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Reactivity of nitrate and organic acids at the concrete–bitumen interface of a nuclear waste repository cell

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H I G H L I G H T S

- Interactions of cement paste and organic acid–nitrate solutions were investigated.
 - Cement leaching imposed alkaline pH (>10) very rapidly in the liquid media.
 - Acetic acid action on cement paste was similar to that of classical leaching.
 - Oxalic acid attack formed Ca-oxalate salts; organic matter in solution decreased.
 - Nitrate was stable under abiotic conditions and with organic matter.
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A B S T R A C T

This study investigates the fate of nitrate and organic acids at the bitumen–concrete interface within repository cell for long-lived, intermediate-level, radioactive wastes. The interface was simulated by a multiphase system in which cementitious matrices (CEM V cement paste specimens) were exposed to bitumen model leachates consisting of nitrates and acetic acid with and without oxalic acid, chemical compounds likely to be released by bitumen. Leaching experiments were conducted with daily renewal of the solutions in order to accelerate reactions. The concentrations of anions (acetate, oxalate, nitrate, and nitrite) and cations (calcium, potassium) and the pH were monitored over time. Mineralogical changes of the cementitious matrices were analysed by XRD. The results confirmed the stability of nitrates in the abiotic conditions of the experiments. The action of acetic acid on the cementitious matrix was similar to that of ordinary leaching in the absence of organic acids (i.e. carried out with water or strong acids); no specific interaction was detected between acetate and cementitious cations. The reaction of oxalic acid with the cementitious phases led to the precipitation of calcium oxalate salts in the outer layer of the matrix. The concentration of oxalate was reduced by 65% inside the leaching medium.

1. Introduction

In France, a significant fraction of long-lived, intermediate-level, radioactive wastes (bituminous wastes) consist of a mixture of inorganic salts immobilised in a bitumen matrix. They are poured in cylindrical steel containers called primary packages. Depending on the disposal concept, these containers are grouped into cuboid reinforced concrete overpacks. These secondary packages

are then placed inside waste cells built at a depth of 450–550 m within a Callovo-Oxfordian clay rock formation, using significant amounts of additional concrete (i.e. lining, shotcrete) (Andra, 2005).

After closure of the cells, water resaturation that probably fills the waste cells from the bottom up (bathtub effect), reaching near-saturation within a few thousand years, should enhance the release of chemical species. Among the compounds probably released into the interstitial aqueous medium are soluble salts (notably nitrates) and organic matter such as organic acids, phenols, etc. contained within the bituminous matrix (Walczak et al., 2001), together with gas (mostly H₂) produced via radiolysis of organic matter and/or anaerobic steel corrosion (black and stainless steel present in primary containers and concrete reinforcement).

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Table 1
CEM V/A cement composition. I.o.i.: loss on ignition.

	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	TiO ₂	Na ₂ O	K ₂ O	MnO	SO ₃	I.o.i.
CEM V/A 42.5 N	46.4	30.0	11.2	3.6	2.8	0.6	0.2	1.2	0.1	2.8	2.1

The presence of nitrates in the vicinity of waste packages may result in oxidising conditions favourable to the mobility of a series of radionuclides (Se, U, Tc, Pu, Np, etc.) [Albrecht et al. \(2013\)](#). However, in the geochemical conditions prevailing in the cell, different redox reactions are likely to occur, including nitrate reduction driving the system back to a reducing environment favourable to safe repository. Reduction of nitrate (NO₃⁻) may occur (i) from abiotic processes, with iron from the steel and/or H₂ acting as electron donors, and surface catalysis provided by the different types of steel and corrosion products present in the waste cell, and/or (ii) from biological catalysis through bacterial activity. The reactions may lead to the formation of nitrite (NO₂⁻), gaseous nitrogen (N₂) and/or ammonium (NH₄⁺), depending on a variety of parameters not yet well understood, particularly in concrete-dominated systems ([Devlin et al., 2000](#); [Truche et al., 2013a,b](#); [Alquier et al., 2014](#); [Libert et al., 2011](#); [Bertron et al., 2013](#)). Both types of reactions (abiotic and biotic) involve electron donors and numerous inorganic and organic candidates are available in the waste cell or in the host rock (organic acids, H₂, zero-valent metals, etc.) [Albrecht et al. \(2013\)](#). All reactions occur in an environment influenced by the alkaline conditions imposed by the concrete phases. The overall project, of which this paper is a part, aims to investigate the reduction of nitrates within a system comparable to a “real” waste-cell where bacterial activity is likely to occur (denitrifying alkaliphilic bacteria) and notably to determine the phenomenology and kinetics of reactions and the role of the electron donor (i.e. organic acids released by bitumen, such as acetic or oxalic acids) in the reactions ([Alquier et al., 2012, 2013, 2014](#)).

However, previous studies have shown that strong interactions occur between cementitious materials and organic acids ([Bertron et al., 2005a,b](#); [Bertron et al., 2007](#); [Larreur-Cayol et al., 2011a,b](#); [Oueslati and Duchesne, 2012](#); [Bertron and Duchesne, 2013](#)). These reactions could modify not only the bioavailability of organic matter – and thus influence the reactivity of nitrates under biotic conditions – but also the composition of the concrete and its ability to buffer the chemical system (i.e. pH).

An important prerequisite was therefore to investigate the interactions of organic acids with the cementitious matrix in the presence of nitrates under aerobic conditions and without bacteria. Reactions and the related equilibria of multiphase systems representative of the bitumen–concrete interface were investigated in simplified batch systems and in short term experiments. CEM V paste specimens were immersed in solutions made of acetic and/or oxalic acids and nitrates that simulated bitumen model leachates. Changes in the cement pastes and liquid phase compositions were investigated.

2. Materials and methods

2.1. Materials

2.1.1. Cement pastes

The specimens were CEM V/A 42.5 (S-V) N CE PM-ES-CP1 cement pastes (slag and fly ash cement from the Airvault Calcia factory, chemical composition given in [Table 1](#)) with a water/cement ratio of 0.40. They were cast in cylindrical plastic moulds 50 mm high and 27 mm in diameter (volume = 28.6 cm³ and surface area = 53.9 cm²) without demoulding oil and were vibrated to evacuate air voids. The specimens were taken out of their moulds 24 h after pouring and stored in water at 20 °C for 28 days. They were then subjected to

the leaching tests described below. In parallel, some control specimens were kept in water at 20 °C.

2.1.2. Bitumen model leachate solutions

Uncertainties remain on the release of organic and inorganic matter by bitumen–salt mixtures. Experimental studies have shown that the degradation of bitumen gives rise to the release of organic matter (naphthalene, alcohols, linear carboxylic acids, aromatics and glycols) and salts (NaNO₃, Na₂SO₄, etc.) ([Walczak et al., 2001](#); [Van Loon and Kopajtic, 1990](#); [Libert and Walczak, 2000](#); [Nakayama et al., 2003](#); [Marien et al., 2008](#); [Walczak, 2000](#); [Kagawa et al., 2000](#)).

On the basis of this literature data, leaching of bitumen was simulated by aqueous solutions made of organic acids and nitrates. Linear carboxylic acids were considered (i) since they are easily assimilated by ([Ma et al., 2012](#); [Daniel et al., 2007](#)) and (ii) because of their probable strong interactions with cement phases. Experiments of bitumen degradation by water uptake and/or radiolysis have shown the presence of acetic, formic and oxalic acids in the leachates ([Walczak et al., 2001](#); [Van Loon and Kopajtic, 1990](#); [Walczak, 2000](#); [Kagawa et al., 2000](#)). Among experimental parameters influencing the quantity and nature of acids are: pH of the leaching solution, irradiation, temperature and duration of experiment and presence or lack of oxygen. In leaching experiments performed at ambient or moderate temperature (≤45 °C), concentrations of acids of the order of ten milligrams per litre have been found in the leachates. Oxalic acid was notably detected after radiolysis of bitumen in the presence of oxygen; in coherence with experiments yielding oxalate production during irradiation of formic acid under oxygen. [Van Loon and Kopajtic \(1990\)](#) concluded that the production of oxalate in the absence of oxygen was questionable. Oxygen initially present in the waste cells after closure will be rapidly consumed either reacting with components of the clay host rock or with metals present in the reinforced concrete, but it must be kept in mind that the waste containers will be stored for several decades in an oxygen-bearing atmosphere.

Calcium salts of formic and acetic acids being highly soluble in water ([Lange and Dean, 1985](#)), it is likely that both acids have similar effects on the cementitious matrix ([Bertron and Duchesne, 2013](#)). In contrast, calcium oxalate salts are only slightly soluble in water ([Seidell, 1919](#); [Streit et al., 1998](#)) and are thus likely to be produced during the attack of cementitious matrix by oxalic acid. Acetic and oxalic acids were therefore considered in the present study.

Two types of model leachate solutions were considered. The first type was made of acetic acid (0.50 mM to 30 mg/L) and sodium nitrate (32.3 mM). The initial pH of this solution, noted as N + OA1, was 4. The second type was a mix of acetic acid (0.33 mM), oxalic acid (0.17 mM) (same total concentration of acids of 0.50 mM) and sodium nitrate (32.3 mM). The pH of this solution, noted as N + OA2, was 3.6. The nitrate concentration (32.3 M) was only an estimate of the likely concentration in a waste cell (results of coupled chemical and transfer modelling) ([Sercombe et al., 2006](#); [Gwinner et al., 2006](#)). [Table 2](#) summarises the composition of the test solutions.

2.2. Experimental set-up and leaching process

The experimental device is shown in [Fig. 1](#). Batch systems were implemented.

Table 2
Compositions of bitumen model leachates.

Solutions	Concentration					pH	
	Acetic acid		Oxalic acid		Nitrate NO ₃ ⁻		
	mg/L	mM	mg/L	mM	mg/L		mM
N+OA1	30	0.50	–	–	2000	32.3	4.0
N+OA2	20	0.33	15	0.17	2000	32.3	3.6

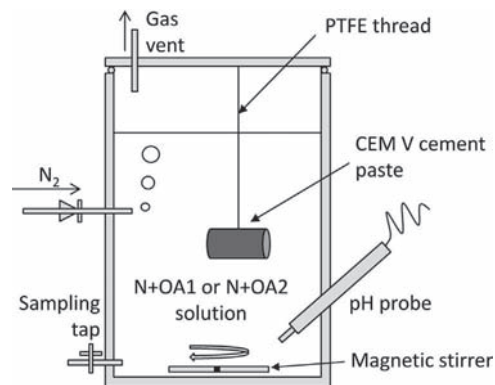


Fig. 1. Experimental set-up.

The reactor, filled with 1 L of nitrate and organic acid solution (N+OA1 or N+OA2) was equipped with an outlet for solution sampling, a gas inlet with check valve (used for N₂ bubbling to impose anoxic conditions inside the reactor similar to those that will prevail inside a repository cell), a gastight tap for a pH probe, and a hermetically closed lid fitted with a gas vent.

The pH probe was connected to a data acquisition system (Consort, D230 Data Acquisition System, v1.1.13). The solution in the reactor was continuously stirred using a magnetic barrel. The cement paste specimen was suspended in the solution by a PTFE thread. The solid/liquid volume ratio was about 3% (similar to that implemented in the biotic part of the study (Alquier et al., 2012)). The experimental device was kept in an air-conditioned room (20 °C) during the whole experiment.

N+OA1 (acetic acid 0.5 mM; NO₃⁻ 32.23 mM) and N+OA2 (acetic 0.33 mM and oxalic 0.17 mM acids; NO₃⁻ 32.23 mM) solutions were renewed daily for 5 days. These short term experiments were chosen because the key phenomena impacting bacterial reaction (explored in the biotic part of the overall study of which this paper is part of (Alquier et al., 2013, 2014)) occur in the very short term of the experiment (because of the very severe conditions rapidly imposed by the cementitious materials in the liquid medium). Moreover, it should be noted that these short term leaching experiments were favoured with the view to limit the severity of the media and ensure microbial growth (and thus microbial activity) in the corresponding biotic testing (Alquier et al., 2013, 2014).

Table 3
HPIC test conditions.

	Eluant (1 mL/min)	Precolumn	Chromatographic column	Suppressor
Anions	KOH (1 × 10 ⁻³ mol/L) elution gradient: 10% mobile phase to 60% mobile phase in 25 min	NG1 (4 mm × 50 mm, Dionex) + IonPac AG11-HC (4 mm × 50 mm, Dionex)	IonPac AS11-HC (4 mm × 250 mm, Dionex)	ASRS 300 (4 mm, Dionex) + CRD 200 (4 mm, Dionex)
Cations	Methylsulfonic acid (30 × 10 ⁻³ mol/L) isocratic (30 min)	NG1, (4 mm × 50 mm, Dionex) + IonPac CG16 (4 mm × 50 mm, Dionex)	IonPac CS16 (4 mm × 250 mm, Dionex)	Suppressor CSRS 300 (4 mm, Dionex)

Table 4
Detection and quantification limits (DL and QL) of ions (μmol/L) (S/N = Signal/Noise).

	Acetate	Oxalate	Nitrite	Nitrate	Potassium	Calcium
DL (3 < S/N)	0.68	0.79	1.74	2.42	0.402	0.764
QL (10 < S/N)	2.04	2.61	6.09	8.06	1.339	2.546

During the first day of exposure, the solution was sampled 4 times (20–25 mL each sample). The solid/liquid ratio changed very little. On days 2–5, a liquid sample was taken from the solution just before renewal. Concentrations of Ca, K, acetate, nitrate and nitrite were measured on each sample.

Control experiments were carried out to investigate the possible sorption of nitrates on the cement paste in the same conditions (NO₃⁻ 32.3 mM, solid/liquid ratio 3%, duration of the experiment: 15 days with no renewal of the solution). No decrease of nitrate concentration was observed in the solution. Moreover, the cementitious specimens were rinsed three times and the rinsing solutions were analysed by HPIC to determine nitrate and nitrite concentration. The concentrations were lower than the detection limits of the equipment (Table 3).

2.3. Analytical methods

2.3.1. Methods for determining ion concentrations of solutions

Concentrations of anions (acetate, oxalate, nitrate and nitrite) and of cations (calcium and potassium) were measured by High Performance Ion Chromatography (HPIC) coupled to a conductimetric detector fitted with chemical suppressor (Dionex ICS-2000 and ICS-3000). The analytical conditions are summarised in Table 3.

Quantification was performed by external calibration over the concentration range 1–40 mg/L with a regression coefficient of 0.999 calculated from peak areas. Repeatability was assessed on 5 injections and was better than 98%. Bias error was between 5 and 10%. The detection limit (defined as injected quantity giving a signal/noise ratio of 3) and quantification limit (defined as injected quantity giving a signal/noise ratio of 10) were calculated for each compound (Table 4).

Liquid samples were filtered at 0.2 μm (Minisart PES, Fisher Scientific) to remove suspended solid matter.

2.3.2. Mineralogical analyses of cementitious specimens

To explore the mineralogical changes, cement paste samples were analysed by X-Ray diffraction (Siemens D5000; copper cathode; anode voltage 40 kV; current strength 30 mA) after the leaching tests. The measurements were performed according to the distance inwards from the plane cylinder surface in contact with the solutions. The first analysis was made on the plane external face of the specimen, which was then abraded with a polishing disc and subjected to the next analysis. The depth of analysis was measured using a calliper square. The last analysis, which was on the core of the specimen, was carried out at a depth of 5 mm (after the specimen had been sawn perpendicularly to its axis). A control specimen was also analysed 5 weeks after pouring.

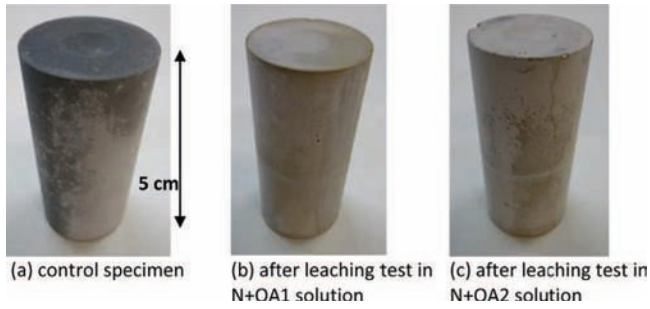


Fig. 2. Macroscopic observation of the cement paste specimens. (a) Control specimen kept in water, (b) specimen after 5 days of leaching by N+OA1 (acetic acid 0.50 mM, nitrate 32.3 mM) solution and (c) specimen after 5 days of leaching by N+OA2 (acetic 0.33 mM and oxalic 0.17 mM acids, nitrate 32.3 mM) solution.

3. Results and discussion

3.1. Macroscopic observations

The cementitious matrix, initially grey, had turned to a yellowish colour at the end of the leaching experiments (Fig. 2). This is characteristic of the leaching of a cementitious matrix by acidic solutions where Fe(III) of hydrated and/or anhydrous phases precipitates in the form of orangey-coloured iron hydroxide. In CEM V-type anhydrous cement, iron is contained in fly ashes and in the C₄AF-phase (brownmillerite) of clinker. Iron-bearing phases of cement hydrate more slowly than silico-calcic phases. In a hydrated cementitious matrix, iron is found in anhydrous residual phases and as partial substitution in hydrates. The outer layer of leached CEM I and CEM V pastes is enriched in iron (relative enrichment) (Bertron et al., 2007; Moudilou, 2000; Pavlík, 1994). Iron in the outer layer is probably contained in residual anhydrous fly ashes, in C₄AF (this phase is more resistant to leaching than other hydrated and anhydrous phases of Portland matrix (Bertron et al., 2005a) and in the silica gel, issued from leached calcium silicate hydrates (main hydrated phase of cementitious matrices).

3.2. Composition and pH of the test solutions

Concentrations of K⁺ and Ca²⁺ of N+OA1 and N+OA2 solutions in cement paste immersion tests are shown versus time in Figs. 3 and 4. Concentrations of OH⁻ ions, calculated from continuous measurement of pH are also represented. Concentrations of

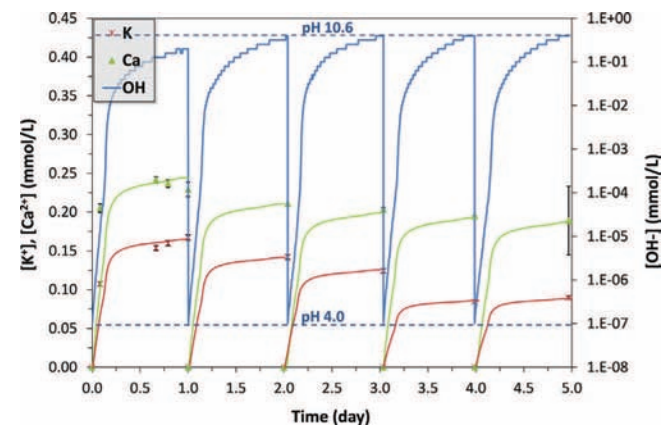


Fig. 3. Concentrations of K⁺, Ca²⁺ and OH⁻ in N+OA1 (acetic acid 0.50 mM; nitrate 32.3 mM) leaching solution. The solution was renewed daily. Solid area/liquid volume ≈ 50 cm²/L. Concentration of OH⁻ was calculated from the pH values. For days 2–5, variations of K and Ca concentrations are based on the final concentration and an evolution similar to day 1.

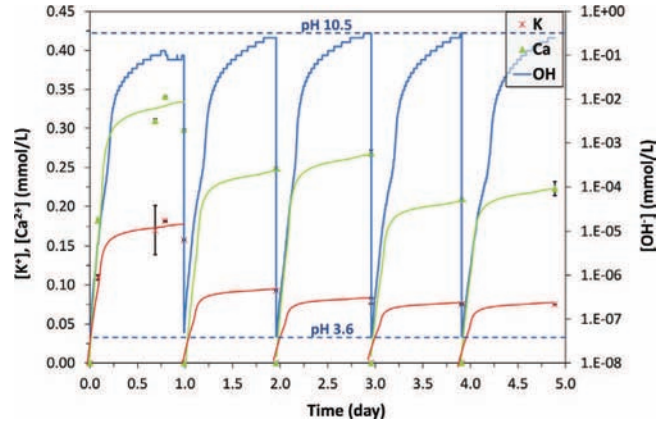


Fig. 4. Concentrations of K⁺, Ca²⁺ and OH⁻ in N+OA2 (acetic 0.33 mM/oxalic 0.17 mM acids; nitrate 32.3 mM) leaching solution. The solution was renewed daily. Solid area/liquid volume ≈ 50 cm²/L. Concentration of OH⁻ was calculated from the pH values. For days 2–5, variations of K and Ca concentrations are based on the final concentration and an evolution similar to day 1.

nitrate, nitrite, acetate and oxalate of the solutions are given in Table 5.

The variations of pH were similar for the five 24-h cycles: from the initial values of 4.0 for N+OA1 and 3.6 for N+OA2, pH increased rapidly during the first 6 h of leaching, to reach about 9.5, then increased slowly to reach 10.6 in N+OA1 and 10.5 in N+OA2 after 24 h (Figs. 3 and 4). Longer reaction times would allow pH to increase even further. Alkaline conditions were thus very rapidly imposed in the leaching medium. The increase in pH was mostly due to the release of hydroxide ions by the dissolving cement paste matrix.

Concentrations of K⁺ and Ca²⁺ varied the same way. During the first leaching cycle, variations followed those of pH and concentrations reached [Ca²⁺] ≈ 0.25 mmol/L and [K⁺] ≈ 0.15 mmol/L in N+OA1 and [Ca²⁺] ≈ 0.33 mmol/L and [K⁺] ≈ 0.17 mmol/L in N+OA2. For leaching days 2–5, concentrations at the end of the cycle decreased progressively to reach [Ca²⁺] ≈ 0.25 mmol/L and [K⁺] ≈ 0.09 mmol/L in N+OA1 and [Ca²⁺] ≈ 0.22 mmol/L and [K⁺] ≈ 0.08 mmol/L in N+OA2 at the end of the 5th leaching cycle.

Concentrations of nitrates in N+OA1 and N+OA2 (Table 5) remained equivalent to the initial value (32.3 mM). Nitrites were not detected in either solution. Moreover, cation chromatograms did not reveal any peak due to ammonium NH₄⁺ produced by abiotic reduction of nitrates under anoxic conditions. Ammonium has notably been observed by (Alquier et al., 2012; Truche et al., 2013a,b) in the presence of various types of steel acting as reaction catalysts. Results obtained in this study indicate that no abiotic reduction of nitrate occurred in the conditions of the experiment.

Table 5

Evolution of concentrations (mmol/L) of anions in N+OA1 and N+OA2 solutions with time of cement paste immersion. Solution renewed daily. Solid area/liquid volume ≈ 50 cm²/L. <DL: lower than the detection limit.

Time (day)	N+OA1 solution			N+OA2 solution			
	[Ac]	[NO ₃]	[NO ₂]	[Ac]	[Ox]	[NO ₃]	[NO ₂]
0.00	0.57	31.6	<DL	0.37	0.17	31.8	<DL
0.08	0.53	31.9	<DL	0.30	0.05	32.1	<DL
0.67	0.62	31.4	<DL	0.26	0.07	31.7	<DL
0.79	0.60	31.7	<DL	0.34	0.07	31.7	<DL
1.00	0.61	31.6	<DL	0.34	0.06	31.8	<DL
2.04	0.55	31.8	<DL	0.32	0.05	31.7	<DL
3.04	0.52	31.7	<DL	0.28	0.06	31.9	<DL
3.99	0.47	31.7	<DL	0.31	0.05	31.7	<DL
4.97	0.56	31.6	<DL	0.30	0.05	31.8	<DL

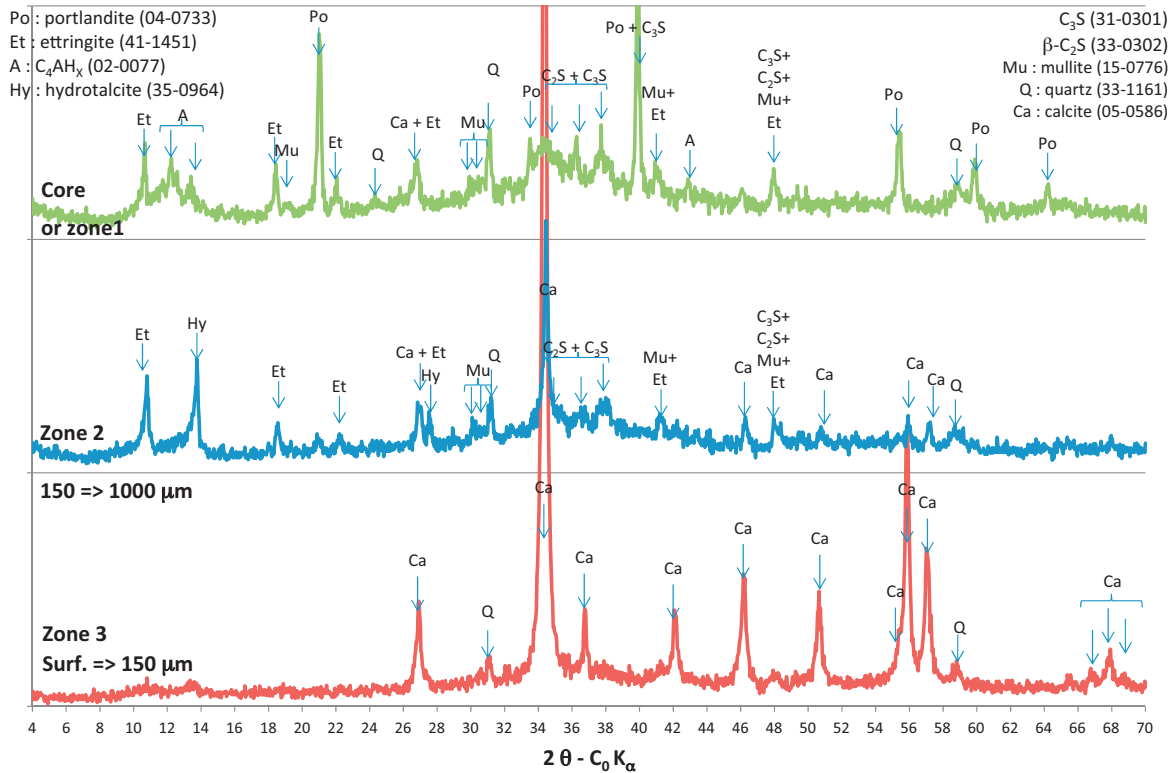


Fig. 5. XRD mineralogical analyses of CEM V paste specimen after 5-day leaching in N+OA1 (acetic acid 0.5 mM, nitrate) solution at various distances in from the surface of the specimen.

Concentrations of acetate in N+OA1 and N+OA2 were almost constant throughout the experiment and were similar to initial concentrations (Table 2). In contrast, the concentration of oxalate, which was initially 0.17 mmol/L, had decreased at the first sampling time (0.08 day ~ 2 h) and remained relatively stable (equal to 0.06 ± 0.01 mmol/L) in the following samples.

3.3. Mineralogical changes in the cement pastes

Figs. 5 and 6 present the mineralogical characterisation by XRD of the CEM V paste specimens at the end of the leaching experiments by N+OA1 and N+OA2 solutions respectively. Diffractograms are presented according to the distance from the surface in contact with the test solution. The analyses showed that alterations led to a mineralogical zonation of the specimens.

Diffractograms of control zones ("core or zone 1" on Figs. 5 and 6) performed at 5 mm depth present typical peaks of anhydrous (C_3S or $3CaO \cdot SiO_2$, C_2S or $2CaO \cdot SiO_2$, mullite $3Al_2O_3 \cdot 2SiO_2$) and hydrated (ettringite $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$, portlandite or $Ca(OH)_2$, hydrated calcium aluminates C_4AH_x or $4CaO \cdot Al_2O_3 \cdot xH_2O$) cementitious phases and of quartz.

The peripheral part of cement pastes immersed in N+OA1 (acetic acid) solution showed two zones with different mineralogical compositions (zones 2 and 3 in Fig. 5). The total thickness of the two zones was about 1 mm. In zone 2 (from 150 μm to 1000 μm from the surface) portlandite had disappeared and a hydrotalcite-type ($Mg_4Al_2(OH)_{14} \cdot 3H_2O$) compound had precipitated. Precipitation of hydrotalcite (carbonated or not) has also been observed by Faucon et al. (1996) in degraded zones of cement paste specimens leached at pH 7. Calcite also precipitated in zone 2, probably because of a re-combination of calcium released by portlandite dissolution with carbonate released by the dissolution of carbonated AFm. Zone 3 (from the surface to 150 μm deep), was more strongly carbonated. All crystallised cementitious phases

had disappeared. This thin carbonated layer was also observed on control specimens kept in water (carbonation of specimen's skin because of ambient CO_2 dissolved in repository water). Neither Ca-acetate nor Na-acetate characteristic peaks were found on the diffractogram.

The peripheral zone of the specimen immersed in N+OA2 (acetic/oxalic acids) solution showed 3 zones with different mineralogical characteristics (zones 2–4 on Fig. 6). These three zones together made up a total a thickness of approximately 1.3 mm. As for specimens immersed in N+OA1, portlandite had disappeared in zone 2 (from 400 μm to 1300 μm deep) where a hydrotalcite-like compound had precipitated together with calcite. Zone 3 (300–400 μm deep) was characterised by ettringite dissolution. Calcite and calcium oxalate mono-hydrate or whewellite ($CaC_2O_4 \cdot H_2O$) had precipitated. The outer layer of the specimen or zone 4 (from the surface to 300 μm deep) showed typical peaks of calcite, whewellite and calcium oxalate tri-hydrate or caoxite ($CaC_2O_4 \cdot 3H_2O$). Neither Ca- or Na-acetate nor Na-oxalate salt peaks were found in the diffractograms.

Precipitation of whewellite in cement paste specimens immersed in oxalic acid solutions (0.28 M) has been observed experimentally by Larreur-Cayol et al. (2011a,b). Ca-oxalate tri-hydrate, mentioned by Streit et al. (1998) is not very stable (Deganello et al., 1981) and is very easily transformed into di- or mono-hydrate Ca-oxalate (Echigo et al., 2005; Tomazic and Nancollas, 1979). Nevertheless, the precipitation of Ca-oxalate tri-hydrate jointly with mono-hydrate has already been observed (Heijnen et al., 1985; Opalko et al., 1997).

Finally, the results of cement paste mineralogical analyses coupled with those of chemical analyses of the solutions showed that the exposure of CEM V paste specimens to N+OA1 solution was similar to a leaching of cement paste (Bertron and Duchesne, 2013; Faucon et al., 1996; Moranville et al., 2004; Duchesne and Bertron, 2013). Acetate ion did not combine with cations released

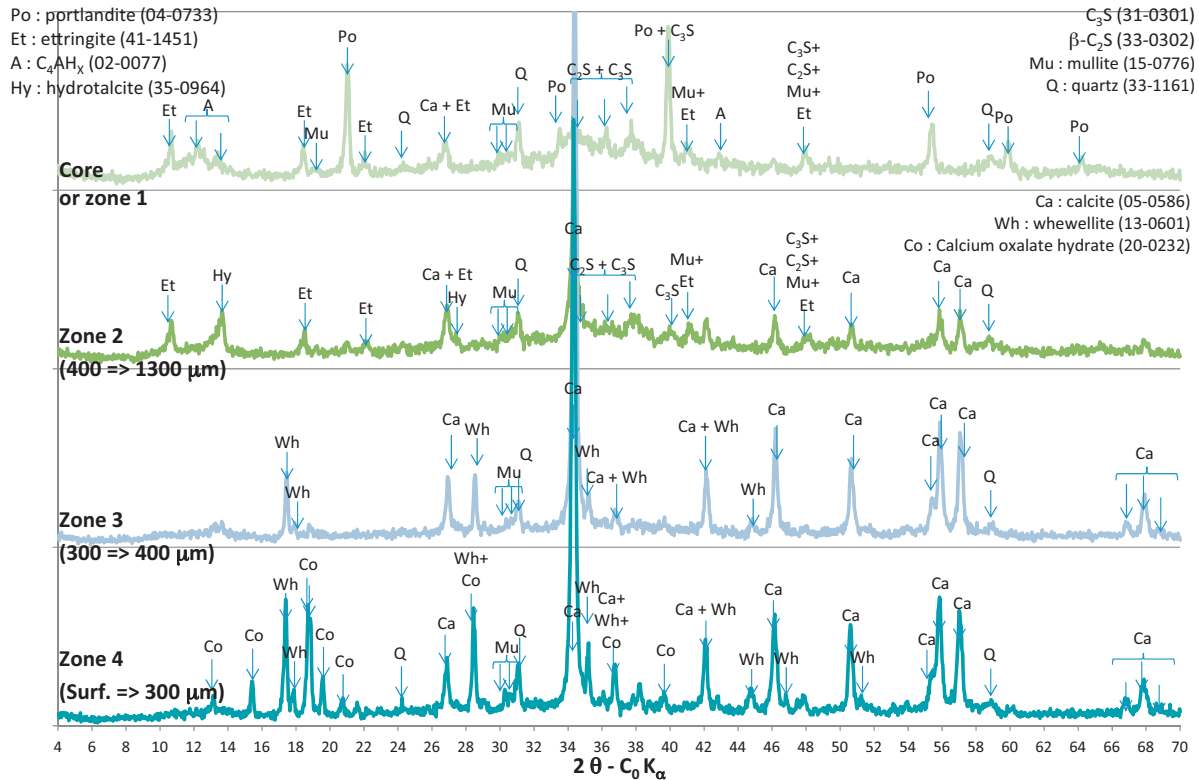


Fig. 6. XRD mineralogical analyses of CEM V paste specimen after 5-day leaching in N + OA2 (acetic 0.33 mM/oxalic 0.17 mM acids, nitrate) solution for various distances in from the surface of the specimen.

by the cementitious matrix. This result is in accordance with those obtained by other authors who have worked on the attack of acetic acid but with different concentrations of acids (Bertron et al., 2007; Oueslati and Duchesne, 2012; Pavlík, 1994). Moreover, it should be noted that a numerical analysis by Larreur-Cayol et al. (2011a,b) suggested that no Ca-acetate aqueous complex forms in solutions with acetate concentrations ranging from 10^{-5} M to 0.3 M. Thus, regarding the frame of the study, the reactions between acetic acid released by bitumen should not modify acetate bioavailability for bacteria that may be present inside the waste cells.

In contrast, when oxalic acid was present in solution, reactions of oxalate anion with cementitious cations (calcium at least) did occur and led to the formation of various forms of calcium oxalate salts. Precipitation of calcium oxalate salt in oxalic acid solution containing calcium has been confirmed numerically by Larreur-Cayol (2012) for a large range of oxalate activity (10^{-5} M–0.3 M). In the present study conducted with oxalic acid concentration of 0.17 mM, 65% of oxalate was combined with cementitious cations. Consequently, with respect to biotic studies conducted in the presence of cementitious matrices, oxalate could be less bioavailable to bacteria.

4. Conclusion

The overall study, of which this paper is a part, aimed to investigate the reactivity of nitrate under biotic conditions (biotic catalysis of nitrate reduction) in the context of repository of long-lived, intermediate-level, radioactive wastes. The aim of the present paper was to investigate the interactions between the various chemical species (nitrates, bitumen model leachates) and the cementitious matrix under abiotic conditions, with the view to determining the chemical conditions to which bacterial candidate species could be exposed in the biotic part of the study. Leaching experiments were conducted on batch systems comprising CEM

V paste specimens in contact with solutions made of nitrate and acetic acid or acetic and oxalic acids (initial pH of 4 and 3.6). Results showed that an alkaline pH (>10) is very rapidly (less than 24 h) established in the aqueous medium. The impact of bitumen model leachates made of acetic acid (0.50 mM) was similar to those found in classical leaching tests of cementitious matrix as no particular interaction between cementitious cations and acetate anions was observed. Thus, in experiments involving bacteria and a cementitious matrix, organic matter would remain in solution and would therefore more probably be available for oxidation and as a carbon source for microorganisms. In contrast, the study conducted with the model leachate made of acetic (0.33 mM) and oxalic (0.17 mM) acids showed a strong interaction between oxalate anions and calcium cations released by the cement paste. 65% of oxalate was combined with calcium to precipitate as calcium oxalate mono- and tri-hydrate salts in the periphery of the matrix. Oxalate would thus be less available for bacteria. Finally, the study confirmed the stability of nitrates under abiotic conditions in the presence of a cementitious matrix and organic matter.

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References

- Albrecht, A., Bertron, A., Libert, M., 2013. Microbial catalysis of redox reactions in concrete cells of nuclear waste repositories: a review and introduction. In: Bart, F., Cau-di-Coumes, C., Frizon, F., Lorente, S. (Eds.), *Cement-Based Materials for Nuclear Waste Storage*. Springer, New York, pp. 147–159.
- Alquier, M., et al., 2012. Etudes expérimentales de la réactivité des nitrates à l'interface bitume-eau cimentaire-ciment en conditions biotiques, Rapport Andra LGC – LMDC – LCA no CRPFSTR120031.

- Alquier, M., et al., 2014. *Halomonas desiderata* as a bacterial model to predict the possible biological nitrate reduction in concrete cells of nuclear waste disposals. *J. Environ. Manag.*, <http://dx.doi.org/10.1016/j.jenvman.2013.10.013>.
- Alquier, M., et al., 2013. Nitrate reducing bacterial activity in concrete cells of nuclear waste disposal. In: L'Hostis, V., Gens, R. (Eds.), *EPJ Web of Conferences*, vol. 56, p. 01003.
- Andra, 2005. *Dossier 2005 Argile, Tome Architecture et Gestion du stockage géologique*. Rapport Andra C.RP.ADP.04.0001B.
- Bertron, A., Duchesne, J., Escadeillas, G., 2005a. Accelerated tests of hardened cement pastes alteration by organic acids: analysis of the pH effect. *Cem. Concr. Res.* 35 (1), 155–166.
- Bertron, A., Duchesne, J., Escadeillas, G., 2005b. Attack of cement pastes exposed to organic acids in manure. *Cem. Concr. Compos.* 27 (9–10), 898–909.
- Bertron, A., Duchesne, J., Escadeillas, G., 2007. Degradation of cement pastes by organic acids. *Mater. Struct.* 40 (3), 341–354.
- Bertron, A., Duchesne, J., 2013. Attack of cementitious materials by organic acids in agricultural and agrofood effluents. In: Mark, A., Alexandra, B., Belie, N.D. (Eds.), *Performance of Cement-Based Materials in Aggressive Aqueous Environments*. RILEM State-of-the-Art Reports. Springer, Netherlands, pp. 131–173.
- Bertron, A., Erable, B., et al., 2013. Catalyse biotique et abiotique de la réduction des nitrates en milieu alcalin dans le contexte du stockage profond des déchets radioactifs. *Matériaux & Techniques* 101 (1), 104.
- Daniel, S.L., Pilsil, C., Drake, H.L., 2007. Anaerobic oxalate consumption by microorganisms in forest soils. *Res. Microbiol.* 158 (3), 303–309.
- Deganello, S., Kampf, A.R., Moore, P.B., 1981. The crystal structure of calcium oxalate trihydrate: $\text{Ca}(\text{H}_2\text{O})_3(\text{C}_2\text{O}_4)$. *Am. Mineral.* 66 (7–8), 859–865.
- Devlin, J.F., Eedy, R., Butler, B.J., 2000. The effects of electron donor and granular iron on nitrate transformation rates in sediments from a municipal water supply aquifer. *J. Contam. Hydrol.* 46 (1–2), 81–97.
- Duchesne, J., Bertron, A., 2013. Leaching of cementitious materials by pure water and strong acids (HCl and HNO_3). In: Alexander, M., Bertron, A., De Belie, N. (Eds.), *Performance of Cement-Based Materials in Aggressive Aqueous Environments*. RILEM State-of-the-Art Reports. Springer, Netherlands, p. 22.
- Echigo, T., et al., 2005. Re-investigation of the crystal structure of whewellite [$\text{Ca}(\text{C}_2\text{O}_4)\cdot\text{H}_2\text{O}$] and the dehydration mechanism of caoxite [$\text{Ca}(\text{C}_2\text{O}_4)\cdot 3\text{H}_2\text{O}$]. *Mineral. Mag.* 69 (1), 77–88.
- Faucon, P., et al., 1996. Leaching of cement: study of the surface layer. *Cem. Concr. Res.* 26 (11), 1707–1715.
- Gwinner, B., et al., 2006. Modelling of bituminized radioactive waste leaching. Part II: Experimental validation. *J. Nucl. Mater.* 349 (1–2), 107–118.
- Heijnen, W., Jellinghaus, W., Klee, W.E., 1985. Calcium oxalate trihydrate in urinary calculi. *Urol. Res.* 13 (6), 281–283.
- Kagawa, A., Fukumoto, M., Kawamura, K., 2000. Influence of chemical and radiolytic degradation of bitumen on its performance for disposal. *J. Nucl. Sci. Technol.* 37 (10), 934–937.
- Lange, N.A., Dean, J.A., 1985. *Lange's Handbook of Chemistry*. McGraw-Hill, New York, NY.
- Larreure-Cayol, S., (Thèse de Doctorat. Doctoral thesis) 2012. *Attaques des matériaux cimentaires par les acides organiques des effluents agricoles et agro-alimentaires*. Université Paul Sabatier, Toulouse.
- Larreure-Cayol, S., Bertron, A., Escadeillas, G., 2011a. Degradation of cement-based materials by various organic acids in agro-industrial waste-waters. *Cem. Concr. Res.* 41 (8), 882–892.
- Larreure-Cayol, S., De Windt, L., Bertron, A., Escadeillas, G., 2011b. Deterioration of cementitious materials by organic acids in agricultural effluents: experiments and modelling. In: 7th International Symposium on Cement Based Materials for a Sustainable Agriculture. CIGR International Symposium, pp. 38–46.
- Libert, M., et al., 2011. Molecular hydrogen: an abundant energy source for bacterial activity in nuclear waste repositories. *Phys. Chem. Earth Parts A/B/C* 36 (17–18), 1616–1623.
- Libert, M., Walczak, I., 2000. Effect of radio-oxidative ageing and pH on the release of soluble organic matter from bitumen. In: ATALANTE 2000 Scientific research on the back-end of the fuel cycle for the 21th century. Avignon, p. 4.
- Ma, J., et al., 2012. Assimilable Organic Carbon (AOC) in soil water extracts using vibrio harveyi BB721 and its implication for microbial biomass. *PLoS ONE* 7 (5), e28519.
- Marien, A., Smets, S., Li, X., Valcke, E., 2008. Processes related to the water uptake by EUROBITUM bituminized radioactive waste: Theoretical considerations and first experimental results. In: Lee, W.E., Roberts, J.W., Hyatt, N.C., Grimes, R.W. (Eds.), *Scientific Basis for Nuclear Waste Management Xxxi*. Materials Research Society, Warrendale, pp. 151–159.
- Moranville, M., Kamali, S., Guillon, E., 2004. Physicochemical equilibria of cement-based materials in aggressive environments—experiment and modeling. *Cem. Concr. Res.* 34 (9), 1569–1578.
- Moudilou, E., (Thèse de Doctorat. Doctoral thesis) 2000. *Cinétiques et mécanismes de relargage des métaux lourds présents en traces dans les matrices cimentaires*. Université d'Orléans.
- Nakayama, S., Iida, Y., Nagano, T., Akimoto, T., 2003. Leaching behavior of a simulated bituminized radioactive waste form under deep geological conditions. *J. Nucl. Sci. Technol.* 40 (4), 227–237.
- Opalko, F.J., Adair, J.H., Khan, S.R., 1997. Heterogeneous nucleation of calcium oxalate trihydrate in artificial urine by constant composition. *J. Cryst. Growth* 181 (4), 410–417.
- Oueslati, O., Duchesne, J., 2012. The effect of SCMs and curing time on resistance of mortars subjected to organic acids. *Cem. Concr. Res.* 42 (1), 205–214.
- Pavlik, V., 1994. Corrosion of hardened cement paste by acetic and nitric acids part II: formation and chemical composition of the corrosion products layer. *Cem. Concr. Res.* 24 (8), 1495–1508.
- Seidell, A., 1919. *Solubilities of Inorganic and Organic Compounds: A Compilation of Quantitative Solubility Data from the Periodical Literature*. D. Van Nostrand Company.
- Sercombe, J., et al., 2006. Modelling of bituminized radioactive waste leaching. Part I: constitutive equations. *J. Nucl. Mater.* 349 (1–2), 96–106.
- Streit, J., Tran-Ho, L.-C., Königsberger, E., 1998. Solubility of the three calcium oxalate hydrates in sodium chloride solutions and urine-like liquors. *Monatshefte für Chemie/Chemical Monthly* 129 (12), 1225–1236.
- Tomazic, B.B., Nancollas, G.H., 1979. A study of the phase transformation of calcium oxalate trihydrate-monohydrate. *Invest. Urol.* 16 (5), 329–335.
- Truche, L., Berger, G., Domergue, L., Albrecht, A., 2013a. Abiotic nitrate reduction induced by carbon steel and hydrogen: implications for environmental processes in waste repositories. *Appl. Geochem.* 28, 155–163.
- Truche, L., Berger, G., Albrecht, A., Domergue, L., 2013b. Engineered materials as potential geocatalysts in deep geological nuclear waste repositories: A case study of the stainless steel catalytic effect on nitrate reduction by hydrogen. *Appl. Geochem.* 35, 279–288.
- Van Loon, L.R., Kopajtic, Z., <http://www.nagra.ch/en/shopproductdetail1.htm/s.level/10390/s.product/29018> 1990. Complexation of Cu^{2+} , Ni^{2+} and UO_2^{2+} by Radiolytic Degradation Products of Bitumen. Nagra.
- Walczak, I., (Thèse de Doctorat. Doctoral thesis) 2000. *Determination des produits organiques d'altérations chimiques et radiochimiques du bitume: applications aux enrobés bitumes*. INSA, Lyon.
- Walczak, I., Libert, M., Camaro, S., Blanchard, J.M., 2001. Quantitative and qualitative analysis of hydrosoluble organic matter in bitumen leachates. *Agronomie* 21 (3), 247–257.