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Nové směry ve zpracování kapalných radioaktivních odpadů obsahujících organická komplexotvorná činidla

New Options for Treatment of Organic Complexants Containing Liquid Radioactive Waste

Summary

A new modular process was developed and tested for treatment of liquid radioactive waste containing organic complexing agents, such as oxalic or citric acids, for final disposal. It combines photocatalytic degradation of organic complexants by means of UV radiation in the presence of titanium dioxide catalyst with subsequent sorption separation of radionuclides onto either selective inorganic-organic absorbers or standard strongly acidic cation resins. As a part of background data collection, important new data on the mechanisms of photocatalytic and radiolytic degradation of citric and oxalic acids were obtained in broad fundamental studies.

The new modular process was successfully demonstrated on laboratory scale for a real spent acidic AP-CITROX decontamination solution from NPP Dukovany, Czech Republic. For spent electrochemical decontamination waste, the applicability of the process was demonstrated even on a bench scale in NPP Jaslovské Bohunice, Slovakia, with a real decontamination waste.

The process developed was found not to be effective for alkaline saline wastes such as NPP evaporator concentrates or Hanford-type waste. In the NPP evaporator concentrates, bulk of the organic complexants was successfully degraded by radiolysis. However, the efficiency of separation of radiocobalt, the most problematic radionuclide in this type of waste, has not significantly improved after radiolytic treatment.

Performance of a simple precipitation-desalination process for regeneration of the spent electrochemical decontamination waste has been tested. Both the macrocomponents and radionuclides could have been separated from the spent solution. After adjustment of oxalic and citric acids concentrations, performance of the regenerated electrolyte was practically the same as of the fresh one.

Souhrn

Byl vyvinut nový modulární proces pro zpracování kapalných radioaktivních odpadů obsahujících organické komplexotvorné látky, jako např. kyselinu šťavelovou nebo citrónovou. Proces kombinuje fotokatalytickou degradaci organických látek UV zářením za přítomnosti oxidu titaničitého jako katalyzátoru s následnou separací radionuklidů pomocí selektivních anorganicko-organických sorbentů nebo standardních silně kyselých měničů iontů. Během souvisejícího širšího základního výzkumu byly získány nové poznatky o mechanismu fotokatalytického a radiolytického rozkladu kyseliny šťavelové a citrónové.

Účinnost nového procesu byla úspěšně ověřena v laboratorním měřítku při experimentech s reálnými odpadními kyselými dekontaminačními roztoky z procesu AP-CITROX vzniklými v jaderné elektrárně Dukovany. Jeho použitelnost pro zpracování kapalných odpadů z elektrochemické dekontaminace byla demonstrována při čtvrtprovozním experimentu s reálným odpadem v jaderné elektrárně Jaslovské Bohunice (Slovensko).

Vyvinutý proces není použitelný pro alkalické solné odpady, jako jsou např. koncentráty z odparek jaderných elektráren nebo odpady z vojenského využití jaderné energie skladované v Hanfordu v USA. Pro rozklad organických komplexotvorných látek v koncentrátech z odparek jaderných elektráren byla úspěšně ověřena možnost vyžití radiolýzy zářením gama nebo urychlenými elektrony. Ani rozklad komplexotvorných látek však nevedl k výraznému zvýšení účinnosti separace radiokobaltu – nejproblematičtějšího radionuklidu v tomto typu odpadů.

V poslední části práce byla ověřena účinnost jednoduchého procesu pro regeneraci použitého elektrolytu z elektrochemické dekontaminace. Metoda je založena na srážení makropomponent a radionuklidů následovaném odsolením roztoku na silně kyselém měniči kationtů v H^+–cyklu a úpravou koncentrace kyseliny šťavelové a citrónové na výchozí hodnoty. Provedené experimenty prokázaly perspektivnost této metody – dekontaminační účinnost regenerovaných roztoků byla prakticky shodná s účinností čerstvých roztoků.

Klíčová slova

Radioaktivní odpady, organická komplexotvorná činidla, ukládání odpadů, regenerace, dekontaminační roztoky, koncentráty z odparky, kyselina šťavelová, kyselina citrónová, fotokatalytická degradace, fotokatalyzátory, oxid titaničitý, radiolýza, peroxodvojsíran, anorganické měniče iontů, kompozitní měniče iontů.

Keywords

Radioactive waste, organic complexing agents, final disposal, regeneration, decontamination solutions, evaporator concentrate, oxalic acid, citric acid, photocatalytic degradation, titanium dioxide photocatalyst, radiolysis, peroxodisulphate, inorganic ion exchangers, composite exchangers.

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1 INTRODUCTION

Technologies for processing of the majority of large amounts of standard operational radioactive waste from such facilities as nuclear power plants (NPPs) and other nuclear fuel cycle facilities are well established and are regarded as technologically mature. Nevertheless, there exist strong driving forces for development and application of new technologies. The motivation behind this streaming is as follows [1]:

- safety aspects and better public acceptance (more stable final waste forms, reduction of waste volume, minimisation of any risks for the population or environment),
- economic factors,
- non-proliferation aspects.

Significant co-ordination efforts in this field are carried on by the International Atomic Energy Agency (IAEA) in Vienna. The two main instruments for this support are

a) maintaining the IAEA Net-Enabled Waste Management Database (NEWMDB) that serves to:
    - support national data collection and their transfer to the IAEA database systems,
    - supply information on the status and trends of radioactive waste management (RWM) worldwide,
    - asses the level of national RWM programmes and assist the planning and decision-making processes;
b) direct support of R&D activities in the field of RWM (co-ordinated research programmes – CRPs).

Standard operational processes for the management of low and intermediate level liquid radioactive waste issuing operation of nuclear installations are usually based on pre-concentration (e.g. evaporation) and solidification of the concentrates. The main disadvantages of such processes are high energy consumption, large amount of non-active matrix materials disposed off with the radioactive waste and the consequently increased requirements on the disposal site space, and last but not least low degree of media, materials and chemicals recycling.

The main recent trends in the management of low and intermediate level liquid radioactive waste target [1-3] are the application of:

- advanced filtration systems (ultrafiltration, osmosis, etc.),
- selective sorbents,
- combinations of these approaches in various modular systems.

When combined with advanced technologies for treatment of filtration materials and sorbents, extremely high volume reduction factors (more than 10 000) may be obtained. As an example of this approach, the “zero liquid radioactive waste release” concept pursued at the NPPs in the USA can be listed. As demonstrated in Fig. 1, twenty-five fold decrease of the total volume of liquid radioactive waste produced at the US NPPs was achieved over a period of 17 years. Among the disadvantages of such advanced technologies their complexness, price, and the fact that the final solidificates usually represent not a low but intermediate level waste may be listed.

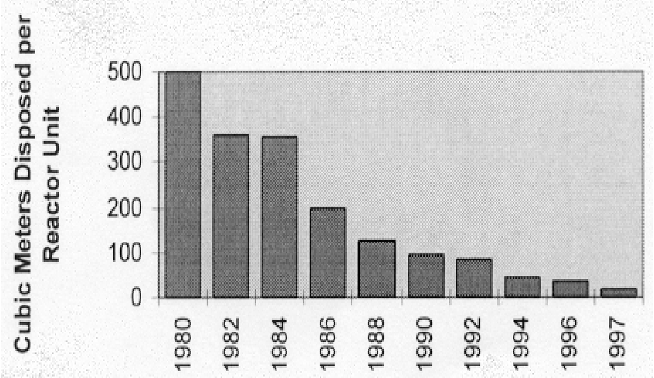

Fig. 1 Development of the volume of liquid radioactive waste disposed in US PWR NPPs [1]

The third of the approaches listed above – combinations of various techniques in modular systems – has been a subject of a recent IAEA CRP. Within this programme the following classification of combined methods for liquid radioactive waste treatment has been suggested [3]:

- Application of *materials with combined properties* (e.g. materials that exhibit both photocatalytic and ion exchange properties);
- Application of a *single stage process incorporating different waste treatment principles or techniques* (e.g. the electrosorption process that combines migration of ions in electrical field with their sorption onto a suitable sorbent);
- Application of *waste treatment systems interrelated sequentially and incorporating above novel materials and single stage processes* (combined multi-stage processes).

One of the standard operational radioactive waste stream types that can still be considered as "problematic" is the waste containing different organic components [4]. Reaching sufficiently high decontamination factors in single-stage processes for treatment of such waste may often not be possible because of the presence of significant concentrations of non-ionic or complexed species.

As the most typical examples of such wastes, namely NPP spent decontamination solutions and evaporator concentrates can be listed. In addition to the oxalic (HOx) and citric (HCit) acids, that are usually contained in standard spent decontamination solutions, more efficient and less corrosive complexants, e.g. nitrilotriacetic acid (NTA), diethylentriaminpentaacetic acid (DTPA), or 2-hydroxyethylendiamintetraacetic acid (HEDTA) have been recently introduced in the advanced decontamination processes [5].

The presence of these substances negatively influences not only the volume but also the quality of the final waste solidificates since it may result in elevated leachability and higher mobility of the cationic (radionuclidic) contaminants. For treating such complex waste formulations, combined processes in more stages have been suggested to offer the most promising solutions [3]. At the CTU in Prague, significant research efforts have been devoted recently to development of new options for treatment of both the spent decontamination solutions and evaporator concentrates [4,6-11].

This paper summarises results obtained by a combination of organic complexants degradation followed by radionuclides separation. Inorganic-organic composite absorbers with a binding matrix of modified polyacrylonitrile [12,13] were used for radionuclidic contaminants separations. For the organic complexants degradation, several methods reported in the literature were tested. They included:

- heterogeneously catalysed photochemical degradation by ultraviolet radiation with the use titanium dioxide photocatalyst [14-16],
- gamma-ray radiolysis [17-19],
- degradation by the action of peroxodisulphate [20].

In addition, preliminary results of the study of decontamination solutions regeneration [21] are briefly reviewed.

2 EXPERIMENTAL

The studies of *photocatalytic degradation of organic complexants* were carried out in a small immersion well photochemical reactor of 80 ml capacity. A 6W low–pressure mercury lamp was used for irradiating the samples by the short-UV range (254 nm) radiation. The suspension was bubbled with air by a membrane pump; the temperature was maintained by a thermostat. Membrane filtration (pore diameter 0.40 μm) was used for the separation of the photocatalysts from the reaction mixture. Titanium dioxide (TiO_2–M, prepared at the Department of Nuclear Chemistry – DNC – of the CTU in Prague from an intermediate in the production of titanium white) was used as a photocatalyst.

For the study of *radiolytic degradation*, PERUN facility operated by Artim, s.r.o., Prague was used to irradiate the samples by γ–radiation of ^{60}Co (dose rate 0.8 kGy/hr). In the study of the influence of type of the radiation, irradiation by 4.5 MeV electrons at an electron accelerator in NRI Řež was used. In both these studies, isotachophoretic analysis was used to determine the degree of organic substances degradation.

For the radionuclides separation studies from AP-CITROX and electrochemical decontamination solutions, absorbers listed in Table 1 were used for the batch experiments. The majority of these materials was synthesized at the DNC CTU [22]. In the experiments with evaporator concentrate, four commercial active charcoal samples (Chezakarb F and S-G, Chemopetrol, Czech Republic; 208 CP charcoal, Sutcliffe Speakman Carbons, UK; American Norit Co, USA, charcoal) and manganese dioxide inorganic absorber were also used. The batch experiments were carried out at the volume of liquid to the mass of absorber ratio V/m = 500 ml/g (AP-CITROX and electrochemical decontamination solutions) or 100 ml/g (evaporator concentrate).

Table 1 Inorganic absorbers used in batch radionuclides separation tests from AP-CITROX and electrochemical decontamination solutions

CODE	COMPOSITION
ZrP	zirconium phosphate
NaTiO	sodium titanate
Na-Y	synthetic zeolite
Mordenite	Mordenite
FeS	iron sulphide
CSbA	polyantimonic acid
NiFC	nickel ferrocyanide
ZrO	zirconium oxide
TiO	titanium oxide

In the dynamic sorption experiments, performance of inorganic-organic composite absorbers, prepared [12] from the inorganic ion-exchangers that performed the best in batch experiments, was tested and compared with standard OSTION KS806 cation exchanger (Spolchemie, Czech Republic). The experiments were performed in SUPELCO Rezorian Cartridges equipped with polyethylene frits both at the bottom and the top of the bed of the absorber (ID ~ 0.86 cm, bed volume BV = 1.2 ml); downward direction of the feed flow was used. The percentage break-through of the radionuclides in single fractions of the effluents was then calculated and plotted vs. the volume of treated solution expressed in the units of bed volumes of the absorbers (BV).

Three types of liquid radioactive wastes were investigated. They included the following simulants or real solutions:

- acidic spent decontamination solution from the second stage of the AP-CITROX process,
- liquid waste from electrochemical decontamination,
- NPP evaporator concentrate.

The characteristics and composition of each of these solution is given below at the start of the respective chapters.

3 RESULTS AND DISCUSSION

3.1 Spent AP–CITROX decontamination solution

This study was performed with both model solutions and a real spent acidic decontamination solution from the AP–CITROX process. The real solution was generated during the steam generator decontamination in NPP Dukovany, Czech Republic. Its composition was as given in Table 2, its radionuclidic composition is shown in Table 3.

Table 2 Real spent acidic decontamination solution from the AP–CITROX process – chemical composition

Compound	Concentration	Compound	Concentration
Oxalic acid Citric acid	8.2 g/l 10 g/l	Iron(III) ions	0.011 g/l

Table 3 Real spent acidic decontamination solution from the AP–CITROX process – radionuclidic composition

Nuclide	Activity [Bq/l]	Nuclide	Activity [Bq/l]
^{110m}Ag	$5.362.10^3$	^{59}Fe	$4.589.10^3$
^{7}Be	$8.587.10^3$	^{54}Mn	$9.402.10^3$
^{57}Co	$1.356.10^3$	^{95}Nb	$6.847.10^3$
^{58}Co	$6.091.10^3$	^{124}Sb	$1.087.10^3$
^{60}Co	$1.684.10^3$	^{65}Sn	$3.584.10^3$
^{51}Cr	$3.915.10^3$	^{95}Zr	$3.587.10^3$

As for most the cases reported in this paper, the studies performed with this solution consisted of a study of photocatalytic degradation of the organic complexants in the solution, study of direct separation of radionuclides from the original solution and a study of radionuclides separation from the solution after degradation of organic complexants.

3.1.1 *Photocatalytic degradation of organic complexants*

A thorough general study of the photocatalytic degradation of organic complexants typical for the decontamination solutions – oxalic (HOx) and citric (HCit) acids – was performed [23]. The results obtained showed that the process was strongly influenced by the experimental parameters such as amount of photocatalyst, temperature, aeration rate (v_{air}), or additions of H_2O_2. As an example of the results obtained, the dependence of the HOx and HCit degradation on the value of initial pH of the solution is shown in Fig. 2.

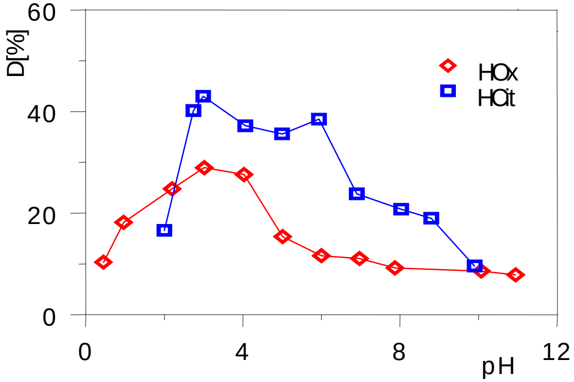

Fig. 2 Dependence of HOx and HCit degradation on the value of initial pH of the solution
(0.01 M HOx, t_{irrad} = 1 hr, 0.005 M HCit, t_{irrad} = 2 hr, 1.25 g/l TiO_2-M, t = 25°C, v_{air} = 25 l/hr)

The main conclusions of this general study may be listed as follows:
- the rate-determining step of the photocatalytic degradation are transport phenomena,
- the kinetics of the photodegradation follows the first order kinetics,
- complexant anion sorption on TiO_2 plays an important role in the photodegradation,
- the photocatalytic activity cannot be easily correlated with physico-chemical parameters of the catalyst.

The further study was directed towards optimisation of the conditions for the degradation of both the complexants. Proceeding of the degradation in optimised conditions is shown in Fig. 3. It can be seen that in these conditions all the oxalic and citric acids were quantitatively degraded within 12 hours.

3.1.2 *Separation of radionuclides from spent AP–CITROX solution*

A screening study of *direct separation of radionuclides* from the real spent solution was performed with nine selected inorganic absorbers (see chapter 2) at three values of pH – the original pH of the solution (pH ~ 1.4), and at pH = 3.6 or pH = 7.0. The main conclusion of this study was [8] that direct separation of radionuclides is not feasible even after the pH adjustment. The values of distribution coefficients were generally insufficient, in solutions with increased

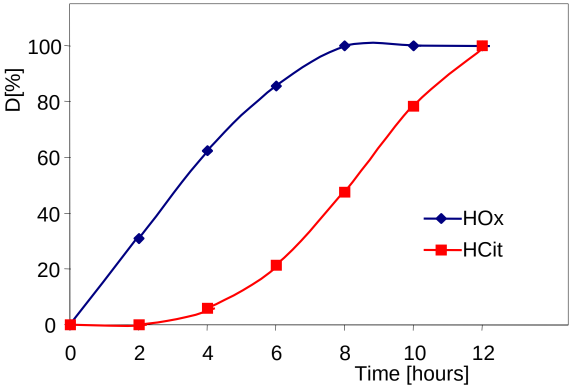

Fig. 3 HOx and HCit photocatalytic degradation under optimum conditions (3.15 g/l TiO_2–M, $T = 45^0C$, $v_{air} = 50$ l/hr, 1 ml of H_2O_2 each 2 hours)

pH, the K_D values were even lower than in the original solution with pH ~ 1.4. The reason for this finding is the increased radionuclides complexation at higher pH. In addition, some of the potentially prospective absorbers exhibited limited chemical stability in the solutions tested, namely in the original acidic solution with non-adjusted pH.

In a study of *separation of radionuclides from the solution, where HOx and HCit were completely decomposed* by means of photocatalysis, both batch and dynamic sorption experiments were performed [6]. The absorbers studied were the same as those tested for direct separation of radionuclides from the original solution. The batch experiments showed that the most prospective absorbers for radionuclide separation from the KDR solution were zirconium phosphate or sodium titanate, followed by crystalline polyantimonic acid, chemical stability of all the tested absorbers in the photodegraded solution was good. As an example of the data obtained, a comparison of distribution coefficients K_D obtained for the original solution and the solution after photodegradation of oxalic and citric acids is shown in Fig. 4.

Two composite absorbers NaTiO–PAN/SF and ZrP–PAN/SF, containing sodium titanate or zirconium phosphate, respectively, as active components, were prepared for the dynamic sorption study. The experiments demonstrated that all the radionuclides started to brake through the columns almost simultaneously. The NaTiO–PAN/SF absorber was found to be more effective, the maximum achievable concentration factor did not exceed 100. Another experiment, performed with a standard strongly acidic cation exchanger (Ostion KS806), revealed that the sorption cycle of such absorber is significantly longer. Practical concentration factors of several hundred to one thousand should be achievable with this material. Examples of the break-through curves obtained in these experiments are shown in Fig. 5.

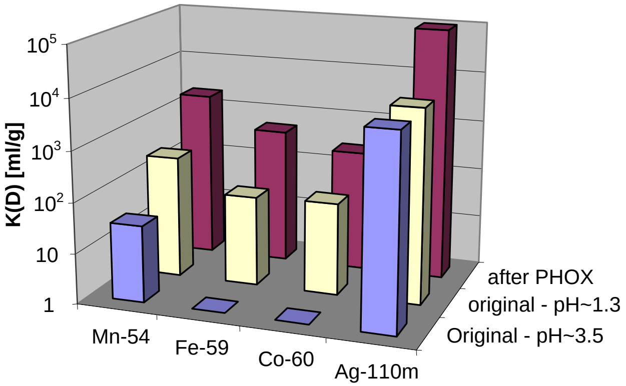

Fig. 4 K_D values in AP-CITROX solution after photocatalytic degradation of organic complexants and in the original non-pH-adjusted (pH~1.3) or pH-adjusted (pH~3.5) solution (V/m = 500 ml/g, 20 hours of contact)

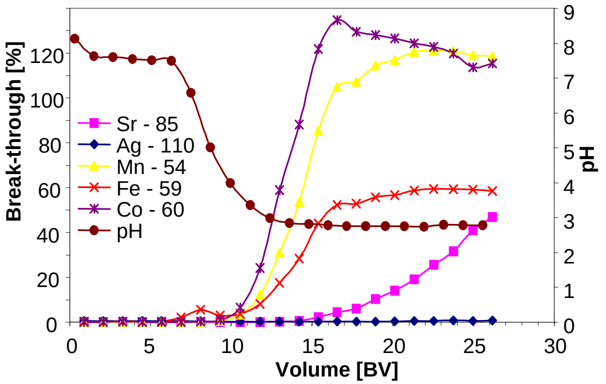

Fig. 5 Break–through curves of selected radionuclides through a column of NaTiO-PAN/SF composite absorber from the real AP-CITROX solution after photodegradation of organic complexants and the dependence of pH of the effluent on the volume of the treated solution (BV = 1.2 ml, absorber grain size 0.25 - 0.4 mm, flow rate 6.2 BV/hr)

On the basis of the experiments described above, an efficient procedure for radionuclides separation from the spent AP–CITROX decontamination solution was proposed. It is a two-step process comprising:

1. degradation of the organic complexants,
2. radionuclides separation onto a strongly acidic cation exchanger.

3.2 Spent electrochemical decontamination solutions

This study was performed with a model solution simulating the real spent electrochemical decontamination solution. The solution was prepared by electrolysing 10 g/l of HOx and 5 g/l of HCit solution in the electrolyser made of the NPP primary circuit equipment steel. The same conditions as in the operational electrochemical decontamination were used (current density 130 mA/cm^2 of the anode surface, total charge per volume unit of electrolyte 44 C/ml and the ratio between the volume of electrolyte and the decontaminated area ~ 31.5 ml/cm^2). During the electrolysis, some 60 % or 25 % of HOx or HCit were degraded, respectively. Similarly to the AP-CITROX solution, a study of photocatalytic degradation of the organic complexants and a study of radionuclides from both the original solution and from the solution after degradation of organic complexants were performed.

3.2.1 Photocatalytic degradation of organic complexants

The main difference between the AP-CITROX and electrochemical decontamination solutions consists in the presence of macroamounts of ions as iron, nickel, chromium, etc. Therefore, an initial general study of the influence of presence of such cations on the efficiency of photocatalytic degradation was performed.

The results obtained [24,25] showed that the degradation of both HOx and HCit proceed faster in the presence of most of the studied cations. This effect was most pronounced for the case of iron(III) ions, where it was confirmed to be a consequence of a different mechanism of the reaction. In the presence of relatively high concentration of iron, Fenton reactions take place under UV irradiation of a system containing semiconductor photocatalyst, which results in a significant increase of the rate of OH$^\bullet$ radicals production. Similar effect was observed in the presence of most of the other studied cations, too. As an example, comparison of the photocatalytic degradation of HCit in systems with and without cobalt ions is shown in Fig. 6.

The further study was directed towards optimisation of the conditions for the degradation of both the complexants in the electrochemical decontamination solution. The degradation in optimised conditions is shown in Fig. 7. It can be seen that in these conditions all the oxalic and citric acids were quantitatively degraded within 4 or 10 hours, respectively. When compared with the AP-CITROX solution (see Fig. 3), it can be seen that the conclusions of the general study were confirmed – due to the presence of iron(III) ions, the degradation of HOx and HCit in the electrochemical decontamination solution proceeds faster.

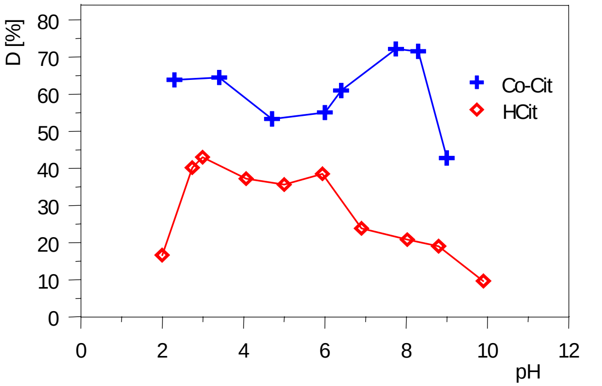

Fig. 6 Degradation of citric acid (HCit) and HCit–Co(II) complexes (D) in the presence of TiO_2–M photocatalyst as a function of pH at the end of the experiment
(0.005M HCit or 0.005M HCit + 0.005M $Co(NO_3)_2$, t_{irrad} = 1 hr, 1.25 g/l TiO_2–M, t = 25^{o}C, v_{air} =20 l/hr)

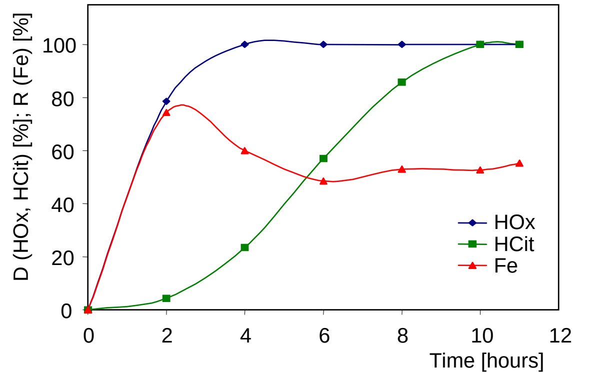

Fig. 7 HOx and HCit photocatalytic degradation (D) and iron removal (R) in the electrochemical decontamination solution under optimum conditions
(3.15 g/l TiO_2-M, T = 22^{0}C, v_{air} = 50 l/hr, 1 ml of H_2O_2 each 2 hours)

3.2.2 Separation of radionuclides from the electrochemical decontamination solution

A screening study of *direct separation of radionuclides* from this solution, performed in a similar way as described above for the AP-CITROX solution, yielded also similar results [8]. The main conclusion was that direct separation of radionuclides is not feasible from this solution, either. Contrary to the experiments with AP-CITROX solution, the chemical stability of most the absorbers tested was relatively good, however, the K_D values measured for the majority of radionuclides of interest were generally low (mean log $K_D < 2$). The only exception to this rule was observed for strontium and the CSbA absorber at pH = 1.8 where extraordinarily high value of the distribution coefficient ($K_D = 2.4.10^5$) was found even in the presence of organic complexants.

In a study of *separation of radionuclides from the solution, where HOx and HCit were completely decomposed* by means of photocatalysis, both batch and dynamic sorption experiments were performed [6]. The distribution coefficients of the radionuclides of interest measured for the best performing materials were about 3 to 8 times lower in the electrochemical decontamination solution than those found for the AP-CITROX solution; the general behaviour of the tested absorbers was similar in both solutions. Based on the distribution coefficients for ^{54}Mn, ^{59}Fe, and ^{60}Co, the Na–Y absorber (synthetic zeolite) was chosen for the dynamic experiments. As an example of the data obtained, a comparison of distribution coefficients K_D obtained for the original solution and the solution after photodegradation of oxalic and citric acids is shown in Fig. 8 for this absorber.

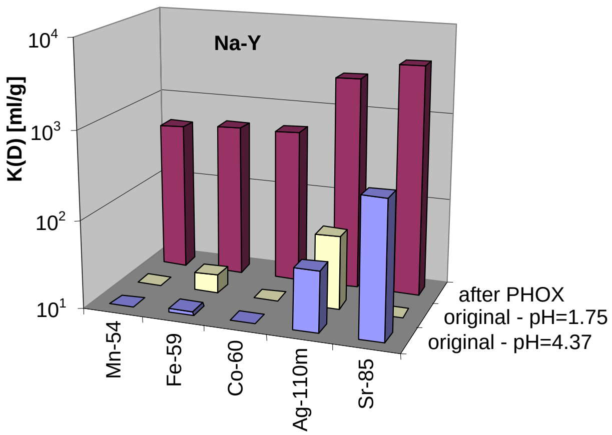

Fig. 8 K_D values in the electrochemical decontamination solution after photocatalytic degradation of organic complexants and in the original non–pH–adjusted (pH=1.75) or pH–adjusted (pH=4.37) solution (V/m = 500 ml/g, 20 hours of contact)

For the dynamic sorption study, NaY–PAN/SF composite absorber, containing synthetic zeolite as the active component, was prepared. Similarly to the results obtained for the AP-CITROX solution, the maximum achievable concentration factor was found to be about 100. In a parallel experiment, performed with a strongly acidic cation exchanger, practical concentration factor of more than 200 was achieved. Examples of the break-through curves obtained in these experiments are shown in Fig. 9 and Fig. 10.

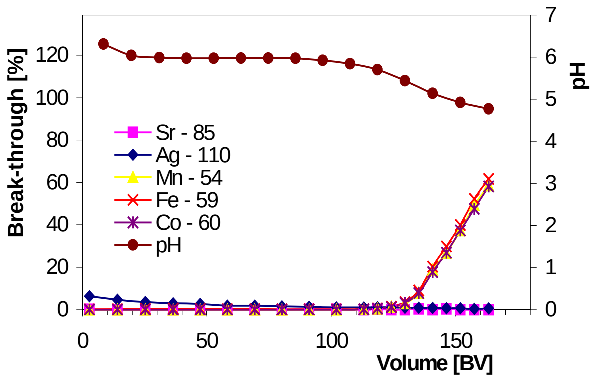

Fig. 9 Break–through curves of selected radionuclides through a column of NaY–PAN/SF composite absorber from the electrochemical decontamination solution after photodegradation of organic complexants and the dependence of pH of the effluent on the volume of the treated solution
(BV = 1.2 ml, absorber grain size 0.25 - 0.4 mm, flow rate 5.7 BV/hr)

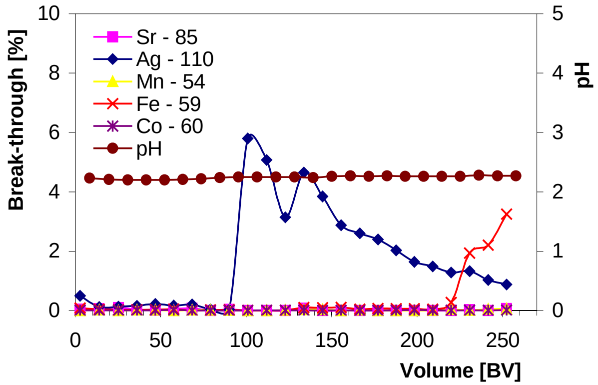

Fig. 10 Break–through curves of selected radionuclides through a column of OSTION KS806 cation exchanger from the electrochemical decontamination solution after photodegradation of organic complexants and the dependence of pH of the effluent on the volume of the treated solution
(BV = 1.2 ml, absorber grain size 0.08 - 0.16 mm, flow rate 5.3 BV/hr)

3.2.3 Demonstration of a process for treatment of electrochemical decontamination solution for final disposal

The results of the experiments described above confirmed that the two-step process comprising photocatalytic degradation of the organic complexants and radionuclides separation onto a strongly acidic cation exchanger is a prospective way even for the treatment of spent electrochemical decontamination solution. The performance of this process was demonstrated in NPP Jaslovské Bohunice, Slovakia [4,6]. Waste prepared by standard electrochemical decontamination of VVER 440 NPP reactor internals was used for this demonstration.

The analyses carried out in the course of the photodegradation revealed that the degradation of organic complexants in the real waste proceeds as well as it did in the simulants used in the laboratory experiments, i.e. the degradation was quantitative already after ~ 12 hrs. As an example of the behaviour of the solution during irradiation, results obtained for one of the batches of the treated solution are listed in Table 4.

Table 4 Behaviour of radionuclides, macroelements, complexants and pH during photocatalysis (total irradiation time 21 hrs)

Nuclide	**Peak [keV]**	**10^3 cps**		**D [%]**
		Electrolysate	**Photocatalysate**	
Sb-124	603	175.9	0.0	100.0
Cs-137	661	18.6	0.0	100.0
Co-58	811	92.1	53.7	41.7
Co-60	1332	945.7	723.0	23.5
Mn-54	834	1064.3	903.3	15.1
Element		**c [mg/l]**		**D [%]**
		Electrolysate	**Photocatalysate**	
Fe		7.289	0.293	96.0
Ni		0.941	0.735	21.9
Cr		2.610	0.763	70.8
Complexant		**c [mg/l]**		**D [%]**
		Electrolysate	**Photocatalysate**	
Oxalic acid		4.16	0	100
Citric acid		3.65	0	100
		Electrolysate	**Photocatalysate**	
pH		1.70	5.11	

D – relative amount removed during photocatalysis

The first conclusion that follows from these data is that the vast majority of iron (~ 95 %) is removed during the photocatalysis. This removal should be ascribed to iron deposition onto the surface of the photocatalyst. An interesting feature is the rather different behaviour of nickel (~ 20 % removed). Significant amount of chromium is removed, too (~ 70 %).

Out of the radionuclides, quantitative removal during the photocatalysis was observed for ^{124}Sb and ^{137}Cs. Some deposition/sorption of radiocobalt and ^{54}Mn onto the photocatalyst takes place, too. From these findings an important conclusion on the nature of the spent photocatalyst follows. As a result of metal ion / radionuclide deposition, this photocatalyst would collect a significant part of the total radioactivity of the treated solution and would hence represent a secondary waste stream.

The results of the sorption part of the test are summarised in Fig. 11. In total, some 300 BV (~ 350 ml) of the electrolysate solution treated by photocatalysis were passed through the column of OSTION KS806 cation exchanger. From the data obtained, it can be seen that, except for nickel, no radionuclides or metal ions broke through in the course of the entire test. Visually, the progress of loading the column with metal ions could be followed as a dark zone expanding through the column. At the end of the experiment, some 5 % of the bed of the exchanger has not been loaded, yet. Hence, it can be supposed, that significant break-through of the metal ions and/or radionuclides would occur soon.

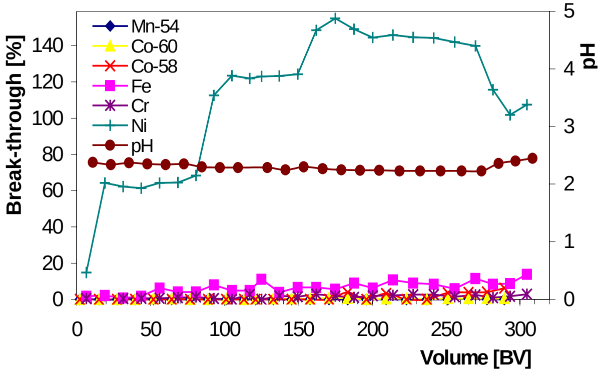

Fig. 11 Break-through curves of radionuclides and metal ions through a column of OSTION KS806 cation exchanger from the real electrochemical decontamination solution after photocatalytic degradation of organic complexants and the dependence of pH of the effluent on the volume of the treated solution (BV = 1.2 ml, absorber grain size 0.08 - 0.16 mm, flow rate 6.0 BV/hr)

It can be concluded that the results obtained are rather promising. Both the photocatalytic degradation and the radionuclide sorption modules performed in the real solution as well as in the preliminary tests with the simulant solutions. Hence practicability of the process was confirmed. If considering practical application of this process, attention should be paid to the spent photocatalyst that would represent an additional secondary radioactive waste stream.

3.2.4 Development of a precipitation-desalination process for regeneration of the electrochemical decontamination solution

The results of published speciation studies [21] demonstrated that iron can be precipitated in the presence of organic complexing agents, in the form of iron hydroxide, and the radionuclides can be either co-precipitated or not depending on the actual value of pH. Based on this fact, a new way for regeneration of the electrochemical decontamination solution was proposed [9,21] as a four-step process comprising

- iron precipitation / radionuclides co-precipitation,
- phase separation,
- cation removal (desalination),
- oxalic and citric acids concentrations adjustment.

The results of the precipitation experiments performed with the electrochemical decontamination solution showed that at pH higher than 10.5 it is possible to remove more than 94 % of iron from solution and to reduce activity of solution down to background values, due to co-precipitation of the radionuclides with iron hydroxide flocks (see Fig. 12). At the same time, nearly all the organics are left in solution after iron hydroxide precipitation.

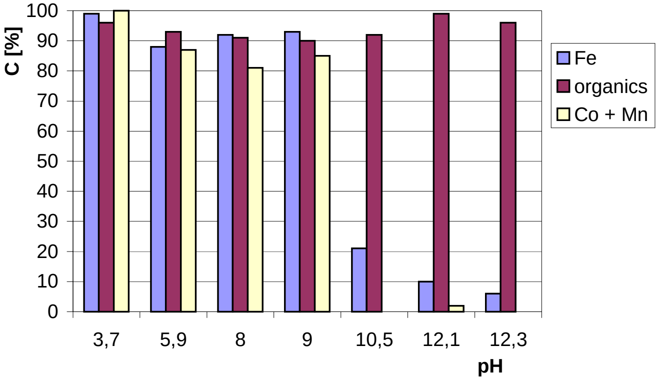

Fig. 12 Effect of pH on the composition of spent electrochemical decontamination solution (C [%] – per cent of component left in the solution at the respective pH)

For the regeneration of the solution for its repeated use, the excessive Na^+ cations should be removed from the solution, which also results in re-acidification of the solution. For this step, simple passing through a column loaded with cation-exchange resin in H^+–form may be used. The regeneration is then finalised by the oxalic and citric acids concentrations adjustment.

The performance of the proposed process was demonstrated in NPP Jaslovské Bohunice, Slovakia [9,21]. The same solution was used as described in the chapter 3.2.3 above. The results of the test are presented in Table 5.

Table 5 Behaviour of radionuclides, macroelements, complexants and pH in the electrolysate regeneration process

Nuclide	**Peak [keV]**	**10^3 cps**		
		Electrolysate	**Supernatant**	**Regenerate**
Sb-124	603	107.7	92.3	85.0
Ag-110m	658	65.1	0.0	0.0
Cs-137	661	21.0	14.0	0.0
Co-58	811	208.6	7.9	3.7
Co-60	1332	1380.2	103.0	71.7
Mn-54	834	1459.7	139.0	102.7
Element		**c [mg/l]**		
		Electrolysate	**Supernatant**	**Regenerate**
Fe		6.825	0.669	0.603
Ni		0.952	0.107	0.088
Cr		2.449	0.996	0.851
Complexant		**c [mg/l]**		
		Electrolysate	**Supernatant**	**Regenerate**
Oxalic acid		3.86	4.86	3.06
Citric acid		3.21	3.21	3.22
		Electrolysate	**Supernatant**	**Regenerate**
pH		1.75	10.20	3.40

Supernatant – solution after iron hydroxide precipitation and phases separation
Regenerate – supernatant treated by desalination/Na^+ separation by ion exchange

From these data, the following conclusions may be drawn:

- some 90 % of the macroelements (Fe, Ni, Cr) are removed during the precipitation step,
- significant amount of the oxalic acid is lost in the desalination / sodium removal step,

- activity of the major contributors to the total activity of the spent solution (radiocobalt, ^{54}Mn, ^{110m}Ag) is decreased by 90–100 % in the precipitation step, it is not further significantly reduced in the sorption desalination / sodium removal step,
- ^{137}Cs is not significantly removed by precipitation while it is quantitatively removed in the desalination / sodium removal step.

After the desalination / sodium removal step, the concentrations of the oxalic and citric acids in the regenerate were adjusted to their original values in the fresh electrolyte. The decontamination efficiency of the regenerated electrolyte was tested and compared to that of the fresh electrolyte in a series of standard decontamination runs. From the results obtained (see Fig. 13) it can be seen that the performance of the fresh and regenerated electrolytes is practically the same - from three out of the total of four samples all the activity was removed within 13 minutes of the decontamination.

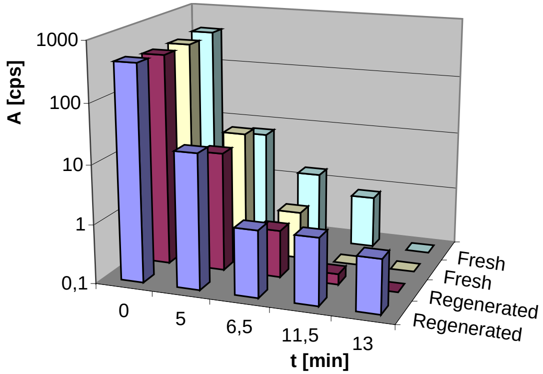

Fig. 13 Comparison of the performance of the fresh and regenerated electrolytes

Generally, it can be concluded that the results of verification of the process designed for the regeneration of the spent electrolyte from electrochemical decontamination were rather promising. No difference in the performance of fresh and regenerated electrolytes was found in the first experiments.

3.3 NPP evaporator concentrate

This study was performed with both model solutions and a real evaporator concentrate from tank 7TW10B03 at the NPP Dukovany, Czech Republic. The major chemical and radiochemical components of the real concentrate are summarised in Table 6, Table 7 lists the composition of the model solution used.

The specific activities of individual radionuclides in the real concentrate are rather low, only the activities of ^{60}Co and $^{134+137}$Cs are high enough to allow easy following their behaviour in radionuclides separation experiments. For the experiments with strontium separation, this real solution had to be labelled with ^{85}Sr.

Table 6 Selected parameters of the real evaporator concentrate used in the experiments

Chemical parameters			**Radiochemical parameters**		
pH		11.27	^{54}Mn	[kBq/l]	0.25
H_3BO_3	[g/l]	74.2	^{59}Fe	[kBq/l]	<0.11
NO_3^-	[g/l]	52.8	^{60}Co	[kBq/l]	12.03
Cl^-	[g/l]	2	^{134}Cs	[kBq/l]	1.35
CO_3^{2-}	[g/l]	10.8	^{137}Cs	[kBq/l]	41.49
SO_4^{2-}	[g/l]	3.5	^{90}Sr	[Bq/l]	6.42
NO_2^-	[g/l]	3.2	^{129}I	[Bq/l]	98.60
Oxalates	[g/l]	1.5	^{63}Ni	[Bq/l]	132
Citrates	[g/l]	1.2	^{99}Tc	[Bq/l]	196
K^+	[g/l]	5.6			
Na^+	[g/l]	46.8			

Table 7 Composition of the full simulated solution of NPP evaporator concentrate (NaOH added ad pH~11.5)

Compound	**H_3BO_3**	**NaCl**	**K_2CO_3**	**$NaNO_3$**	**Na_2SO_4**	**$NaNO_2$**	**HCit**	**HOx**
c [mol.l^{-1}]	0.832	0.056	0.180	0.852	0.038	0.069	0.006	0.017

As for most the cases reported in this paper, the studies performed with this solution consisted of a study of degradation of the organic complexants in the solution, study of direct separation of radionuclides from the original solution and a study of radionuclides separation from the solution after degradation of organic complexants.

3.3.1 Degradation of organic complexants

In a study aimed at the *degradation of organic complexants*, efficiency of radiolysis (gamma radiation, 0.8 kGy/hr, total dose up to 300 kGy) and degradation by the action of peroxodisulphate was tested. Because of the lack of relevant data in literature, a broad fundamental study of HOx and HCit radiolytic degradation was performed. As an example of the data obtained, comparison of the effect of irradiation by γ–rays (^{60}Co) or accelerated electrons (4.5 MeV) is shown in Fig. 14.

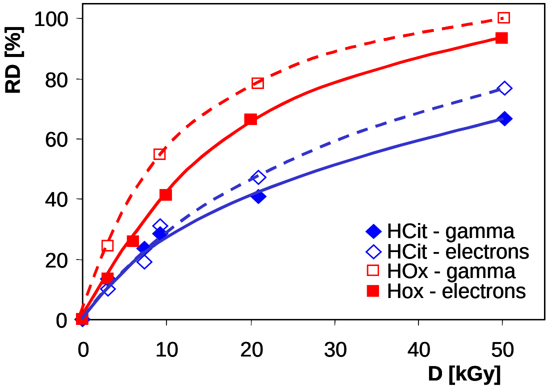

Fig. 14 Comparison of the degradation (RD) of oxalic (HOx) and citric (HCit) acids under irradiation by γ–rays (^{60}Co) or accelerated electrons (4.5 MeV)
(D - absorbed dose, 0.005 M HCit or 0.01 M HOx)

The main conclusions of the first part of this study can be summarised as follows:

- the effect of γ–rays and accelerated electrons is comparable,
- saturation of the solution by NO has a positive effect on the degradation rate,
- saturation of the solution by N_2 has a negative effect on the degradation rate,
- the effect of presence of modifiers (TiO_2) is unclear,
- HOx degradation decreases monotonously with increased salinity (nitrates or borates concentration)
- HCit degradation passes a maximum at 0.01M NO_3^- and then steadily decreases, while monotonous decrease was observed with increasing BO_3^{3-} concentration.

Interesting results were obtained in the study of the dependence of radiolytic degradation of organic substances on pH of the solution. It was found that HOx degraded easily in the acidic range while the efficiency of its degradation decreased rapidly with increasing pH. The pH dependence is much less pronounced for HCit. Qualitative comparison of the shape of these dependences with the dependence of abundance of individual species of HOx or HCit on pH (see Fig. 15) seems to indicate that for both HOx and HCit the partly dissociated forms seem to be the most vulnerable to degradation.

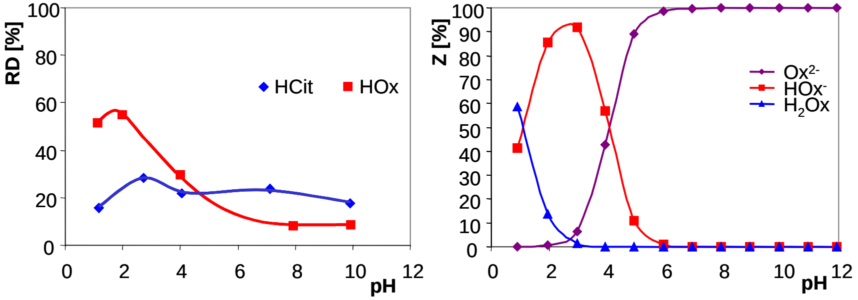

Fig. 15 Degradation (RD) of citric (HCit) and oxalic (HOx) acids under irradiation by γ–rays and abundance of (Z) of oxalic acid species as a function of pH
(absorbed dose D = 10.9 kGy, 0.005 M HCit or 0.01 M HOx)

This fundamental study revealed two factors that represent a significant obstacle for the applicability of radiolytic degradation of organic complexants on the specific case of evaporator concentrate. They are:

- decreased efficiency of the degradation in alkaline pH range and
- decreased efficiency of the degradation in the presence of high concentration of salts.

In an experiment performed with a real evaporate that was irradiated up to an absorbed dose D=300 kGy, 62 % of HCit and 92 % HOx was degraded. This degradation was higher than in a parallel experiment performed with the full simulant. Among the potential reasons for this observation mutual compensation of some antagonistic factors such as the negative influence of high pH and high salinity or positive influence of some minor components may be suggested.

A brief study revealed that degradation by the action of peroxodisulphate is more efficient than the radiolytic degradation. In the solutions of pure organic substances, both the citric and oxalic acids were completely decomposed in one hour under optimised conditions, similar results were obtained even for the simulated and real evaporator concentrate solution. However, it should be noted that addition of another substances into the solution with already high concentration of salts is a non-negligible disadvantage of peroxodisulphate treatment.

3.3.2 Separation of radionuclides from the evaporator concentrate

Direct selective *separation of ^{137}Cs and ^{85}Sr* radionuclides was demonstrated to be achievable even from the original evaporator concentrate not treated for the degradation of organic complexants. (TiO+FC212)–PAN composite absorber containing a mixture of titanium dioxide and potassium-cobalt hexacyanoferrate as active components may be applied for such separation [26].

Because of its unclear and complex speciation, *separation of cobalt* turned most complicated. A study of the influence of degradation of organic substances on the efficiency of cobalt separation on 11 inorganic absorbers and charcoals was performed with the original concentrate and the concentrate treated by radiolysis (300 kGy). In most cases, the generally low K_Ds increase after irradiation for inorganic absorbers and decrease for the samples of charcoals. This finding is in agreement with the expected decrease in abundance of complexed forms of cobalt after degradation of the organic complexants. However, in both solutions the highest K_Ds were observed for the charcoals. This is most probably due to the fact that in saline alkaline solution the cobalt released from the organic complexes will not stabilise in cationic form but will form various neutral species, like hydroxocomplexes or pseudocolloids, which are not readily sorbed on ion-exchangers.

These findings were confirmed also in dynamic sorption experiments. An example of the break-through curves measured is shown in Fig. 16. It can be seen that the performance of a sorption column did not change significantly after partial degradation of the organic complexants and it still remains insufficient for practical application.

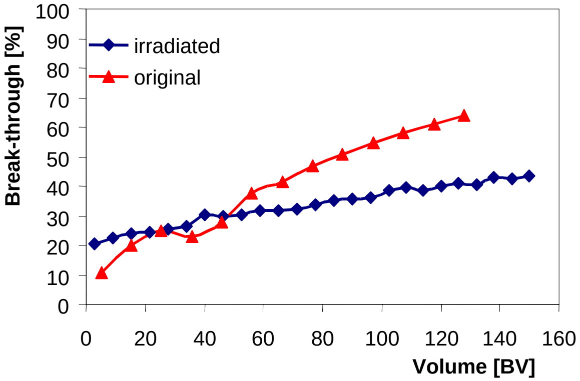

Fig. 16 Break-through curves of radiocobalt through a column of Chezakarb F charcoal from the original evaporator concentrate and the concentrate after partial radiolytic degradation of organic complexants (BV = 1.2 ml, absorber grain size 0.4 - 0.8 mm, flow rate 4–5 BV/hr)

4 CONCLUSIONS AND OUTLINE OF FUTURE RESEARCH AND EDUCATION DIRECTIONS

In this study, a new modular process for treatment for final disposal of liquid radioactive waste containing organic complexing agents, such as oxalic or citric acids, was developed and tested. It combines photocatalytic degradation of organic complexants by means of UV radiation in the presence of titanium dioxide catalyst with subsequent sorption separation of radionuclides onto either selective inorganic-organic absorbers or standard strongly acidic cation resins.

As a part of background data collection, important new data on the mechanisms of photocatalytic and radiolytic degradation of citric and oxalic acids were obtained in broad fundamental studies. The finding that in photocatalytic systems in the presence of significant concentrations of iron Fenton reactions, which lead to a significant increase of the rate of $OH^{\bullet}$ radicals production, take place has a direct impact to the applicability of this process to certain types of waste (e.g. the electrochemical decontamination waste).

The new modular process was successfully demonstrated on laboratory scale for a real spent acidic AP-CITROX decontamination solution from NPP Dukovany, Czech Republic. For spent electrochemical decontamination waste, the applicability of the process was demonstrated even on a bench scale in NPP Jaslovské Bohunice, Slovakia, with a real waste produced in the course of test decontamination of VVER 440 NPP reactor internals. It has been concluded that both the photocatalytic degradation and the radionuclide sorption modules performed in the real solution as well as in the preliminary tests. If considering practical application of this process, attention should be paid to the spent photocatalyst that would represent a secondary radioactive waste stream.

The process developed was found not to be effective for alkaline saline wastes such as NPP evaporator concentrates or Hanford-type waste. In the NPP evaporator concentrates, bulk of the organic complexants was successfully degraded by radiolysis. However, the efficiency of separation of radiocobalt, the most problematic radionuclide in this type of waste, has not significantly improved after radiolytic treatment.

A possibility to further reduce the volume of finally disposed waste was verified in a test of a simple precipitation-desalination process for regeneration of the spent electrochemical decontamination waste that has been proposed by Belarussian group in the framework of INCO Copernicus “SUSRAD” project [9,21]. Both the macrocomponents and radionuclides could have been separated from the spent solution. After adjustment of oxalic and citric acids concentrations, performance of the regenerated electrolyte was practically the same as of the fresh one.

In full agreement with the general trends reviewed in the Introduction, the prospective direction of R&D in the field of treatment of liquid radioactive waste containing organic complexing agents, leading to minimisation of the finally disposed waste, is development of technologies for regeneration of spent solutions for their re-use. Depending on the basic characteristics of the solutions (pH, salinity), two prospective pathways may be foreseen:

- New regeneration technologies based on efficient separation of both the macrocomponents and the radionuclides should be developed for spent decontamination solutions. By recycling the solutions, both the volume of the waste and the discharge of organic complexing agents would be minimised.
- For the NPP evaporator concentrate the most plausible direction seems to be boric acid separation in the first stage, followed by raffination of the separated H_3BO_3 for its re-use in the NPP primary circuit and a separate treatment of the remaining solution with decreased salinity and pH, if possible down to the free release limits.

For the maximum efficiency, the research should make full use of the potential of the modern and emerging experimental techniques that allow the studies to be re-focused from the description of macroscopic down to molecular level properties. Among these tools, application of Time Resolved Laser Fluorescence Spectroscopy for the complexation studies is already under consideration.

Education in the field of liquid radioactive waste management has been, and should remain to be, a constituent part of the Masters and Ph.D. degree courses of Nuclear Chemical Engineering or Nuclear Chemistry, respectively, at the Department of Nuclear Chemistry of the Faculty of Nuclear Sciences and Physical Engineering of the CTU in Prague. The prospective directions of fostering education in this field may be outlined as follows:

- *Education by Research* – the most effective way of transfer of the cutting edge knowledge is inclusion of the students into research project. Such activities should start as early as possible in the curricula, because they represent one of the most efficient instruments for motivating the students.
- *Theoretical education as a part of the regular curricula* – to bring the most up-to-date information to all the students, not only those involved in the research, frequent update of the courses and including selected subjects into practical exercises should be pursued.
- *Continued Education* – there are two target groups to be addressed with the information on the current status of this politically and sociologically sensitive topic:
  - Specialists from the industries (NPP or service decontamination companies employees) should attend specialised courses comprising both theoretical and practical education.
  - General public that may be educated in various ways, as e.g. courses at the University of the 3rd Age, or by popularisation activities.

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Curriculum vitae

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- Separation of radionuclides from complex waste matrices (2003-2006, chief scientific investigator), International Atomic Energy Agency, Vienna RB 12433/R0

- Development of solid phase extractants for radiochemical activation analysis, (2004-2006, chief scientific investigator), Grant Agency of the Czech Republic, GA 203/04/0943
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- Supervising and guiding PhD students (2 graduated, 6 running), masters' degree projects (7 graduated), research projects (9) a semestrial projects (8); 4 of the students won awards in competitions at international conferences.

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- Member of the following Learned societies:
    - Czech Chemical Society - Chairman of the Nuclear Chemistry section
    - I.M.Marci Spectroscopic Society - member
    - Česká Technika - member
- Chairman / Member of the Scientific of Organising Committees of multiple conferences and symposia:
    - 13th and 14th Radiochemical Conferences (RadChem'98 and RadChem 2002, Mariánské Lázně, Czech Republic) - chairman of the Organising Committee

- Scientific Committee member of the „1st FECS European Chemistry Congress“ (August 2006, Budapest).
- Co-chairman of the Organising Committee of three International Symposia organised by Florida State University, Tallahassee, USA,
- Co-chairman of one international seminar organised by the Czech chemical society.
- Advisory board member of two international conferences.
- Organiser of “Nuclear Chemistry” sessions on two Czech Chemical Society congresses.

Publications:

Author or co-author of 3 chapters in international monographs, more than 80 original papers in scientific journals or conference proceedings, 3 university or specialised courses textbooks, and more than 90 research reports. By March 2004, Web of Science lists 80 references to the above-enumerated papers.

Co-editor of one technical document (TECDOC) published by the International Atomic Energy Agency, two Proceedings of international conferences published in an international professional journal, and two Booklets of Abstracts of international conferences.