_{\text{H}_2} \sim 40$  bar and  $T = 74$  °C. 100 mg  $\text{UO}_2$  is present in the solution purged with 5%  $\text{O}_2$  in Ar prior to pressurizing with  $\text{H}_2$ .

### Acknowledgements

Swedish Nuclear Fuel and Waste Management Co. is gratefully acknowledged for financial support.

### References

- [1] SKBF/KBS, Swedish Nuclear Fuel Supply Co., Stockholm, 1983.
- [2] T.E. Eriksen, U.-B. Eklund, L. Werme, J. Bruno, *J. Nucl. Mater.* 227 (1995) 76.
- [3] J. Bruno, E. Cera, M. Grivé, U.-B. Eklund, T.E. Eriksen, SKB-Technical Report TR-99-26, 1999, p. 1.
- [4] N.R. Smart, D.J. Blackwood, L. Werme, SKB-Technical Report TR-01-22, 2001, p. 1.
- [5] J. Bruno, E. Cera, M. Grivé, L. Duro, T.E. Eriksen, SKB-Technical Report TR-03-03, 2003, p. 1.
- [6] A.B. Ross, B.H.J. Bielski, G.V. Buxton, D.E. Cabelli, C.L. Greenstock, W.P. Helman, R.E. Huie, J. Grodkowski, P. Neta, in: *NDRL/NIST Solution Kinetics Database*, 1992.
- [7] R.C. Merritt, *The Extractive Metallurgy of Uranium*, Colorado School of Mines Research Institute, Golden, 1971.
- [8] J.A.T. Smellie, M. Laaksoharju, P. Wikberg, *J. Hydrol.* 172 (1995) 147.
- [9] J.C. Robbins, *CIM Bull.* 71 (1978) 61.
- [10] I. Grenthe, F. Diego, F. Salvatore, G. Riccio, *J. Chem. Soc., Dalton Trans.* 11 (1984) 2439.
- [11] F.A. Forward, J. Halpern, *Can. Min. Metall. Bull.* 56 (1953) 645.
- [12] E.L. Stephen, N.S. Hatfield, R.S. Peoples, H.A.H. Pray, in: C.L. Young (Ed.), *Solubility Data Series*, Pergamon, Oxford, 1981.
- [13] H.A. Pray, C.E. Schweickert, B.H. Minnich, *Ind. Eng. Chem.* 44 (1952) 1146.
- [14] B. Bunji, B. Zogovic, in: *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy*, vol. 3, 1958, p. 350.