

# RADIOLYTIC DEGRADATION OF ORGANIC COMPLEXANTS IN LIQUID RADIOACTIVE WASTES

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## Abstract

Considerable volumes of liquid waste containing organic complexing agents such as oxalic or citric acids are generated during operational decontamination or decommissioning of nuclear facilities. Their presence complicates any procedure for the separation or concentration of radionuclides and also negatively influences the safety of final waste storage and disposal. Degradation of such organic complexants, for example their radiolytic disintegration, could be one of the pathways how to break down the complexes of the radionuclides and make them available for subsequent separation. A series of experiments was performed, aimed at the study of radiolytic degradation of organic complexants by gamma radiation. A Co-60 source (0.8 kGy/h) was used throughout the study. The dependence of the degradation of citric acid, oxalic acid and their mixture on pH, concentration of the organic substances, presence of other ions, and the total absorbed dose was determined. In the case of citric acid, the radiolysis does not seem to be depended on pH value. On the other hand, the degradation of oxalic acid depends on the form present in the solution. In agreement with the presumptions, the percentage of degradation increases with absorbed dose and decreases with increasing concentration of organic substances. The presence of salts in high concentration was found to have inhibitive influence onto the degradation of organic substances.

## Introduction

Almost any liquid radioactive waste produced during Nuclear Power Plant (NPP) operation contains decontamination solutions. Substances like EDTA, citric or oxalic acid belong among the most usual components of such solutions (1). These strongly complexing agents bind radionuclides and increase their mobility (2). Moreover, solutions containing organic substances are not completely compatible with matrices used in waste solidification processes. Degradation of organic substances is one of pathways to improve the waste management. Waste solutions that underwent organics degradation should be more compatible with solidification matrices and much more: radionuclides released from complexes should exist in the solution in ionic forms that are propitious for their separation by sorption on ion-exchange resins or inorganic absorbers (1).

Degradation of organic substances into carbon dioxide and water is the most advantageous method of disintegration of treated substances. Existing decomposition processes may be classified as thermic (e.g. incineration) (3), oxidative (e.g. wet air oxidation (4), ozonization (5)), chemical (e.g. digestion with acids) (3), photochemical (3), biologic (3) or radiolytic (6). In our laboratory, extensive efforts were devoted to the studies of photocatalytic degradation methods, recently (8). However, these methods are known not to be effective in alkaline saline media, similar to the Handford-type wastes of NPP evaporator concentrates (8). The methods efficient even in such conditions include e.g. radiolysis (6), ozonolysis (5) or degradation by the action of peroxodisulphate (7).

The aim of this work was to study the possibility of degradation of organic complexants by means of gamma radiation. The dependence of the degree of radiolysis of citric (HCit) and oxalic (HOx) acids were studied on various parameters (pH value, absorbed dose, initial concentration of organic substances and concentration of inorganic substances) in solutions containing only organic acids or solutions simulating alkaline liquid radioactive wastes with high content of salts (NPP evaporator concentrates).

## Methods

Following solutions of organic substances were prepared for the study of radiolysis:

- ⇒ solutions of pure HCit or HOx of various concentrations (0,001 M, 0,005 M, 0,01 M, 0,05 M) and non-adjusted pH value
- ⇒ solutions of 0.005 M HCit and/or 0.01 M HOx at various pH values (non-adjusted, pH~1, ~4, ~7, ~10)
- ⇒ solutions of 0.01 M HCit and/or 0.01 M HOx with various content of nitrate and/or borate ((0,01 M, 0,1 M, 1 M, 2 M) and non-adjusted pH value

In addition to these solution, simplified or full (see Table 1) simulants of NPP evaporator concentrate were exposed to the action of  $\gamma$  radiation of Co-60 source (0.8 kGy/h). The 15 ml aliquots of these solutions were irradiated by doses of about 3, 7, 10, 20, 50, 100 or 300 kGy. Studies of the dependence of radiolysis of organic substances on various parameters were performed at constant absorbed dose 10 kGy.

Table 1: Composition of the full simulated solution of NPP evaporator concentrate.

substance	H <sub>3</sub> BO <sub>3</sub>	NaCl	K <sub>2</sub> CO <sub>3</sub>	NaNO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	NaNO <sub>2</sub>	HCit	HOx	NaOH
concentration [mol.l <sup>-1</sup> ]	0.832	0.056	0.180	0.852	0.038	0.069	0.006	0.017	ad pH~11.5

The irradiation was performed in Perun facility containing Co-60 source, operated by ARTIM company (Prague, Czech Republic). The degrees of radiolysis of organic substances were determined by isotachophoretic analysis, Ionosep analyzer (Recman, Czech Republic) was used.

## Results and Discussion

In agreement with our presumption, the degree of degradation of organic acids was found to increase with absorbed dose. Oxalic acid is decomposed faster than the citric one in solutions containing only the pure complexants. However, in solutions containing also inorganic ions citric acid is decomposed more easily than the oxalic one. Figure 1 and Figure 2 clearly demonstrate the negative influence of the presence of inorganic ions on the degree of degradation of oxalic and citric acids. Inorganic substances seem to hinder the decomposition of the complexants. This phenomenon can be explained by the following mechanism of the reaction: during radiolysis of water, the macro component of the irradiated system, hydroxyl radicals are produced. When organic substances are the only one component of the solutions, the radicals react with these organic molecules with high effectiveness. If other compounds are present in solutions (namely in concentrations exceeding those of the organic complexants), the probability of the reaction between organic molecule and hydroxyl radical is reduced.

Figure 1: The dependence of the relative amount of undecomposed HOx (*ND*) on absorbed dose (*D*) in the following solutions: 0,01 M HOx (■), 0,005 M HCit + 0,01 M HOx (□), simplified simulant (●) and simulant (×)

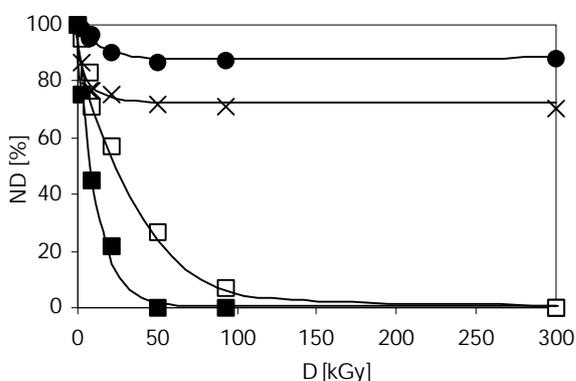
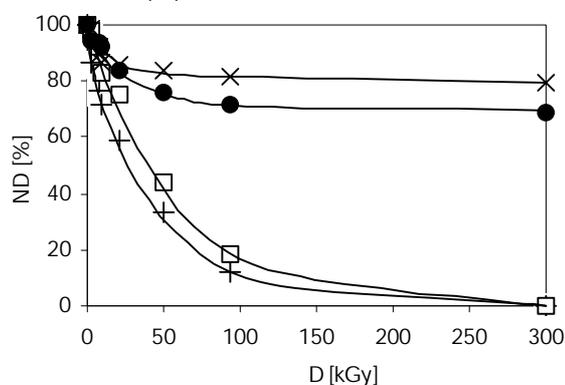


Figure 2: The dependence of the relative amount of undecomposed HCit (*ND*) on absorbed dose (*D*) in the following solutions: 0,005 M HCit (+), 0,005 M HCit + 0,01 M HOx (□), simplified simulant (●) and simulant (×)



Another conclusion that follows from the results presented in Figures 1 and 2 is that with the increasing absorbed dose, the increase of the degradation gradually slows down and finally almost stops. This phenomenon can be again explained by the mechanism of the reaction. With the proceeding degradation, the number of organic molecules decreases to level when the probability of reaction between the organic molecule and hydroxyl radical becomes very small and other ways of this radical stabilization prevail.

In the case of citric acid, the degradation of this organic compound does not seem to depend significantly on the pH value of the solution (Figure 3). When comparing the results presented in Figure 3 with the citric acid speciation (Figure 4), we can conclude that the partly dissociated forms of citric acid (ions  $\text{H}_2\text{Cit}^-$  and  $\text{HCit}^{2-}$ ) are the most vulnerable to degradation.

On the other hand the degradation of oxalic acid was found to be highly depended on the pH value of the solution (Figure 5). When comparing the dependence of degradation of the oxalic acid with its speciation (Figure 6), it can be seen that, similarly to the citric acid, it is the partly dissociated form of oxalic acid (ion  $\text{HOx}^-$ ) that is the easiest to degrade (in the acidic pH range, the degree of degradation of oxalic acid is more than five times higher than in alkaline conditions).

In the next part of this study, the degrees of degradation of organic substances were found to decrease with increasing their initial concentrations (Figure 7). Since for this case interpretation by the total decomposed quantity of the organic substances is more appropriate, its dependence on the initial concentration of organic substances is shown in the same figures, too. Again, the decreasing rate of the increase of decomposed quantity of the organic substances with their increasing initial concentration ("saturation" effect) is in accordance with the expected reaction mechanism - the maximum possible decomposed quantity of organic substances is given by the total number of hydroxyl radicals produced by radiolysis of water, that is independent of the initial concentration of organic substances.

Figure 3: The dependence of the degree of degradation of HCit ( $RD$ ) on  $pH$  in the following solutions: 0,005 M HCit (+) and 0,005 M HCit + 0,01 M HOx ( $\square$ )

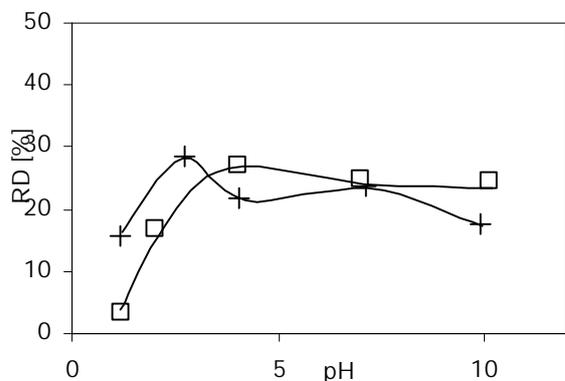


Figure 4: The dependence of abundance of HCit species ( $Z$ ) on  $pH$ :  $\text{Cit}^{3-}$  (+),  $\text{HCit}^{2-}$  ( $\blacksquare$ ),  $\text{H}_2\text{Cit}^-$  ( $\square$ ),  $\text{H}_3\text{Cit}$  ( $\bullet$ )

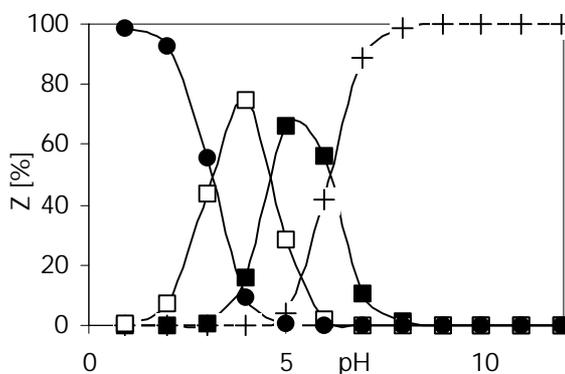


Figure 5: The dependence of the degree of degradation of HOx ( $RD$ ) on  $pH$  in following solutions: 0,01 M HOx ( $\blacksquare$ ) and 0,005 M HCit + 0,01 M ( $\square$ )

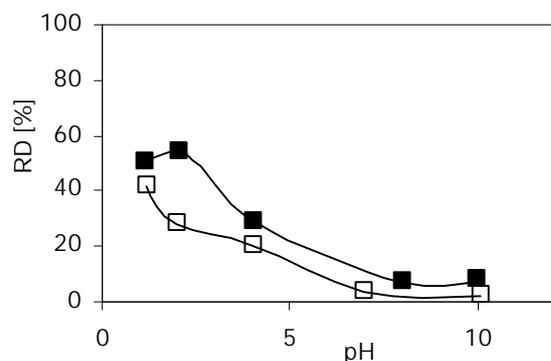


Figure 6: The dependence of abundance of HOx species ( $Z$ ) on  $pH$ :  $\text{Ox}^{2-}$  (+),  $\text{HOx}^-$  ( $\blacksquare$ ),  $\text{H}_2\text{Ox}$  ( $\square$ )

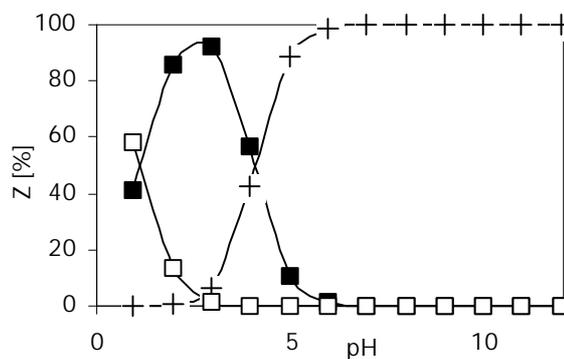


Figure 7: The dependence of the degree of degradation of HCit (◆) and HOx (■) (*RD*) and decomposed quantity of HCit (□) and HOx (●) (*n*) on initial concentration of organic substances (*c*) in 15 ml of solution

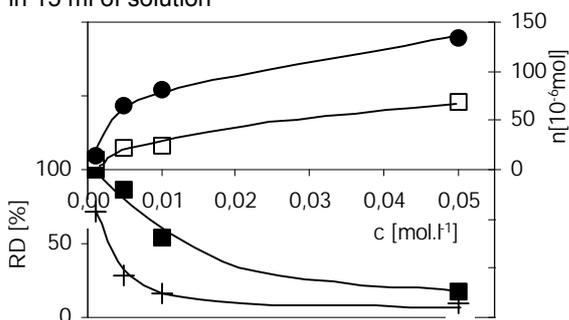


Figure 8: The dependence of the radiation chemical yields (*G*) of HCit (◆) and HOx (■) on initial concentration of organic substances (*c*)

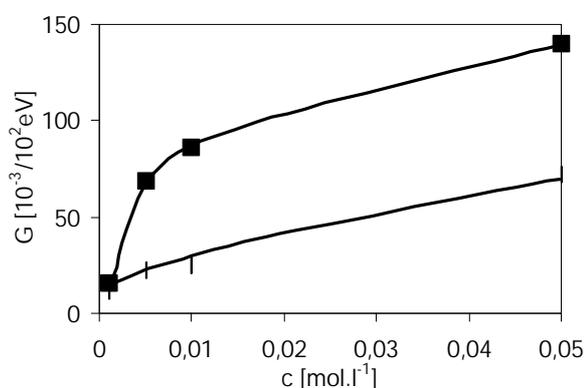


Figure 9: The dependence of the degree of degradation of HOx (*RD*) on concentration of inorganic substances (*c*) in the presence of nitrates (+), borates (■) and HCit+nitrates+borates (●)

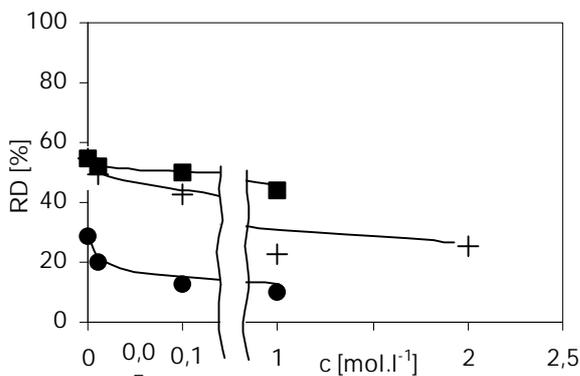
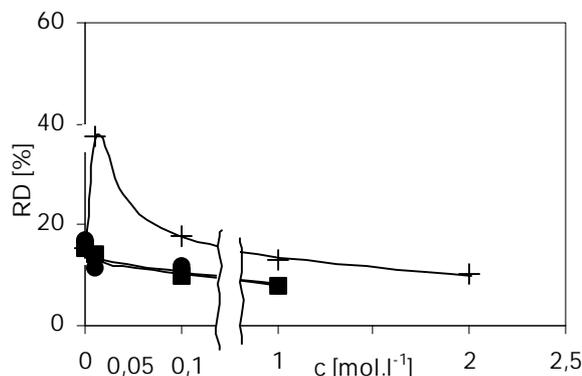


Figure 10: The dependence of the degree of degradation of HCit (*RD*) on concentration of inorganic substances (*c*) in the presence of nitrates (+), borates (■) and HOx+nitrates+borates (●)



The results presented in Figure 7 enabled also calculation of the radiation chemical yields (Figure 8). In agreement with the radiation chemical yield definition, their dependence on the initial concentration of organic substances was found to be similar to the dependence of the decomposed quantity of organic substances on the same parameter.

Borate and nitrate ions (major components of VVER type NPP evaporator concentrates) were chosen for the study of influence of inorganic ions on the degradation of organic substances. The degree of degradation of organic substances was found to decrease monotonously with increasing concentration of borate ions (Figure 9). The influence of nitrate ions is more complex (Figure 10): the degree of degradation of oxalic acid decreases monotonously with their increasing concentration (similarly to the case of borate ions), but in the case of citric acid a significant positive influence of the presence of low concentrations of nitrate ions on the degradation of organic substances can be seen.

## Conclusions

The most important results obtained in this study, can be summarized as follows:

- ⇒ The degree of radiolysis of organic substances increases with increasing absorbed dose, according to logarithmic dependence.
- ⇒ The absolute quantity of decomposed organic substances increases with their initial concentration according to logarithmic dependence (for constant absorbed dose).
- ⇒ Oxalic acid is decomposed more easily in acidic conditions than in the alkaline ones (for constant absorbed dose). Partly dissociated form of oxalic acid is the most vulnerable to degradation.

⇒ The dependence of degradation of citric acid on the pH value of the solution is not as clear as in the case of oxalic acid. However, the partly dissociated forms seem to be the most degradable, too.

⇒ The degree of degradation of oxalic acids decreases monotonously with increasing concentration of inorganic ions. The dependence of the degradation of citric acid on the concentration of nitrate ions passes a maximum at nitrate concentration 0,01M and then monotonously decreases, too.

⇒ Relatively high radiation yields were obtained for both the citric ( $G = 71 \cdot 10^{-3}/10^2 \text{eV}$ ) and oxalic ( $G = 139 \cdot 10^{-3}/10^2 \text{eV}$ ) acids at their concentration  $0.05 \text{ mol} \cdot \text{l}^{-1}$  in solutions with natural non-adjusted pH (2,23 or 1,52 respectively).

From these results, it can be concluded that the radiolytic degradation of citric oxalic acids may be practicable in acidic solutions with no or low content of inorganic salts. Application of this method for treatment of alkaline solutions with high content of salts, as e.g. NPP evaporator concentrates or Hanford-type defense liquid radioactive waste, does not seem to be prospective.

### Acknowledgements

This work was supported by Czech Ministry of Education, Youth and Sports project J04/98:210000020 and was a part the IAEA CRP "New Developments and Improvements in Processing of 'Problematic' Radioactive Waste Streams".

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