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Electron beam irradiation of r-SANEX and i-SANEX solvent extraction systems: analysis of gaseous products

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Abstract. 1-Octanol/kerosene mixtures and water contacted with organic solvents were used as model solutions for r-SANEX and i-SANEX extractions systems. Investigations aimed on a quantitative evaluation of gaseous products generated in these systems under exposure to an electron beam irradiation. Influence of O_2, HNO_3 and the presence of model ligands and complexes on the radiation chemical yields was studied. Relatively high $G(H_2)$ values (up to 420 nmol·J^{-1}) for the organic phase compromise the safety issues of the extraction process and should be considered on the stage of extraction apparatus design. Based on the obtained results gaseous hydrocarbons seem to have negligible impact on safety issue. The upper limit of $G(H_2)$ values in water contacted with organic phase was established to be 85 nmol·J^{-1}. This value is relatively low, however, the literature data indicate that $G(H_2)$ values measured in aqueous solutions are over twice higher for α-particles irradiation than for electron beam or γ-irradiation. Thus, further investigations of these systems are necessary.

Key words: electron beam irradiation • radiolytic gaseous products • gas chromatography • SANEX extraction systems

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Introduction

Management of a spent nuclear fuel is a critical issue of the modern nuclear industry. The main problem is long-term radiotoxicity and the heat load of transuranium elements produced in nuclear reactors as a result of neutron capturing by uranium fuel. Thus, it is necessary to separate and recycle highly radioactive, long-lived isotopes from nuclear wastes. Separation of plutonium and uranium from the spent nuclear fuel in plutonium and uranium recovery by extraction (PUREX) process has been used by the industry for many years [1]. It reduces potential radiotoxicity hazard of wastes from approximately 200 000 years to 10 000 years. Further reduction to about 300 years can be achieved by removing of minor actinides [2]. Development of the selective actinide extraction (SANEX) process based on triazinylpyridine N-donor ligands was the largest breakthrough in the actinide separation chemistry in the recent decades [3]. Radiation chemistry of this system is one of the key factors for the industrial application. Extraction of minor actinides can be significantly affected by radiation damages of the system on several ways. Decreasing of extraction efficiency and loading capacity due to ligand radiation degradation, influence of irradiation products on extraction efficiency, changes of physical properties of solvent (third phase formation, changes of viscosity) are the most important factors. This is rather unlikely that gaseous products of irradiation

may have a dramatic impact of extraction efficiency, however, they can severely compromise safety issue of SANEX process. This is mainly due to a high flammability and explosiveness of generated molecular hydrogen (H_2) and gaseous hydrocarbons.

The present work was focused on determination of radiation chemical yields of gaseous products generated from irradiated regular SANEX (r-SANEX) and innovative SANEX (i-SANEX) extraction systems [4, 5]. In both systems, organic and aqueous phases are in contact during the extraction. The main reason of the radiation damages in these systems is irradiation by α-particles. Since the penetration range of α-particles is very short, major damages take place in the phase containing source of α-emitter. Partitioning of the radioactive isotopes makes uneven distribution of the radioactivity between phases. Moreover, contact time of each phase with radioactive isotopes is different. Thus, both phases are exposed to the different effective radiation doses. For these reasons we decided to investigate each phase separately. A mixture of 1-octanol and kerosene was used as a model organic phase. Even though fraction of 1-octanol modifier is rather low in usually applied organic phase (up to 30 vol.% [3]) we decided to extend our investigation to full range of concentration from 0 to 100% of 1-octanol in kerosene to cover malfunction operation or human error. Radiolytic gaseous products generated from both organic and aqueous phases were analyzed before and after contacting with each other. Influence of oxygen (O_2), nitric acid (HNO_3), model triazinylpyridine ligand and its metal complexes was under investigation. 6,6′-Bis(5,5,8,8--tetramethyl-5,6,7,8-tetrahydobenzo-1,2,4-triazin-3-yl)-2,2′-bipyridine (CyMe$_4$BTBP), a European reference molecule for development of r-SANEX processes [3], dissolved in organic phase, was used as an extractant in r-SANEX system. Whereas a water soluble 2,6-bis(5,6-di(sulfophenyl)-1,2,4--triazin-3-yl)-pyridine (HSO$_3$-Ph-BTP) played a role of model complexing agent for i-SANEX extraction. At this stage of the study we focused mainly on the determination of the dependency between quantity of gaseous products and the initial composition of phases. Impact of the irradiation products accumulation and their possible transfer between phases will be a subject of the future investigations.

Experimental

All gas standards, for chromatography, were purchased from Sigma-Aldrich with the highest available purity. Solvents: 1-octanol (99%) and kerosene (purum) from Sigma-Aldrich were used without further purification. Water purified in the Direct-Q 3 UV (Merck Millipore) system was used in all experiments. 6,6′-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-1,2,4-triazin-3-yl)-2,2′-bipyridine (CyMe$_4$BTBP, 99%) was synthesized according to the procedure published elsewhere [6] by Dr A. W. Smith (University of Reading, UK) and kindly donated to us. 2,6-Bis(5,6-di(sulfophenyl)-1,2,4-tri-

azin-3-yl)-pyridine (HSO$_3$-Ph-BTP) was purchased from Technocomm Ltd. (UK) with purity 99% and used as received.

Approximately 4 ml of solvent were placed in ~14 ml, special septa cap vials, prior to irradiation. In case of samples containing extractant or metal complexes only ~1 ml of solvent were used in vials with volume ~2 ml. The exact volumes of vials were obtained by measuring mass of water in fully filled, septa cap vessels. The free volume was calculated by subtraction of the volume taken by sample (measured by mass) from the vial volume. Samples were purged, depending on needs by air or argon (Ar).

Electron beam irradiations were carried out using Elektronika 10/10 accelerator with ~7 μs pulses, the dose ~20 Gy per pulse, and pulse repetition of 400 Hz. Energy of incident electrons was about 10 MeV which corresponds to LET equal to 0.19 keV·μm^{-1} [7]. In principle, all studies of radiation resistance of the extraction systems used in the nuclear fuel cycle were performed with the absorbed doses ranged from tens kGy to several MGy, and with dose rates up to about 15 kGy·h^{-1} [3, 8]. In our experiments, the absorbed doses were limited to ~85 kGy in order to apply a reasonable short irradiation time. A total absorbed dose (corrected for the mass density of sample) was measured by the alanine dosimetry based on a Bruker e-Scan system. Due to accelerator dose rate (~3 MGy·s^{-1}) relatively high concentrations of radicals and radical ions in very short pulse time are generated. At limited point, it resembles high concentration of intermediates generated in tracks of α-particles. Major radiation degradation of r-SANEX and i-SANEX systems is caused by the latter type of particles. All samples were kept for 0.5 h after irradiation with periodical gentle shaking. The main reason was to reach physical equilibria. It was crucial since the temperatures of the samples increase to about 40°C during irradiation.

Gas analysis was carried out on Porapak Q and MS 5A columns, using Shimadzu GC-2014 and Shimadzu GC-14B chromatographs with TCD and PDHID detectors. Measurements were performed by an injection of the small fraction (20–70 μl) of the gaseous sample from the vial headspace above the liquid phase to the instrument. Injections were performed by the valve equipped Hamilton syringe.

Radiation yields (G) were calculated as an average of 3 to 5 independent measurements taken at the single dose. Standard deviation of G values were lower than 15%.

The content of water in samples was determined by Karl-Fischer coulometric titration method (C20 Coulorimetric KF Titrator, Mettler Toledo).

Results and discussion

Organic phase

A general reaction scheme for the radiolysis of organics begins with the ionization and excitation of their constituent parts. H_2 – a typical gaseous product

of organics irradiation – can be formed either in a subsequent reaction from the electronically excited states of molecules or from the electron deficient species often called 'holes'. It is well known that a homolytic cleavage of bonds in excited organic molecules is not fully random in spite of the high energy of the incident particles. Chemical bonds with the relatively low dissociation energies, such as tertiary C-C or C-H are the most vulnerable to scission. As a result of the homolytic cleavage of the C-H bonds, hydrogen atoms (H$^{\bullet}$) are produced. Typically, H$^{\bullet}$ abstract H-atoms from another organic molecule forming H_2. A direct recombination of two H$^{\bullet}$ is rather unlikely due to their low concentration unless their reactions in tracks of high LET particles are concerned. Similarly, a cleavage of C-C bonds in alkane chains leads to formation of alkyl radicals which – after recombination – may end up as gaseous alkanes. There are several reactions leading to H_2 formation, which are connected with the post-ionization radical-ion mechanism. The most important reactions are: (i) dissociation of radical-cations; (ii) neutralization of radical-cations by electrons (including geminate recombination) followed by formation of electronically excited states; and (iii) deprotonation of radical-cations followed by proton neutralization to form H$^{\bullet}$.

The $G(H_2)$ dependency on composition of Ar saturated 1-octanol in kerosene diluent is presented in Fig. 1 (series A). This is the most often used diluent in the SANEX system [3]. Obtained values range from 420 nmol·J^{-1} for neat kerosene to 380 nmol·J^{-1} for neat 1-octanol. These data correspond quite well to the published results for the components of this system as it is described below.

Kerosene is a commercial name of one of the rectification fraction of petroleum. It is composed mainly of normal and branched alkanes and cycloalkanes. Aromatic and unsaturated hydrocarbons normally do not exceed 30% by volume [9–11].
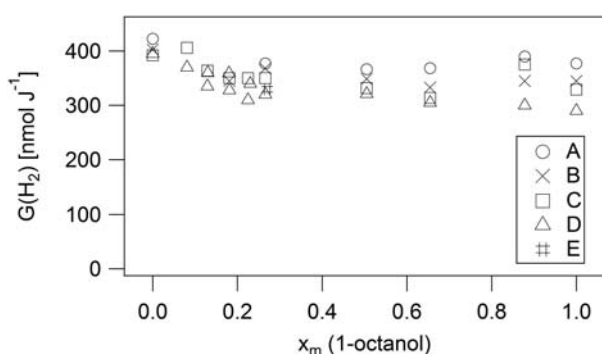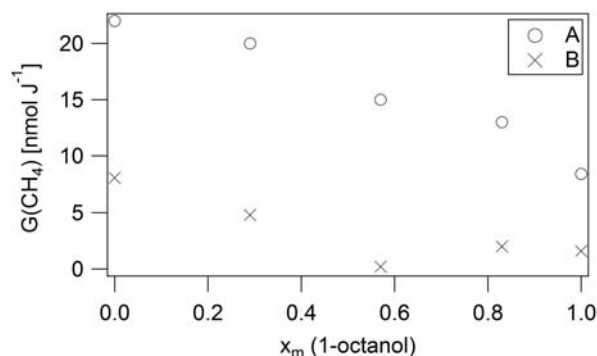

Fig. 1. The $G(H_2)$ dependency on 1-octanol concentration in kerosene. A: Ar saturated 1-octanol/kerosene diluent, B: air saturated 1-octanol/kerosene diluent, C: air saturated 1-octanol in kerosene solution in contact with water (the ratio of organic to aqueous phase volume was equal to 1), D: air saturated 1-octanol in kerosene solution in contact with 1 M HNO$_3$ (ratio of organic to aqueous phase volume was equal to 1), E: air saturated solution of CyMe$_4$BTBP (5.1 mM) in 1-octanol/kerosene (27/73 mass) contacted with an aqueous solution of Eu^{3+} (5 mM) in HNO$_3$ (1 M, ratio of organic to aqueous phase volume was equal to 1).

$G(H_2)$ values in the γ and electron beam irradiated liquid n-alkanes are in the range of 430–545 nmol·J^{-1} [7, 12, 13]. In general, these values are lower for branched alkanes. For instance, $G(H_2)$ is equal to 210 nmol·J^{-1} for 2,2-dimethylbutane [7] comparing with 520 nmol·J^{-1} for n-hexane [12]. Unsaturated alkanes reveal also lower $G(H_2)$ values: for 1-hexene, $G(H_2)$ is equal to 83 nmol·J^{-1} [14]. Aromatic compounds are significantly more stable towards radiation than aliphatic ones. The $G(H_2)$ for benzene is quite low and equal to 3.9 nmol·J^{-1} [15]. Moreover, aromatic compounds show so-called radiation protection effect. The stabilization influence of the aromatic ring extends to the alkyl groups in the same molecule [16], or even to aliphatic compounds mixed with aromatic ones [7, 17]. The G values in alkane/aromatic systems are lower than those calculated from linear interpolation between the values obtained for neat components and the electron fraction (stopping power) of each component of the system [7, 18]. A presence of aromatic compounds in organic phase is the main reason of a relatively low $G(H_2)$ comparing to n-alkanes. It is also worth to note that variation in aromatics contents in commercially available kerosene may have a dramatic effect on $G(H_2)$ values in this solvent.

$G(H_2)$ values, obtained by γ-irradiation, of liquid normal alcohols (C1 to C4) vary between 460 and 560 nmol·J^{-1} [7]. Corresponding values for 28 MeV α-particle irradiation are lower and fall into the range 281–372 nmol·J^{-1} [19]. For this type of irradiation $G(H_2) = 361$ nmol·J^{-1} was measured for 1-octanol.

The radiation chemical yield of methane ($G(CH_4)$) in a deaerated 1-octanol/kerosene solvent decreases from 22 to about 6 nmol·J^{-1} with increasing of 1-octanol mass fraction from 0 to 1 (Fig. 2, series A). The highest radiation yield of ethane ($G(C_2H_6)$) equal to 14 nmol·J^{-1} was obtained for neat kerosene. At the 1-octanol concentration above 50%, the $G(C_2H_6)$ values are below detection limit of our experimental setup. These values can be explained based on literature information recorded for electron beam irradiated alkanes and alcohols. The $G(CH_4)$ value decreases from 40 nmol·J^{-1} for n-pentane to 4 nmol·J^{-1} for n-hexadecane [7, 12, 20]. Significantly higher values were observed for branched alkanes. The $G(CH_4)$ values of 2-methylpentane and 2,2-dimethylbutane are equal to 52 and 124 nmol·J^{-1},

Fig. 2. The $G(CH_4)$ dependency on 1-octanol concentration in kerosene. A: Ar saturated 1-octanol/kerosene diluent, B: air saturated 1-octanol/kerosene diluent.

respectively, whereas for n-hexane 16 nmol·J^{-1} [7, 12, 20]. For alkyl substituted benzenes, the values $G(CH_4)$ are lower than 2 nmol·J^{-1} [7]. The $G(CH_4)$ measured in γ-irradiated methanol and ethanol are equal to 70 and 60 nmol·J^{-1}, respectively, whereas for 1-propanol and 1-butanol, CH$_4$ was not detected [7]. In the case of 28 MeV α-particles irradiation, the corresponding $G(CH_4)$ values for methanol, ethanol and 1-propanol were 37, 45 and 7.0 nmol·J^{-1}, respectively, whereas in 1-octanol the $G(CH_4)$ was equal to 2.2 nmol·J^{-1}, under the same experimental conditions [13, 19].

Obtained radiation yields of gaseous products, in the deaerated conditions, do not precisely reproduced real conditions of the irradiated extraction system. O$_2$ is a well-known scavenger of electrons and also affects radical reactions of the diluent. However, due to exposition to a high dose rate, one can expect fast depletion of O$_2$ in organic phase. Therefore, the radiation chemical yields of gaseous products in deaerated samples can be used as the highest measured limit. Direct observation of the O$_2$ effect on radiation chemistry of organic diluent was investigated based on air saturated sample. Results are shown in Fig. 1 (series B). Negligible difference (within experimental error) between $G(H_2)$ values for aerated and deaerated samples is due to a low concentration of O$_2$ in organic phase. It is likely that major H$_2$ formation is a consequence of very fast reactions, taking place in the spurs of ionization (high concentration of intermediates). Apparently at these conditions, the scavenger is not capable to affect this kind of reactions.

However, a presence of air did not affect $G(H_2)$ values but it had a significant impact on the radiation chemical yields of gaseous hydrocarbons. In the presence of air, the $G(CH_4)$ values observed in a neat kerosene decreased from 22 nmol·J^{-1} to about 8 nmol·J^{-1} (Fig. 2, series B). For mass fraction of 1-octanol higher than 40%, $G(CH_4)$ values were below detection limit of our experimental setup. The disrupted ratios of [O$_2$] to [N$_2$] after irradiations were used to calculate consumption of O$_2$. The radiation chemical yields of the O$_2$ consumption $G(O_2)$ changed linearly from –53 nmol·J^{-1} for a neat kerosene to –12 nmol·J^{-1} for a neat 1-octanol, whereas $G(CO_2)$ decreased from 11 to 0 nmol·J^{-1}, respectively. At the same experimental conditions, the radiation chemical yields of water formation ($G(H_2O)$) increase from 0 for a neat kerosene to 150 nmol·J^{-1} for a neat 1-octanol. The obtained G values strongly suggest the formation of peroxides in air-saturated kerosene.

The $G(H_2)$ values obtained for the aerated 1-octanol/kerosene solution remained the same within an experimental error when the organic phase was contacted with water prior to irradiation. This is not surprising at the low concentration of 1-octanol since solubility of water in kerosene is very low (Fig. 3). Due to this fact, a direct ionization of water molecules is very unlikely and thermodynamics of the investigated system does not allow for neither energy transition from organic molecules nor radical or radical-ion reactions involving water molecules.
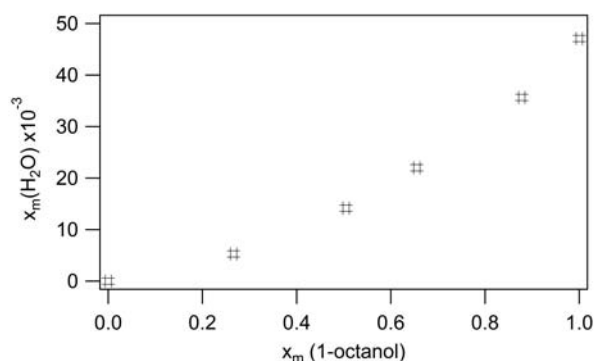

Fig. 3. Water solubility as a function of 1-octanol mass fraction in a mixture of kerosene and 1-octanol.

However, solubility of water in investigated system significantly increases with increasing of 1-octanol fraction (Fig. 3) and reaches mass fraction 0.047 for neat 1-octanol. At these conditions a direct ionization of water molecules is possible and leads to highly reactive intermediates such as hydrogen and hydroxyl radicals (H·, ·OH), eventually. Presence of these intermediates may alter mechanism of radiation induced reactions in an organic phase but apparently, an efficiency of H· generation from water was not sufficient enough to influence $G(H_2)$ values (Fig. 1, series C).

Solubility of HNO$_3$ in 1-octanol/kerosene solution was investigated by Geist [21] for the system with the organic to aqueous phase volume ratio equal to 1. According to the authors, the concentration of HNO$_3$ in kerosene (contacted with 1 M aqueous solution of HNO$_3$) should not be higher than 1 mM whereas in 1-octanol is about 90 mM. These results explain profiles of $G(H_2)$ shown in the Fig. 1 (series D). At low concentration of 1-octanol, HNO$_3$ dissolved in this diluent is not capable to affect fast reactions in spurs of ionization. However, for the higher concentrations of HNO$_3$, scavenging reactions involving precursors of H$_2$ (1 and 2) [22, 23] are more pronounced.
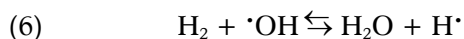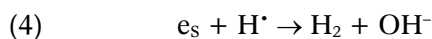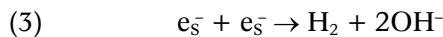
(1) $e_s^- + NO_3^- \rightarrow NO_3^{2-}$

(2) $H^\cdot + NO_3^- \rightarrow HNO_3^-$
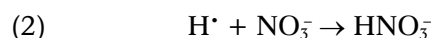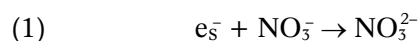
Gaseous alkanes were under detection limit in the presence of HNO$_3$. Neither the presence of CyMe$_4$BTBP ligands nor its Eu^{3+} complex did not affect formation of H$_2$ in the investigated systems (Fig. 1, series E).

Aqueous phase

Radiation chemistry of water is one of the key factors of the safety and the efficiency of the nuclear industry. This is one of the main reasons of extended research in the field of radiation chemistry of this medium. Mechanism of radiation induced reactions in water consists of over 30 reactions [24]. It starts from the ionization of water molecules leading to formation of electrons and holes (H$_2$O$^{+\cdot}$). Electrons after thermalization, in favorable

condition, can be solvated and holes $H_2O^{+\bullet}$ which deprotonates quickly resulting in $HO^{\bullet}$ and H_3O^+ formation. Reactions (3)–(5) are responsible for H_2 formation in irradiated water. Particularly, at the higher pressure H_2 can be consumed to the certain extend in the reaction (6).

$$(3) \qquad e_s^- + e_s^- \rightarrow H_2 + 2OH^-$$

$$(4) \qquad e_s + H^{\bullet} \rightarrow H_2 + OH^-$$

$$(5) \qquad H^{\bullet} + H^{\bullet} \rightarrow H_2$$

$$(6) \qquad H_2 + {}^{\bullet}OH \leftrightharpoons H_2O + H^{\bullet}$$

$G(H_2)$ values obtained in water contacted with organic phase (mixture of 1-octanol with kerosene) are shown in the Fig. 4. The $G(H_2)$ for water contacted with kerosene was about 44 $nmol \cdot J^{-1}$. Solubility of kerosene in water is very limited. Thus, the value obtained corresponds quite well with the published results for a neat water 45–52 $nmol \cdot J^{-1}$ [7, 25–28]. The $G(H_2)$ values increase to about 85 $nmol \cdot J^{-1}$ with increasing 1-octanol concentration in the organic phase. Apparently, a presence of 1-octanol in an aqueous phase stimulates the formation of H_2.

The influence of O_2 on the formation of gaseous products was investigated in aerated samples. Within an experimental error the results obtained were identical to those measured in deaerated samples. A similar phenomenon was observed earlier in a neat water [28]. Even though, O_2 is a very good scavenger of $H^{\bullet}$ and e_s^- – precursors of molecular H_2 – it is not capable of affecting a fast reaction in spurs due to a limited solubility in water (2.5 mM for O_2 saturation [28].

Decreasing of $G(H_2)$ values in water in the presence of HNO_3 is due to the occurrence of reactions (1)–(2), and described earlier by Nagaishi and Katsumura [22, 23].

Neither SO_3-Ph-BTP (up to 18 mM) nor complex of Eu^{3+} (up to 1 mM) with HSO_3-Ph-BTP (18 mM) affect the $G(H_2)$ values.

It is worth to note that the results presented do not address all the problems associated with radiation generation of gaseous products in SANEX system. Even though H_2 formation takes place in spurs of ionization and thus it is insensitive to relatively low concentration of scavengers, accumulation of the radiolytic products can affect its generation.
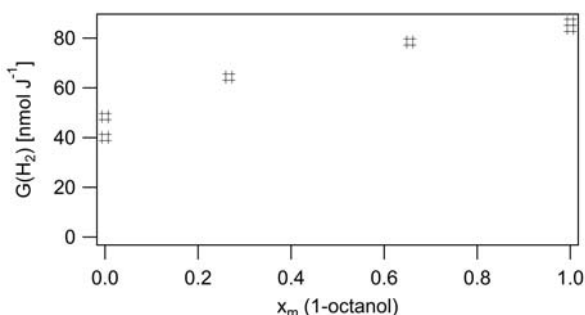
Fig. 4. The $G(H_2)$ in irradiated water contacted with 1-octanol/kerosene organic phase saturated with Ar as a function of 1-octanol fraction.

For instance, G values of diols, aldehydes and ketones are relatively high in alcohols [19, 29]. These products are more or less hydrophilic and during the extraction are transferred to the aqueous phase which may increase the upper limit of $G(H_2)$. Moreover, there are substantial differences in $G(H_2)$ values of aqueous systems obtained by different type of radiation. For instance, $G(H_2)$ in water exposed to an electron beam or γ-irradiation were in the range 45–52 $nmol \cdot J^{-1}$ [7, 25–28] whereas an α-particle irradiation leads to higher than twice values 100–115 $nmol \cdot J^{-1}$ [30]. Thus, further investigations are necessary.

Conclusions

The upper limit of $G(H_2)$ for the electron beam irradiated 1-octanol/kerosene solution was found to be equal to 420 $nmol \cdot J^{-1}$. Taking into account a wide flammability range of H_2 (4–75% by vol. in air [31–34]), it is highly advisable to take an appropriate design intent of extraction apparatus to avoid its dangerous accumulation. An impact of gaseous hydrocarbons on a safety issue of SANEX extraction seems to be negligible. This is due to the relatively low radiation yields (upper limit of $G(CH_4)$ equal to 22 $nmol \cdot J^{-1}$) as well as a narrow range of flammability of these gases (5–15% by vol. in the air [31, 34]). Some indirect effects such as poisoning of H_2 catalytic recombiners by hydrocarbons can be taken into consideration. Some fluctuation in the radiation chemical yields of products may be observed since the composition of kerosene is not strictly determined and differs to a certain extent depending on a source of petroleum and producer.

The upper limit of $G(H_2)$ for aqueous system was found to be 85 $nmol \cdot J^{-1}$. This value is not as high as in the case of organic phase but still may compromise safety issues of extraction. It is worth to note that the values obtained can be much higher for α-particles irradiation. The $G(H_2)$ values recorded for a neat water exposed to an electron beam or γ-irradiation were in the range 45–52 $nmol \cdot J^{-1}$ [7, 25–28] whereas an α-particle irradiation leads to values which are twice as high, and equal to 100–115 $nmol \cdot J^{-1}$ [30]. Moreover, our investigations do not concern transfer between phases, i.e. of hydrophilic, radiolytic products from the organic phase to the aqueous phase or the accumulation of other products which may affect H_2 generation. Thus, it is crucial to investigate these systems more deeply toward a better understanding of the impact of the heavy ions impact and radiolytic product accumulation on gaseous products.

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