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Original Scientific Paper

Preparation of Uranium Dioxide by Electrochemical Reduction in Carbonate Solution and Subsequent Precipitation. II.*

Precipitation of Uranium(IV) from Sodium Carbonate Solutions

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The precipitation of uranium(IV) from sodium carbonate solutions has been studied. Uranium(IV) has been prepared by electrochemical reduction at controlled constant potential at the mercury cathode. From the stable solution uranium(IV) precipitates as hydrous oxide. The dependence of the degree of precipitation of uranium(IV) on the composition of the solution is given, considering the carbonate to uranium concentration ratio, the total sodium carbonate concentration, and the *p*H of the solution. The precipitation was induced and performed also by raising the temperature up to 60° C. Experimental limits of the solubility of uranium(IV) carbonate complexes, at 60° C and at *p*H = 9.5 and 10.3, indicate the possibility of the existence of the uranium(IV) in solution predominantly as the $[U(OH)_2(CO_3)_4]^{-6}$ complex.

INTRODUCTION

The importance of uranium dioxide as nuclear fuel material, as well as an intermediate in uranium recovery from ore leach solutions and fuel reprocessing, has brought the methods of its preparation into focus of the investigations in our laboratory. Uranyl carbonate solutions have been frequently the subject of investigations and the literature on uranyl carbonate solutions is relatively abundant.[1]

The over-all stability constant of uranyl bis-carbonate complex was determined as $\log \beta_2 = 15.6$[2] and 14.6[3] from solubility and the change in free energy, respectively. Data on the last consecutive stability constant of the uranyl tri-carbonate complex vary with the method applied in the determination. Paramonova and coworkers determined the value of $\log K_3 = 7.0$ using ion exchange techniques,[4] and 5.5 by potentiometric titration.[5] Blake and coworkers[6] obtained the value of 3.5 from spectrophotometric measurements. Available data on the behaviour of uranium(IV) in carbonate solutions are scarce probably because the most difficult problem was how to prepare the instable uranium(IV) and dissolve it in alkaline carbonate solutions.

The only available data on the hydrolysis of uranium(IV) are those of Kraus and coworkers[7] on the behaviour of uranium(IV) in chloride and per-

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* Part I. see ref. 10.

chlorate solutions. They claim the existence of the first hydrolytic species $U(OH)_3^+$ which above $pH = 2$ undergoes further hydrolysis to yield a polymer of the composition $U(OH)_4$ without intermediate hydrolytic specia. Polymerization of the uranium species in solution can be observed by the change in colour from the bright green of the simple ionic forms to the black of polymers $[U(OH)_4]_n$.

The soluble uranium(IV) carbonate complexes exist in narrow concentration ranges of carbonate and uranium, depending on *p*H and temperature. In comparison to uranium(VI) their solubility is appreciably lower. In the present work the problem of preparation of uranium(IV) carbonate solutions is solved by application of the electrochemical reduction of uranyl carbonate complexes at a mercury cathode by controlled potential electrolysis.[9,10] The preparation performed in this way does not change the carbonate concentration and pH of the solution, provided the cathodic compartment of the electrolysis cell is separated from the anodic one by a cation exchange membrane.

The reduced solution bears the whole amount of uranium in the four-valent state, and represents the starting material of the present investigations. The precipitation of uranium has been studied from two general aspects. First, to find-out the upper solubility limit of uranium, in order to enable maximum productivity of the electrolysis cell and precipitation equipment. This is the aspect of preparation of stoichiometrically defined uranium dioxide for ceramic nuclear applications. Second, to find-out the lower limit of solubility of uranium(IV) which should enable the recovery of uranium from ore leaching solutions. In the first case the concentration of carbonate (and its cost) is immaterial and has to be considered from the point of view of chemical equilibria only. In the second case, the concentration and consumption of sodium carbonate could impair the process considered. The optimum concentration of carbonate in leach solutions is a matter of geological considerations. On the other hand any cyclic process of ore leaching involves large volumes of liquid with strictly controlled concentrations of solute.

EXPERIMENTAL

Uranyl carbonate solutions were prepared by dissolution of ammonium diuranate in sodium carbonate-bicarbonate solutions of the desired *p*H and concentration. The dissolved uranyl in final solutions was determined from aliquots by polarographic analysis in orthophosphoric acid.[11]

Uranium(IV) carbonate solutions were prepared therefrom by controlled constant potential electrolysis in a two compartment cell as described before.[9,10] The electrochemical reduction was completed to at least 98% of the total uranyl present, when the background current was reached. From the deeply green coloured solution of uranium(IV) carbonate aliquots of 10 ml were taken into appropriate test tubes. To the same tubes preelectrolysed carbonate solutions or redistilled water, free of oxygen, was added. The surface of the solution in the test tubes was protected by a thin layer of chemically pure paraffin oil. Sets of the test tubes prepared in this way were placed into constant temperature baths. Comparative parallel experiments were performed at 20, 40, 60 and 80°C. Soon it was discovered that the precipitation experiments at 80°C showed irreproducible results, due to the rapid reoxidation of uranium(IV) at this temperature. The results at 40° indicated only slight differences in comparison with those at 20°C. Thus the larger part of the work was performed at 20° and 60°C.

The samples were held at constant temperatures for at least 2 and at most 4 hours. This interval was found to yield reproducible results of precipitation and the reoxidation of the uranium(IV) was found to be negligible. Aliquots were taken from the clear supernatant liquor for the polarographic analysis. By the aid of calibration diagrams the difference between the unprecipitated standard sample and the precipitated one allowed to calculate the degree of precipitation, estimated to an average error of about 2%.

Analyses on the bicarbonate and carbonate content of the precipitation systems were made by automatic acidimetric titration using a Radiometer Titrigraph. The same instrument was used for the *p*H determinations with a type B (low sodium error) Radiometer glass electrode.

All solutions were prepared from highest purity grade chemicals and bidistilled water.

RESULTS

The percentage of uranium precipitated at *p*H=9.5 in dependence on the total concentration of uranium originally present is shown in Fig. 1. The

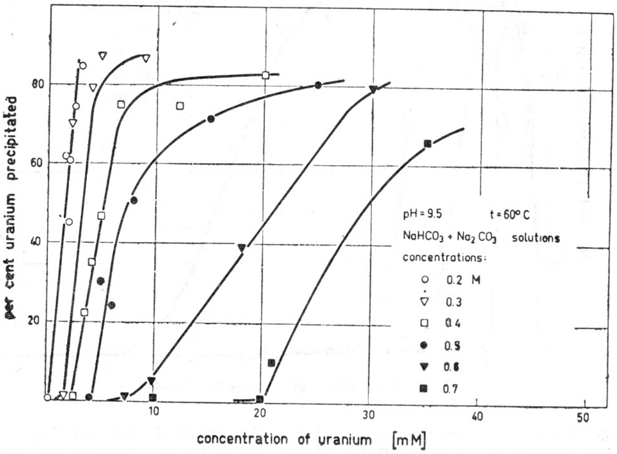

Fig. 1. The percentage of uranium precipitated in dependence on the initial uranium(VI) concentration. Sodium carbonate bicarbonate solutions of various total carbonate concentrations, *p*H = 9.5. Precipitation at 60°C.

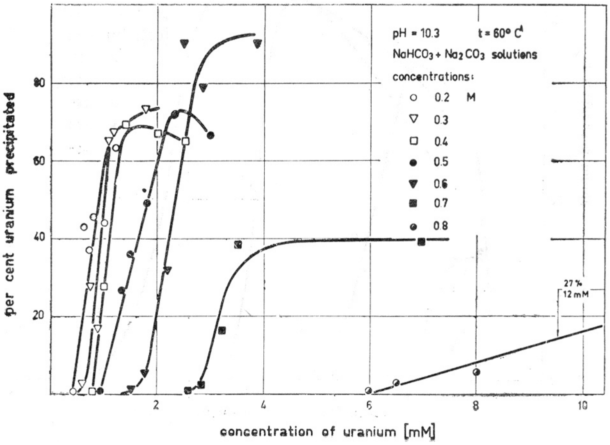

Fig. 2. The percentage of uranium precipitated in dependence on the initial uranium(VI) concentration. Sodium carbonate-bicarbonate solutions of various total carbonate concentrations, *p*H = 10.3. Precipitation at 60°C.

diagram includes experiments done at constant total concentrations of carbonate, ranging from 0.2 to 0.7 molar. It is evident that the yield of precipitation expressed as percentage of the uranium originally present is lowered as the concentration of carbonate increases. At low concentrations of carbonate, e.g. 0.2*M*, the appearance of a sharp precipitation limit is observed. Increased concentrations of carbonate not only enable higher concentrations of uranium(IV) to be dissolved but a sharp precipitation limit is missing also. Fig. 2. represents the corresponding results for the higher *p*H 10.3. There is a clear resemblance to the former diagram, except for the shift in the relevant uranium concentrations to much lower values.

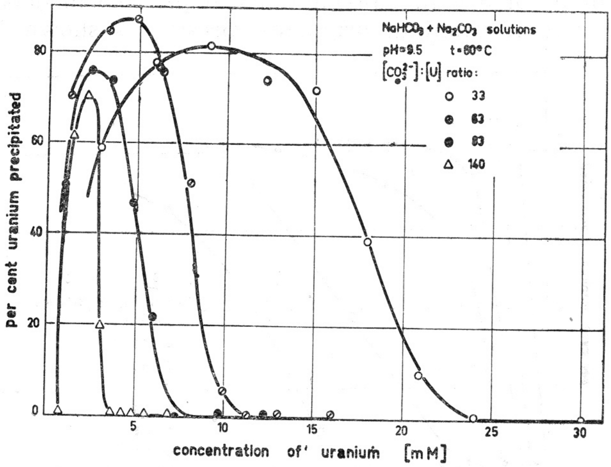

Fig. 4. The percentage of uranium precipitated in dependence on the initial uranium(VI) concentration and varied total carbonate to uranium molar ratios. Solutions with constant *p*H = 9.5 Precipitation at 60°C.

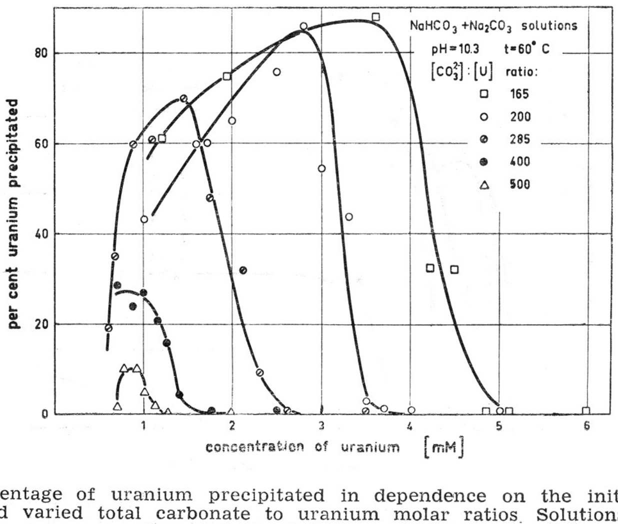

Fig. 4. The percentage of uranium precipitated in dependence on the initial uranium(VI) concentration, and varied total carbonate to uranium molar ratios. Solutions with constant *p*H = 10.3. Precipitation at 60°C.

The sharp limits of precipitation are again seen at the lowest concentrations investigated. It should be noted that solutions of uranium much below 1m*M* (0.24g/1) are considered unsuitable for all practical applications.

Figs. 3. and 4. show the extent of precipitation of uranium in dependence on the initial concentration in the solution at constant concentration ratios of carbonate to uranium. In Fig. 3. the results for *p*H 9.5 are shown. There the molar carbonate to uranium concentration ratios of 33, 63, 83, and 140 are indicated. The curves exhibit distinct maxima. If the points of maximum precipitation are taken into account it may be seen that the carbonate concentrations in this points lie between 0.3 and 0.35 molar total carbonate. The same observation is made for the experiments at *p*H = 10.3 which are shown in Fig. 4. There the points of maximum precipitation are not as clearly defined, but they correspond to values between 0.4 and 0.6 molar total carbonate At this higher *p*H the precipitation is extended to higher carbonate to uranium ratios.

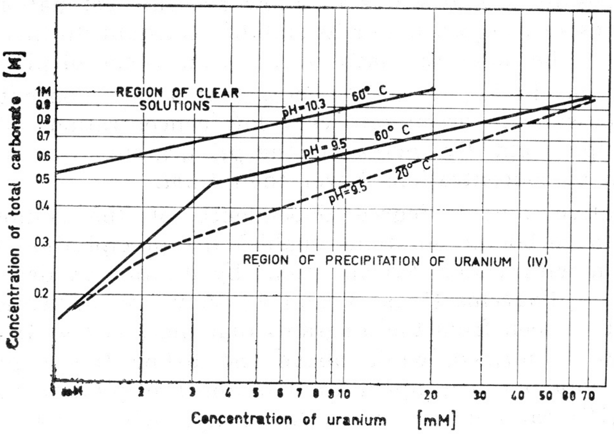

Fig. 5. Limits of precipitation of uranium from carbonate solutions in log. concentration of carbonate *vs.* log. concentration of uranium coordinates.

The results of the present work on precipitation are summarized in Fig. 5. Only the limits of precipitation are shown in log coordinates of carbonate concentrations *vs.* uranium concentration. The diagram indicates the difference in the solubility limits for solutions with initial *p*H = 9.5 at 20 and 60°C as well as for *p*H 10.3 at 60°C. For the precipitation by increasing temperature a relatively broad concentration region is at disposal. The shift of the solubility limit to higher carbonate concentrations is clearly shown for solutions with higher *p*H. The diagram shows two straight lines with a slope of 1/4 at 60°C. At low concentrations of uranium and total carbonate, at *p*H 9.5 and 60°C there is a part of the line with the slope 1/1, indicating a change of the predominant uranium(IV) complex species in the solution. The limit of precipitation at 20°C (24 hours after mixing) indicates the limit of concentrations suitable for electrolysis without precipitation occurring in the electrolysis cell.[10]

DISCUSSION

One of the aims of the present work was to investigate concentration, temperature and *p*H conditions under which the electrochemical reduction of uranium(VI) results in stable carbonate solutions of uranium(IV). All solutions above the dashed line in Fig. 5. fulfill these conditions. At the same time it is shown that precipitation of uranium(IV) can be achieved by increased *p*H or temperature.

In the literature there is scarce indication of possible uranium(IV) carbonate complexes. McLaine *et al.*[3] supposed that the most probable uranium(IV) carbonate complex form may be the $[U(CO_3)_5]^{6-}$.

The present results show a negative fourth degree dependence of uranium(IV) precipitation on carbonate concentration. Taking this into account as well as the difference in solubility limits[12] by changing *p*H of the solution, $[U(OH)_2(CO_3)_4]^{6-}$ can be assumed as the probable predominant species. The only value listed for the solubility product of uranium(IV) hydroxide is that of Latimer,[8] $\log K_{so} = -45$, apparently for the room temperature. The present results are to scarce to allow accurate estimation of either the form of the present complex ion or its stability constant. In this respect further work remains to be done especially over a wide range of *p*H values.

The diagrams in Fig. 1. and 2. show that at low concentrations of carbonate it is possible to precipitate very low concentrations of uranium with a relatively high yield. By increasing the *p*H uranium was successfully precipitated even at concentrations lower than 1m*M*.

The negative fourth degree dependence of the solubility limits of uranium(IV) in carbonate solutions enables the precipitation of uranium by simple dilution with water. Precipitations by dilution (hydrolysis) were performed and the diagrams (Figs. 3. and 4.) show the percentage of uranium precipitated. It is seen from the diagrams that there is always a region where the precipitate is formed, while above and below this region only stable solutions are obtained. The upper limit of the precipitation range represents the uranium(IV) carbonate complex solubility, while the lower limit is determined by the solubility product of the uranium(IV) hydroxide. Moreover it is shown that it is possible to precipitate uranium(IV) at all the concentrations encountered in practice, if appropriate concentration ratios of uranium to carbonate are maintained.

The time of precipitation should be limited when elevated temperature is applied because of the relatively rapid reoxidation of uranium(IV). It is a fortunate circumstance that the uranium(VI) formed by reoxidation is completely soluble at this conditions, thus only the yield of precipitations would be impaired. Accurate determination of the ratios of specia present in the solution might be performed only in controlled inert atmosphere.

The composition of the precipitates in the wet state is not defined. Washed and dried in inert atmosphere (purified nitrogen) at 200°C they show the X-ray characteristics of the predominantly cubic form of uranium dioxide. This observation is supported by the coulometric analysis[13] which shows the O/U ratios to be from 2.04 to 2.09.[14]

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IZVOD

Priprava uranova dioksida elektrokemijskom redukcijom u karbonatnim otopinama i naknadnim taloženjem. II. Taloženje urana(IV) iz otopina natrijeva karbonata

M. Branica, V. Pravdić i Z. Pučar

Ispitivano je taloženje urana(IV) iz otopina natrijeva karbonata u raznim koncentracionim odnosima. Iz stabilnih otopina u kojima je uran(IV) kompleksno otopljen taloži se, povišenjem temperature do 60^0, ili povišenjem *p*H, ili razrijeđenjem otopine, talog uran(IV) oksid hidrata. Prikazane su granice taloženja u koordinatama koncentracije urana prema koncentraciji karbonata. Eksperimentalni rezultati ukazuju da je predominantna specija kompleksno otopljenog urana(IV) vjerojatno $[U(OH)_2(CO_3)_4]^{6-}$.

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ZAGREB

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