

# IMMOBILIZATION OF RADIOACTIVE WASTE IN CEMENT: IODINE BINDING BY CEMENTITIOUS MATERIALS UNDER HIGHLY ALKALINE CONDITIONS

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This work is directed to assess iodine interactions with hardened cement paste (HCP) under highly alkaline conditions ( $\text{pH} > 12$ ) with/without a reductant. For this purpose, a series of  $K_d$  (distribution coefficient) experiments using  $^{127}\text{I}$  as a tracer were performed. The  $K_d$  values of iodine were in the order of  $172\text{--}1095\text{ mL g}^{-1}$  in the batch experiment without a reductant, and in the order of  $83\text{--}92\text{ mL g}^{-1}$  in the experiment with a reductant. The percentage of iodine leached out from HCP throughout the experiment suggested its very strong binding with cementitious materials. The obtained results allow supposing that chemical speciation of iodine has influence on the interaction of iodine with HCP under highly alkaline conditions.

**Keywords:** iodine, cement, sorption, desorption,  $K_d$

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## 1. Introduction

Function of the repository engineered barrier system is to ensure safe disposal of radioactive waste and to prevent uncontrolled migration of radionuclides outside the control area. The migration of radioactive nuclides from the repository through the containers and engineered barriers is induced because of their disintegration by groundwater, microorganisms, cement degradation, and corrosion. Final disposal of long-lived radioactive waste in the repositories implies the long-term risk related to their potential spreading in the surrounding solid and liquid phases.

Solidification of low and intermediate level radioactive waste by cementitious materials is one of the most frequently applied techniques prior to the near-surface or underground disposal [1–3]. Cement (concrete) is used to construct the engineered barriers of the repository as backfill material in vaults and tunnels. High mechanical capacity, low hydraulic conductivity and high radionuclide retention capacity are characteristic of cement. The most abundant cement mineral in hardened cement paste (HCP) is calcium silicate hydrate (CSH) [1–3], which is capable of im-

mobilizing many radionuclides. The interaction of groundwater with hardened cement paste can bring about a chemical alteration therein, and further degradation of concrete [4, 5]. Degradation of hydrated cement involves dissolution and leaching related to processes such as carbonation (dissolution of portlandite) and decalcification (ionic leaching from dissolution of portlandite and calcium-silicate-hydrate) [5]. These processes induce gradual changes in the composition of the pore water, from typical “young” cement leachate with a pH above 13 to leachate with a pH lower than 10 [6]. It has been shown that calcium silicate hydrates are a determining factor in the immobilization of di-, tri-, and hexavalent radionuclides in cementitious materials [1–3].

Several mechanisms have been postulated for the radionuclide immobilization in cement pore water, including precipitation as a simple salt, co-precipitation with other phases, lattice incorporation, chemisorption/physical adsorption, complex and colloid formation in the aqueous phase [7]. The retention of radionuclides in the cement matrix is determined by the formation of solubility-limiting phases because of chemical reactions of radioactive species with cement components [7].

Iodine-129 is a fission product present in the spent fuel from nuclear power plants and it is considered as a key mobile radionuclide for the disposal of spent fuel and high-level radioactive waste [8–10]. The behaviour of iodine in the geomeia is of particular importance because of its long half-life ( $^{129}\text{I}$ ,  $T_{1/2} = 1.57 \cdot 10^7$  years), its radiotoxicity, and its chemistry [11]. Since iodine is very much soluble, it easily migrates along water pathways if it enters the environment [12]. The knowledge of the extent of the iodine interaction with engineered barriers is of vital importance in modelling the iodine release from irradiated nuclear reactor fuel elements stored in underground vaults.

A number of studies on the mechanism of the iodine uptake in cementitious materials have been conducted [12–16]. Most of the studies have focused on the investigations of the potential of individual cement minerals to immobilize iodine and elucidation of a molecular-scale mechanism for the  $\text{I}^-/\text{IO}_3^-$  interaction with HCP and CSH. The iodine species uptake by cement and CSH was studied using XAS and EXAFS [14]. The authors concluded that redox reactions did not influence sorption of the iodine species by HCP and CSH. Moreover, the EXAFS/XANES studies demonstrated that CSH was not the phase controlling  $\text{IO}_3^-$  uptake in HCP.

The objective of this study was to investigate iodine interactions with cementitious materials under ambient highly alkaline conditions ( $\text{pH} > 12$ ) with/without reductant  $\text{Na}_2\text{S}_2\text{O}_4$  because the interaction of iodine under ambient conditions remains poorly characterized. For this purpose, a series of  $K_d$  and sorption/desorption kinetics experiments, using  $^{127}\text{I}$  as a tracer, was performed. The concentrations of iodine in a solution were measured by ICP-MS (inductively coupled plasma mass spectrometer). The distribution coefficient  $K_d$  for  $^{127}\text{I}$  in a cement-water system was determined.

## 2. Experiment

### 2.1. Materials

Solutions were made from reagent grade chemicals in deionized water prepared by the water purification system TKA LAB MICRO (conductivity  $0.055 \mu\text{S cm}^{-1}$ ;  $\text{TOC} < 10$  ppb). Polyethylene centrifuge tubes used in the batch sorption experiments were washed, left overnight in a solution of  $0.1 \text{ mol L}^{-1}$  HCl, and thoroughly rinsed with deionized water prior to use. For the sorption studies, concentration of KI in solution was  $3.15 \cdot 10^{-6} \text{ mol L}^{-1}$ . All experiments were carried out under ambient conditions, but the samples were protected from the sunlight to avoid photochemical reaction of the iodine species.

All batch experiments were performed in triplicate and all experimental data are the averages of triplicate determination. The relative errors of the data were about 10%.

### 2.2. Measurements

Measurements of  $^{127}\text{I}$  and major cation concentrations were carried out with an inductively coupled plasma sector field mass spectrometer (ELEMENT2, *Thermo Scientific*, Germany). All parameters regarding the ICP-SFMS (inductively coupled plasma sector field mass spectrometer) are shown in Table 1 below.

Table 1. General parameters of the ICP-SFMS.

ICP-SFMS	
Plasma power	1350 W
Cool gas	$14.00 \text{ L min}^{-1}$
Auxiliary gas	$0.7 \text{ L min}^{-1}$
Sample gas	$1.2 \text{ L min}^{-1}$
Sample time	0.05 sec
Spray chamber	Cyclonic
Nebulizer	X type, $400 \mu\text{L min}^{-1}$
Scan type	EScan
Sample and skimmer cones	Nickel

Measurements of the iodine speciation were carried out with the high pressure liquid chromatography (HPLC) system (Agilent 1100, Germany) coupled to an inductively coupled plasma sector field mass spectrometer ELEMENT2 equipped with a cyclonic spray chamber (*Glass Expansion*, Australia). All parameters regarding the ICP-SFMS and the sample introduction system are shown in Table 1.

The ion HPLC system was equipped with a ZORBAX SAX anion exchange column ( $4.6 \times 150 \text{ mm}$  5-Micron, *Agilent Technologies*, USA) and in addition we used a ZORBAX SAX guard column ( $4.6 \times 12.5 \text{ mm}$ ). Samples were injected with a 1 mL injection loop. Pre-cleaned 10 mL plastic syringes were used to fill the sample loop. Phthalic acid  $0.01 \text{ mol L}^{-1}$  6.5 pH solution was used as an eluent for this system. In the first step iodine was pre-concentrated on the column using only UPW (ultra pure water) (0–5 min) followed by the elution with  $0.01 \text{ mol L}^{-1}$   $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$  (5–10 min). The flow speed was  $1 \text{ mL min}^{-1}$ . Chromatographic data analysis software (Xcalibur, *Thermo Scientific*, Bremen, Germany) was used for the peak integration.

The redox potential (Eh) and pH of solutions were measured using the WTW pH-meter pH 315i with a combined glass/reference electrode calibrated against standard buffers pH 4 and pH 7 (HANNA pH standard buffer solutions, *Sigma-Aldrich Chemie*) with a measurement error of  $\pm 0.01$ .

### 2.3. SEM and XRD characterization

Commercial Portland cement (CEM II/A-LL 42.5 W, *Akmenės Cementas*, Lithuania) was used for iodine sorption/desorption experiments. The specific surface area of the cement was  $410 \text{ m}^2 \text{ kg}^{-1}$  [13]. The particle sizes of cement were determined with the SEM Helios NanoLab 650 (*FEI*, Netherlands). Based on the SEM analysis, particle sizes of cement were in the range of 3.06–87.90  $\mu\text{m}$ .

XRD analysis of Portland cement was performed by means of the X-ray diffractometer D8 Advance (*Bruker AXS*, Germany).

The peaks (Fig. 1) marked by [▼] correspond to the calcium silicate oxide in a cement sample. The peaks marked by [x] and [●] belong to the brownmillerite and calcium aluminum oxide, respectively.

Chemical composition of cement (Table 2) was determined with a fluorescent X-ray spectrometer with wave dispersion (WD-XRF) AxiosmAX (*PANalytical*, Netherlands) supplied with the software Omnia (*PANalytical*) for standard-less quantitative analysis.

The main components of cement obtained by X-ray fluorescence were CaO (68.57%),  $\text{SiO}_2$  (14.60%),  $\text{Fe}_2\text{O}_3$  (4.54%),  $\text{Al}_2\text{O}_3$  (3.28%), MgO (2.33%),  $\text{K}_2\text{O}$  (1.17%). The Ca/Si ratio in cement was found to be 0.14.

### 2.4. Preparation of HCP

HCP with the water/cement ratio  $W/C = 1:3$  was prepared in accordance with Tits et al. [18]. The samples of HCP were prepared in polyethylene centrifuge tubes

Table 2. Chemical composition of Portland cement (CEM II/A – LL 42.5 W).

Element	Concentration, %	Compound formula	Concentration, %
O	35.0	O	1.4
Na	0.1	$\text{Na}_2\text{O}$	0.2
Mg	1.4	MgO	2.3
Al	1.7	$\text{Al}_2\text{O}_3$	3.3
Si	6.9	$\text{SiO}_2$	14.6
P	0.03	$\text{P}_2\text{O}_5$	0.08
S	1.2	$\text{SO}_3$	3.1
K	1.0	$\text{K}_2\text{O}$	1.2
Ca	49.0	CaO	68.6
Ti	0.2	$\text{TiO}_2$	0.3
Cr	0.01	$\text{Cr}_2\text{O}_3$	0.02
Mn	0.05	MnO	0.07
Fe	3.2	$\text{Fe}_2\text{O}_3$	4.5
Ni	0.01	NiO	0.02
Cu	0.03	CuO	0.03
Zn	0.02	ZnO	0.03
Sr	0.1	SrO	0.1

under Ar conditions. Cement was mixed with deionized water (TKA LAB MICRO system, conductivity  $0.055 \mu\text{S cm}^{-1}$ ; TOC < 10 ppb) and left to hydrate at room temperature (relative humidity 70%) approximately for 4 months. A powder material was prepared by crushing the bulk material in a mortar under ambient conditions and then it was air-dried. Figure 2 shows the XRD pattern of hydrated Portland cement. The

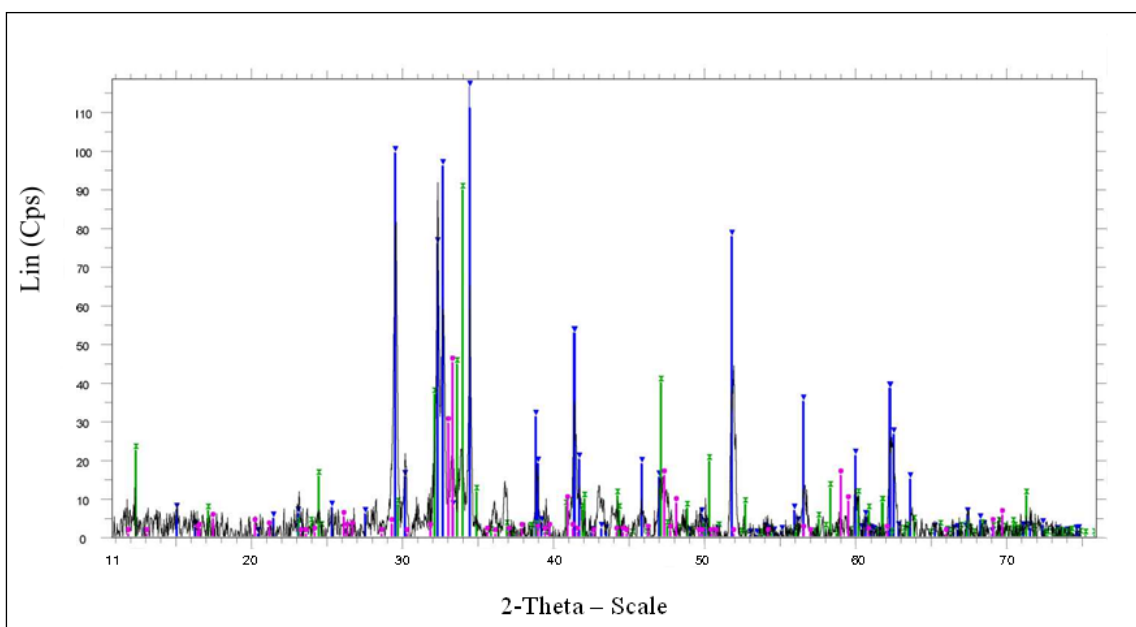


Fig. 1. XRD pattern of Portland cement ([▼] calcium silicate oxide –  $\text{Ca}_3(\text{SiO}_4)\text{O}$  – Rhombo.H.axes; [x] brownmillerite –  $\text{FeAlO}_3(\text{CaO})_2$  – orthorhombic; [●] calcium aluminum oxide –  $\text{Ca}_3\text{Al}_2\text{O}_6$  – orthorhombic).

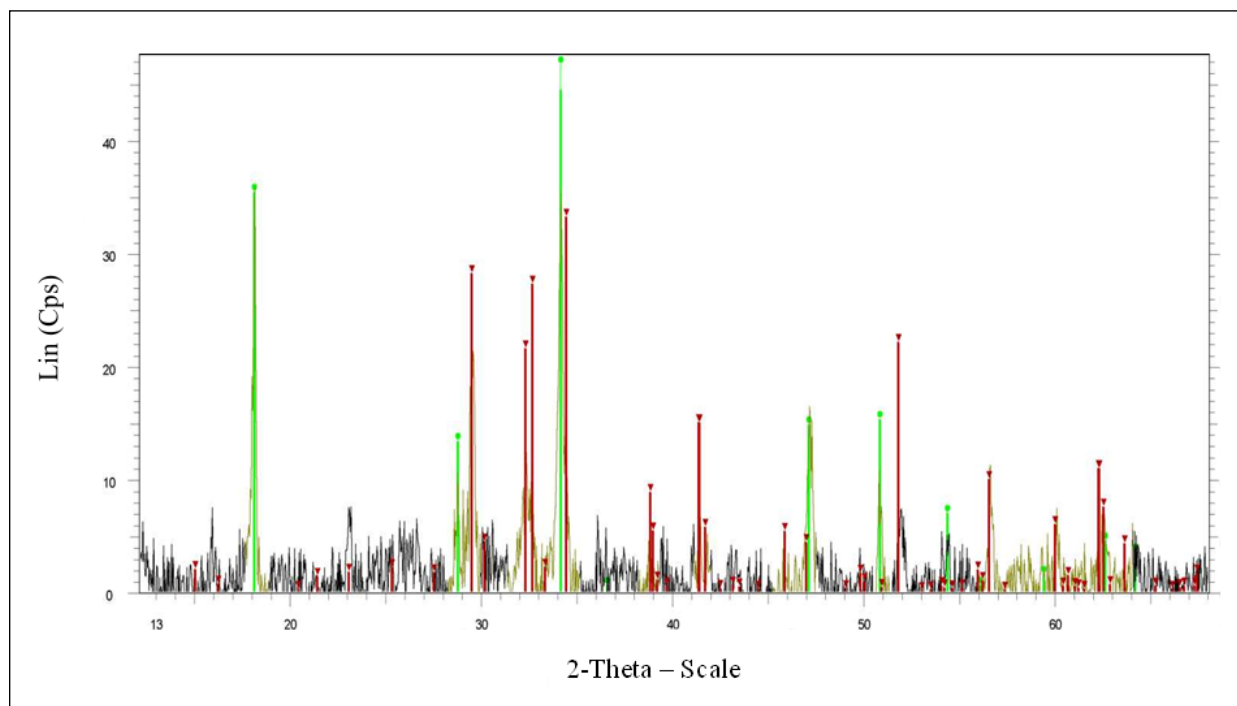


Fig. 2. XRD pattern of hydrated Portland cement ([●] portlandite, syn –  $\text{Ca}(\text{OH})_2$  – 34.15%, [▼] calcium silicate oxide –  $\text{Ca}_3(\text{SiO}_4)\text{O}$  – 23.05%).

peaks marked by [●] are the characteristics of portlandite ( $\text{Ca}(\text{OH})_2$ , 34.15%) and the peaks marked by [▼] correspond to calcium silicate oxide ( $\text{Ca}_3(\text{SiO}_4)\text{O}$ , 23.05%) in a cement sample.

### 2.5. Preparation of cement pore water

In order to retard the degradation of cement during the batch experiment cement pore water (CPW) was prepared using a method reported by Tits et al. [1]. One gram of hydrated cement powder was added to 25 mL of deionized water to obtain a solid to liquid (S/L) ratio of  $0.04 \text{ g mL}^{-1}$ . The suspensions were mixed for 2 weeks on an end-over-end shaker. Liquid phase separation was achieved by centrifuging the samples for 1 hour at 5000 rpm on an Eppendorf (Germany) centrifuge.

The main elements in the solution equilibrated with cement were: Ca 93.40%, Fe 2.31%, Sr 2.17%, Na 1.35%, Ba 0.44%, Ti 0.30%, Si 0.02%.

### 2.6. Procedures

Batch experiments were conducted to determine the distribution coefficient  $K_d$  for iodine in cement under alkaline conditions. All the experiments were carried out under ambient conditions. Both  $K_d$  and sorption kinetics studies were performed in two series of experiments, with/without a reducing agent  $5 \cdot 10^{-3} \text{ mol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_4$ . All experiments were done in plastic 50 mL

vials to prevent iodine sorption by walls. Deionized water and CPW were used as working solutions. Sorption of iodine on hydrated HCP was investigated using three slightly different approaches. In the first one ( $K_d$  experiment, batch I), 25 mL of deionized water was added to 1 g of powdered HCP, and the suspensions were shaken for 2 weeks in an end-over-end shaker. Then, iodine ( $\text{I}^-$ ) was added from a stock solution (KI, Merck) to reach the concentration of  $3.15 \cdot 10^{-6} \text{ mol L}^{-1}$ . The suspensions were thoroughly stirred, and the pH/Eh value was monitored, the vials were corked up, and allowed to shake for 7 days. After equilibration, an aqueous phase was separated and the concentration of iodine was measured with ICP-SFMS.

In the second series of experiments (batch II), 1 g of powdered HCP was mixed with 25 mL of CPW,  $3.15 \cdot 10^{-6} \text{ mol L}^{-1}$  of iodide was added and the suspensions were shaken for 7 days. The third series of experiments (batch III) were performed in parallel with the batch II experiment but using deionized water. The set of duplicate experiments was performed with reductant  $\text{Na}_2\text{S}_2\text{O}_4$  ( $5 \cdot 10^{-3} \text{ mol L}^{-1}$ ).

All sorption kinetic experiments were carried out according to the same scheme as mentioned above within 1, 2, 6, 14, 42 days.

For desorption experiments, the suspensions of cement were centrifuged (5000 rpm, 30 min) at the end of the sorption experiments. The residual cement

was poured with deionized water. Then the suspensions were stirred in an end-over-end shaker and centrifugation was done under the same conditions as in the sorption experiment.

### 2.7. Calculations

The amount of iodine sorbed on cement and the distribution coefficient  $K_d$  were calculated from the following equations [15]:

$$\text{Sorption } \% = \frac{C_0 - C_{\text{eq}}}{C_0} \times 100\%, \quad (1)$$

$$K_d = \frac{C_0 - C_{\text{eq}}}{C_{\text{eq}}} \times \frac{V}{m}, \quad (2)$$

where  $C_0$  is the initial concentration of iodine,  $C_{\text{eq}}$  is the final concentration of iodine in a supernatant after centrifugation,  $m$  is the mass of cement,  $V$  is the volume of aqueous phase.

## 3. Results and discussion

The pH/Eh was measured regularly at the beginning of the experiment, and then at the end of the experiment. The pH ranged between 12.2 and 12.5 throughout the experiment in all batch systems; the initial Eh of the suspensions was  $-313$  mV, during the first 24 hours it decreased to  $-328$  mV and remained relatively stable during the course of the experiment. Constant pH value of  $>12$  indicates pH buffering by portlandite ( $\text{Ca}(\text{OH})_2$ ) [20, 21], which was formed in cement (34.5%; Fig. 2)

after 4 months of hydration. The pH evolution during cement degradation was shown by Jacques et al. [6], who found that pH higher than 12.5 of the pore water of cement was related to high concentrations of  $\text{Na}^+$  and  $\text{K}^+$  ions. The dissolution of portlandite reduces pH of cement pore water to 12, eventually the pH of 10 or lower than 10 is controlled by different cement phases (e. g. C-S-H, calcite).

HPLC analysis of iodine shows that the iodine speciation remained unchanged in the solution during the experiment. Figure 3 presents the iodine speciation within the batch I experiment. From Fig. 3 one can see that after 42 days in the pH range from 12.2 to 12.5 iodide was iodine species. This result is consistent with similar results observed by other authors, e. g. Kaplan et al. [22]. However, under highly elevated oxidizing and basic conditions, iodate may also exist [14], but our experiments showed that ambient experimental conditions inhibited the alteration of iodine speciation.

The effect of addition sequences on iodine sorption on HCP was studied. The addition sequence is different in equilibrating HCP with deionized water for an appropriate period of time and then adding iodide (batch I experiment); spiking iodide to CPW/deionized water and then adding powdered HCP (batch II and III experiments). The results indicated that the sorption of iodine on HCP under experimental conditions was not influenced by the addition sequence. The graphic image of sorption kinetics of iodine on HPC is shown in Fig. 4.

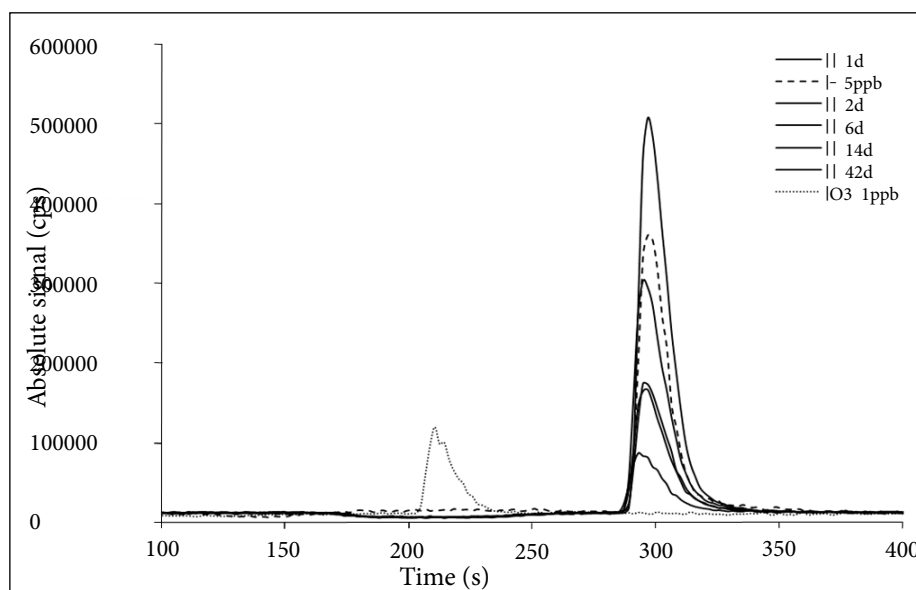


Fig. 3. Iodine aqueous species in solution equilibrated with hydrated HCP (batch I, pH 12.18–12.50;  $-313$  mV  $< Eh < -328$  mV) within 42 days of the batch experiment (the height of the iodide peaks corresponds to the labels order in the legend).

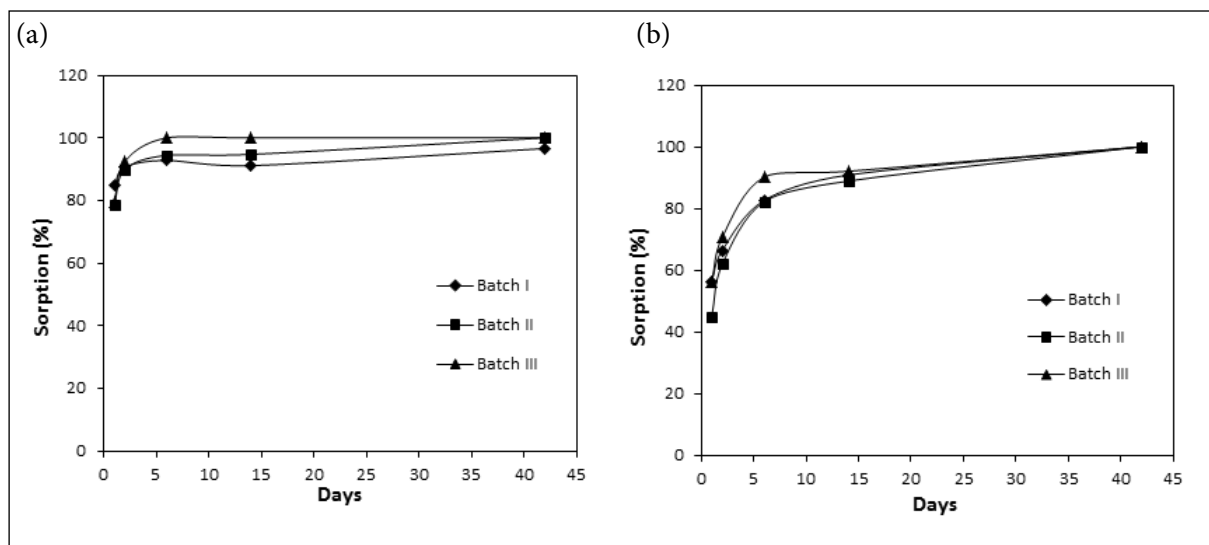


Fig. 4. Kinetics of iodine ( $I^-$ ) sorption on HCP: (a) pH 12.18–12.50,  $c(I^-) = 3.15 \cdot 10^{-6} \text{ mol L}^{-1}$ ,  $m/V = 0.04 \text{ g mL}^{-1}$ ; (b) pH 12.18–12.50,  $c(I^-) = 3.15 \cdot 10^{-6} \text{ mol L}^{-1}$ ,  $m/V = 0.04 \text{ g mL}^{-1}$ ,  $5 \cdot 10^{-3} \text{ mol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_4$ .

The sorption of iodine on hydrated cement was mainly attained within one day (24 hours) in the batch experiments without reductant, while the steady value of sorption was achieved during 42 days (Fig. 4(a)). The results of the sorption of iodine in the presence of reductant indicate that the uptake process was not so fast, but equilibrium was achieved within 42 days as well (Fig. 4(b)). More detailed results of the sorption, based upon the calculations (Eq. 1), are given in Table 3.

By comparing the results of both types of sorption experiments (with/without reductant, Table 3), the sorption of iodine on HCP under the investigation conditions (pH 12.2–12.5) was slightly different. The results showed that after one day 45–56% of iodine, when in a reduced form as iodide ( $I^-$ ), was immobilized in cement. Hereinafter the amount of iodide in an aqueous phase decreased exponentially till it was completely removed from the solution within 42 days. The results obtained in the batch experiments without a reductant show that the bulk amount of iodine was also removed from the solution after one day of

its interaction with HCP but sorption of iodine was slightly higher (79–85%). Because the HPLC analysis of iodine shows that the iodine speciation remained unchanged in the solution during the experiment, the result of sorption experiments lets one to consider that an alteration of the iodine speciation may occur on the boundary layer of cement and this alteration influenced the iodine behaviour in HCP.

The experiments were conducted in order to obtain the  $K_d$  values of iodine species in the cement system under the given experimental conditions (equilibration time = 7 days). The  $K_d$  values (Eq. 2) of iodine were obviously higher in the batch experiment without a reductant, and they ranged from  $172 \text{ mL g}^{-1}$  in the batch II experiment to  $203 \text{ mL g}^{-1}$  and  $1095 \text{ mL g}^{-1}$  in the batch I and batch III experiments, respectively. The  $K_d$  values of iodine in the experiment with a reductant were 83, 85 and  $92 \text{ mL g}^{-1}$  in the batch I, batch II and batch III experiments, respectively. The obtained results allow supposing that chemical speciation of iodine has influence on the interaction of iodine with cementitious materials under hyperalkaline conditions.

Table 3. Percentage of iodine sorption on hardened cement paste (HCP) in the batch systems with/without reductant  $5 \cdot 10^{-3} \text{ mol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_4$ .

Sorption time, days	Sorption, % ( $I^-$ , without reductant)			Sorption, % ( $I^- + 5 \cdot 10^{-3} \text{ M Na}_2\text{S}_2\text{O}_4$ )		
	Batch I	Batch II	Batch III	Batch I	Batch II	Batch III
1	$85 \pm 9$	$79 \pm 9$	$80 \pm 9$	$56 \pm 7$	$45 \pm 7$	$56 \pm 7$
2	$91 \pm 10$	$90 \pm 9$	$93 \pm 10$	$66 \pm 8$	$62 \pm 8$	$71 \pm 8$
6	$93 \pm 10$	$94 \pm 10$	<MDL*	$83 \pm 9$	$82 \pm 9$	$90 \pm 10$
14	$91 \pm 10$	$95 \pm 10$	<MDL	$91 \pm 10$	$89 \pm 9$	$92 \pm 10$
42	$97 \pm 10$	<MDL	<MDL	<MDL	<MDL	<MDL

\* Method Detection Limit.

The reversibility of the iodine uptake by HCP was tested in the desorption experiment. Desorption was started within the first 6 days and a steady state in the iodine desorption was attained within 42 days (Fig. 5).

The percentage of iodine leached out from HCP throughout the experiment suggested its very strong binding with cementitious materials. The amount of iodine obtained in solutions after leaching did not exceed 1–3% within 42 days. Moreover, the results indicate that the amount of desorbed iodide (batch experiment with  $\text{Na}_2\text{S}_2\text{O}_4$ ) was approximately two times higher than that of iodine in the batch experiment without a reducing agent.

Evans et al. [7] in the review summarizes the literature data of the binding mechanisms of different radionuclides to cement and states that sorption and/or lattice incorporation is the main mechanism of the iodine uptake in cement. According to Ojovan et al. [23] physical adsorption is a significant factor for immobilization of radionuclides by cement. Sorption mechanisms depend on the chemical speciation of the radionuclide, and the chemical and physical forms of solid phase [7].

Our sorption/desorption batch-type experiments have shown that iodine immobilization in hydrated

HCP strongly depends on the chemical speciation of iodine.  $K_d$  values obtained in the experiment without a reductant are from 2 to 11 times higher than those in the batch experiment with a reductant. In addition, desorption experiments showed that iodide was easily leached out from cement (~2–3%) in comparison with iodine (~1%) leached out from cement in the batch experiment without a reductant. These results confirmed the lesser affinity of cement phases for  $\text{I}^-$  versus other speciation of iodine [12–14, 19]. For example, the published data indicate that cement has much stronger affinity for iodate than iodide because of a more complex structure of the iodate anion with the surrounding oxygen acting as bridges with the complex cement substrate [7]. As Atkins et al. [24] propose, greater affinity of cement phases for  $\text{IO}_3^-$  over  $\text{I}^-$  is because of direct bonding between CSH and  $\text{IO}_3^-$  or for the precipitation of  $\text{Ca}/\text{IO}_3^-$  containing solid phases. However, the investigation of iodine species ( $\text{IO}_3^-/\text{I}^-$ ) uptake by HCP and a CSH phase under highly alkaline conditions, studied by *K*-edge X-ray absorption spectroscopy, showed that CSH was not the phase controlling  $\text{IO}_3^-$  uptake in HCP [14].

The investigations of iodine speciation in solution equilibrated with HCP showed that no changes of iodine oxidation state occurred within 42 days

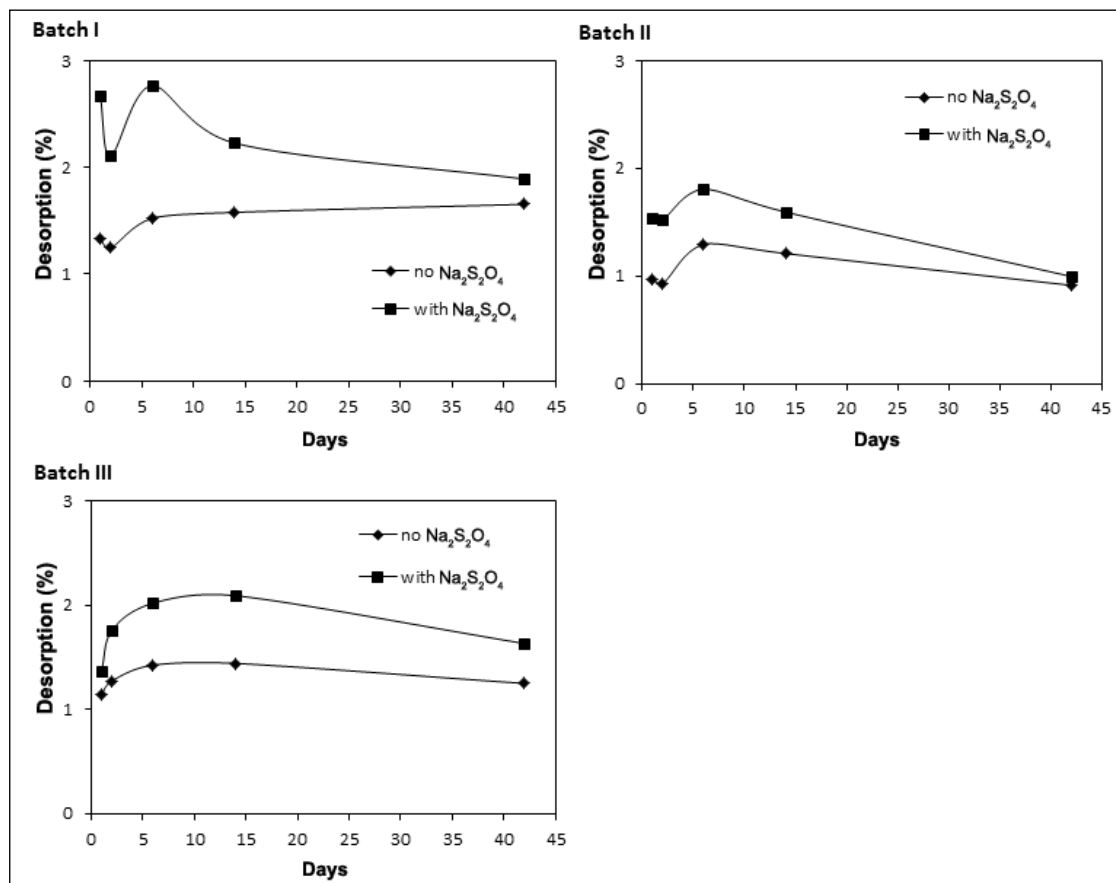


Fig. 5. Kinetics of iodine desorption from HCP with deionized water within 42 days.

of experiments. The obtained results allow supposing that the alteration of iodine speciation can occur in the lattice of cement and leads to formation of solubility-limiting phases by reaction with cement components. In addition, immobilization of iodine by cement under alkaline conditions could result from the substitution of  $\text{SO}_4^{2-}$  by  $\text{I}^-$  [24] or adsorption by oxides and metal hydroxides because of their high zero points of charge (ZPC). Iron and aluminum oxides are distinguished for adsorption of anionic species [25]. Portland cement used in our batch experiments is mainly composed of CaO (68.6%) and  $\text{SiO}_2$  (14.6%) as calcium silicate oxide,  $\text{Ca}_3(\text{SiO}_4)\text{O}$ , and calcium aluminum oxide,  $\text{Ca}_3\text{Al}_2\text{O}_6$ . After hydration 34.1% of portlandite,  $\text{Ca}(\text{OH})_2$ , and 23.0% of calcium silicate oxide,  $\text{Ca}_3(\text{SiO}_4)\text{O}$ , were obtained in hardened cement paste (HCP). In our experiment portlandite is responsible for the alkalinity of HCP suspension. We suppose that incorporation of iodine to cement may occur because of replacing the  $\text{OH}^-$  by  $\text{I}^-$  and formation of a new hydrate [16]. Based on these observations the mechanisms of sorption of iodine by cement under oxidizing highly alkaline conditions remain ambiguous, therefore, further comprehensive structural and chemical analysis is necessary to obtain the knowledge of iodine sorption mechanisms.

#### 4. Conclusions

The present experimental work studied the iodine uptake by hardened cement paste under highly alkaline aerobic conditions. The sorption of iodine by cement is governed by its speciation. HPLC analysis of the iodine shows that the iodine speciation remained unchanged in the solution during the experiment. The results of sorption experiments showed that after one day of the experiment 45–56% of iodine, when in a reduced form as iodide ( $\text{I}^-$ ), and 79–85% of iodine in the batch experiments without a reductant were immobilized in HCP. The obtained results allow supposing that the alteration of iodine speciation can occur in the lattice of cement and leads to formation of solubility-limiting phases by reaction with cement components.  $K_d$  values obtained in the experiment without a reductant are from 2 to 11 times higher than those in the batch experiment with a reductant. Strong binding of iodine with cementitious materials was demonstrated by the desorption experiment. The amount of iodine obtained in the solutions after leaching did not exceed 1–3% within 42 days.

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## RADIOAKTYVIŪJŲ ATLIEKŲ KIETINIMAS CEMENTU: JODO JUNGTTIS SU BETONU STIPRIAŠ ŠARMINĖJE APLINKOJE

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### Santrauka

Radioaktyviųjų atliekų saugyklų inžinerinių barjerų funkcija – užtikrinti ilgalaikį ir saugų pavojingų atliekų laikymą užkertant kelią nekontroliuojamam radionuklidų sklidimui į aplinką. Potencialus radionuklidų sklidimas per saugyklų inžinerinius barjerus gali atsirasti dėl oksiduojančio / redukuojančio aplinkos poveikio ir dėl to susidarančių radioaktyviųjų elementų cheminių savybių pokyčių. Radioaktyviųjų elementų sulaikymas kietinančioje matricoje yra svarbi sąlyga, leidžianti užtikrinti efektyvų radioaktyviųjų atliekų saugojimą.

Darbe buvo tiriama jodo ( $^{127}\text{I}$ ) sorbcijos į hidratuotą cementą ir išplovimo iš jo kinetika, proceso priklausomybė nuo elemento cheminės formos stipriai šarminėje ( $\text{pH} > 12$ ) terpėje naudojant / nenaudojant reduktorių  $\text{Na}_2\text{S}_2\text{O}_4$ . Nustatytas jodo pasiskirstymo tarp kietos ir skystos fazės koeficientas ( $K_d$ ). Eksperimentinėje sistemoje be reduktoriaus jodo  $K_d$  kito 172–1095  $\text{mL g}^{-1}$  ribose, sistemoje su reduktoriumi jodido ( $\text{I}^-$ )  $K_d$  siekė 83–92  $\text{mL g}^{-1}$ .

Eksperimento rezultatai rodo, kad stipriai šarminėje aplinkoje jodas yra efektyviai fiksuojamas cemento matricoje ir jo sorbcija priklauso nuo jodo oksidacijos laipsnio.