

Aluminium Determination and Speciation Modelling in Groundwater from the Area of a Future Radioactive Waste Repository

CONSTANTIN MARIN^{1,*}, ALIN TUDORACHE^{1,2}, LUMINIȚA VLĂDESCU²

¹Emil Racoviță Institute of Speleology of the Romanian Academy, 13 Calea 13 Septembrie, 050711 Bucharest, Romania

²Faculty of Chemistry, University of Bucharest, 2-14 Blv. Regina Elisabeta, 030018 Bucharest, Romania

A study of aluminium concentration distributions in natural groundwater has been conducted, by considering samples collected from the area located in the neighbourhood of Saligny village (Cernavodă -Romania). A GF-AAS method has been developed, tested and used for aluminium content determination. Based on the complete analysis results of the considered groundwater samples, the distribution of the aluminium inorganic species in groundwater has been evaluated. In order to determine the aluminium speciation in the analyzed waters, besides the chemical species included in the PHREEQC code databases, also other ionic associations that aluminium formed with Si species, SO_4^{2-} , F^- , Na^+ and K^+ ions were considered. The distribution of the water saturation index values calculated on this basis suggests that some mineral species of the red clay layers tend to render soluble when the groundwater is mixed with the surface water.

Key words: aluminium, determination, speciation, groundwater, saturation index

Aluminium is the most abundant metal in the earth crust (8.3%), being surpassed in terms of chemical elements general abundance only by oxygen (45.5%) and by silicon (25.7%). It is a major constituent of a large variety of volcanic and metamorphic rocks. In the natural environment, the aluminium stable oxidation state is +3. However, because of its small radius and of its high electrical charge, the Al^{3+} ion is easily involved in a large variety of reactions of hydrolysis and of association with many inorganic ligands, which results in a quite rich speciation of this element. The most important and the most abundant ionic associations are derived through the aluminium interaction with the water environment within which it occurs, being thus formed a series of aluminium-hydroxo species, but also several aluminium associations with Na^+ , F^- , SO_4^{2-} or $\text{SiO}_{2(\text{aq})}$ [1].

The contamination of groundwater with various metal chemical species derived from anthropogenic activities is an investigation field which in the recent years made the object of intensive studies, the latter circumstance being a consequence of the corresponding high toxicological potential and of the undesirable effects exerted on the associated ecosystems, and – last but not least – of the effects exerted on the general health condition of the human communities which use the concerned water supplies [2-4].

In order to determine the total aluminium concentrations in samples of either fresh or waste water, a multitude of analytical techniques are currently utilized. Specifically, aluminium concentrations may be assessed by means of spectrometric methods using Pyrocatechol Violet [5, 6], Chrome Azurol S [7] reagents, as well as by means of catalytic methods with Gallocyanine [8] or Indigo Carmine [9] reagents. Spectrofluorimetric methods are largely used as well, with: Chromotropic acid [10, 11], 8-hydroxyquinoline-5-sulfonic acid [12], Lumogallion [13] as fluorogenic chelating agent, or in combination with solvent extraction [14, 15]. Aluminium concentration was also determined by chemiluminescence method with Luminol [16]. Among the electrometric techniques used for the analysis of aluminium in natural waters, there are

mentioned potentiometry with the ion-selective electrodes [17, 18] and various voltametric methods [19].

Yet the atomic absorption spectrometry (AAS) and the inductively coupled plasma spectrometry (ICP) are the most frequently used methods in aluminium determination [20]. When employing the atomic absorption spectrometry, flame atomization is as a general rule used in order to determine large concentrations of aluminium [21], while for small or trace concentrations, electrothermal atomization is recommended [22]. A series of specific work approaches have been tested, especially in order to eliminate the matrix effects by using matrix modifiers, such as potassium dichromate [23] or zirconyl chloride [24].

One of the basic approaches in groundwater geochemistry interpretations is to assume that all dissolved species are in equilibrium. This assumption permits the use of thermodynamic models of aqueous solutions to calculate the distribution of the dissolved species. In this respect, there has to be mentioned in the first place the Helgeson-Kirkham-Flowers (HKF) model [25], that allows to assess the stability constants and the reference thermodynamic parameters for a multitude of chemical species of the aluminium, over a very wide range of temperatures and pressures [26]. The HKF model can be used for devising a thermodynamic data-base which displays a remarkable internal consistency. Additionally, aluminium speciation has also been performed by resorting to the ion specific interaction model which uses Pitzer formalism [27].

The low and intermediate level radioactive wastes generated by the operation and decommissioning of Cernavodă Nuclear Power Plant are planned to be disposed into a new repository located on Saligny site (Cernavodă-Romania). The repository will be near surface type, with multiple barriers, including red clay layers rich in aluminium. The disposal of radioactive waste needs to be carried out in a manner that provides an acceptable level of safety and which can be demonstrated to comply with the established regulatory requirements and criteria.

The main objective of the present study was to evaluate the nature and level of inorganic chemical species of aluminium in groundwater from Saligny area where the

* email : constmarin@gmail.com, Tel.: +40-021-3181425

low and intermediate level radioactive wastes generated at Cernavodă Nuclear Power Plant are planned to be disposed into a new future repository. To this purpose, there has been developed and tested in laboratory an analytical approach aimed at assessing the aluminium concentrations by means of atomic absorption spectrometry with electrothermal atomization using a graphite furnace, GF-AAS. The indicated approach was employed in the analysis of groundwater samples, collected from aquifers subject to different geological and hydro geological characteristics. Aqueous speciation calculations were performed by using the computer program PHREEQC with the included thermodynamic database LLNL (Lawrence Livermore National Laboratory). That database was significantly upgraded with thermodynamic parameters retrieved from a multitude of scientific publications, parameters which were required in order to characterize the new species of aluminium considered by the present evaluation.

Experimental part

Sampling

Hydrogeological setting of the sampling sites

An area extending between the Danube and the Black Sea - Danube Channel, in close vicinity of the Nuclear Power Plant at Cernavodă, is being currently considered for the development of a future weakly and medium active waste repository (Saligny FWMAWR). In terms of lithology, the repository area consists of a succession of more or less continuous horizons. Considered from the ground surface downward, those horizons include mainly loessoid clays, red clays, kaolinitic and marly clays, glauconitic and kaolinitic sands, altered and fractured limestone of Berriasian age with clayey insertions. The clay minerals (montmorillonite, smectite, illite, kaolinite) are prevalent in the median section of the sedimentary deposit, the corresponding percentages diminishing toward larger depths. On the other hand, carbonate minerals (calcite, dolomite) occur at all horizons, the corresponding percentages increasing from the upper to the lower horizon.

Sampling techniques

In order to provide a characterization of the site in terms of groundwater hydrology, groundwater samples have been

collected during August 2007 from 15 piezometric observation drillings and wells (fig. 1).

The depths to the groundwater level range between 4 and 52 m. In all cases samples were collected using bailers. The recommended bailers cleaning procedure [28] was followed. When collected, water samples were filtered *in situ* by means of a Chromatography Research Supplies filtering system, provided with a manual Nalgene vacuum pump. MCE-Millipore membranes, mixed cellulose esters, of 0.45 μm porosity and of 47 mm diameter have been used for filtering. Each membrane filter was washed in ultra-pure water before the experiment and used only once. During filtration, the first 250 mL of solution were discarded, thus allowing the saturation of the membrane surface prior collecting the filtrate. Filtered water samples have been collected in HDPE Nalgene sampling bottles, and for the subsequent determination of aluminium they were acidified with Ultrapur[®] 60% nitric acid to pH 2 and stored at 4°C.

Reagents

All the reagents used were supplied by Merck and they were of analytic purity. Solutions were prepared with ultra-pure water (TKA MicroPure system). Suprapur[®] (Merck) 65% nitric acid ($d = 1.39 \text{ g/mL}$) was used for the pH adjustment of the collected samples. A solution of 0.05 M HCl prepared from 37% HCl ($d = 1.19 \text{ g/mL}$) was standardized in laboratory with di-sodium tetra borate decahydrate (Merck). Reference material for the Al, Fe, Na, K, Mg, and Ca determination by AAS were CertiPUR[®] (Merck). These materials are prepared in 0.5 M HNO₃ and contain 1000 mg/L of ion of interest.

Equipment and analytical procedures

The determination of total aluminium concentrations was performed with a Perkin-Elmer atomic absorption spectrometer, model AAnalyst 700, provided with a deuterium arc background correction, equipped with an AS-800 autosampler, an HGA-800 graphite furnace, and a Lumina Single-element HCL-Aluminum source lamp (Perkin-Elmer). Pyrolytically coated tubes with integrated platforms (Perkin-Elmer) were used. The instrumental settings and analysis temperatures are listed in table 1. The signal was measured in the peak area mode. Each

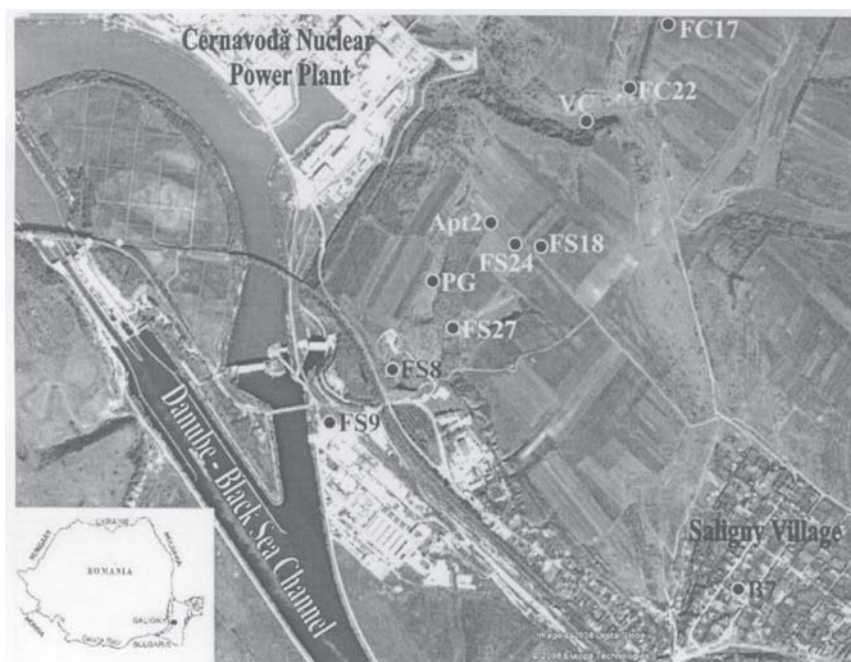


Fig. 1. Location map indicating groundwater sampling sites

Table 1
OPERATING PARAMETERS FOR THE GF-AAS DETERMINATION
OF ALUMINIUM CONCENTRATION

Instrumental conditions			
Wavelength (nm)	309.0		
Slit (nm)	0.7		
Applied current (mA)	25		
Energy	55		
Mode	AA-BG		
Calibration	Nonlinear		
Standards ($\mu\text{g/L}$)	10, 30, 60		
Matrix modifier ($5 \mu\text{L}$)	1.0% $\text{Mg}(\text{NO}_3)_2$		
Furnace temperature program			
Step	Temp ($^{\circ}\text{C}$)	Ramp time (s)	Hold time (s)
Pre-drying	100	5	20
Drying	140	15	15
Ashing	1700	10	20
Atomization	2500	0	5
Clean-out	2600	0	6

completed determination was followed by a 6 s clean-up step of the graphite tube at 2600°C .

In most cases the water samples were analyzed directly, with an injected sample volume of $20 \mu\text{L}$. Certain samples required preliminary dilutions, since the dilution capability of the auto-sampler was exceeded. The atomic absorption signal was measured as a peak area mode against an analytical calibration curve. The calibration lines were traced using solutions prepared from standard solutions CertiPUR[®] (Merck). All the solutions were prepared with ultra-pure water (TKA Ultra Pure System GenPure, electric resistance $18.2 \text{ M}\Omega \times \text{cm}$).

The methods accuracy, precision and sensitivity were tested by using the reference matter provided by Perkin-Elmer groundwater and wastewater pollution control certified reference materials (Trace Metals I – 15 elements). The performance of the employed analytical procedures was determined according to the IUPAC [29, 30] and EURACHEM recommendations [31] (table 2).

The water temperature was measured at the sampling site by using a Crison portable thermometer TM65 with Immersion probe Pt 1000 sensor (measuring error $\leq 0.2^{\circ}\text{C}$, reproducibility $\pm 0.1^{\circ}\text{C}$). When samples were being collected, a Crison PH 25 portable instrument has been used in order to perform all pH measurements (Electrode with integrated Temperature Probes ATC, NIST-traceable

pH buffer solutions of pH 4.01 and 7.00), according to international recommendations [32].

The Na, K, Mg, Ca and Fe concentrations in water samples were determined in laboratory by means of flame - atomic absorption spectrometry, FAAS, by using standard methods (ISO 9964, SR ISO 7980 and SR 13315). The total alkalinity has been assessed by electrometrical titration with 0.25 M and 0.05 M HCl solutions by a Gran titration procedure [33]. In most cases, determinations were made within 24 h of sampling. The dissolved silica content was determined spectrometrically with molybdate [34]. Nitrate was analyzed by a UV spectrometric method [35]. Sulphate was determined turbidimetrically [36]. All these determinations have been conducted by means of a molecular absorption spectrometer in the visible and ultraviolet spectra, of the Perkin-Elmer Lambda 25 model. In order to measure total fluoride ion concentration, an ion-selective procedure was used (SR ISO 10359-1). The chloride was analyzed by the mercury (II) thiocyanate spectrophotometric method [37].

The total dissolved solids (TDS) content was calculated as the sum of the total dissolved-ion concentrations, by additionally making the adjustment of bicarbonate to carbonate ions [38]. The speciation calculations were performed by means of PHREEQC, version 2.15.0.2697 [39]. Surface water and groundwater densities were calculated with the Clegg-Whitfield relations [40] for the inter-conversion of concentration scales, based on the measured temperatures.

Results and discussions

The analytical results concerning the main cations and anions concentrations of the analyzed groundwater samples are indicated in table 3. The molal ionic strengths average for the water samples collected from the wells in the *Saligny* FWMAWR site amounts to $0.0157 \text{ mol}\cdot\text{kg}^{-1}$.

In terms of aluminium concentrations assessments, an important methodological issue has to be mentioned. The generation of colloids, prevalently as a result of aluminium hydrolysis, has a significant operational outcome. Colloids penetrate the $0.45 \mu\text{m}$ filtering membrane [41-43]. When water samples filtered in that way are analyzed by means of spectrometric methods (AAS or ICP), both phases – solution and colloidal – will be analyzed together, resulting in a positive deviation of the charges balance.

Aqueous speciation calculations were performed by using the computer program PHREEQC with the included thermodynamic database LLNL (Lawrence Livermore National Laboratory, California, USA) that corresponds to

Table 2
ANALYTICAL PERFORMANCE PARAMETERS OF GF-AAS METHOD USED
FOR ALUMINIUM CONCENTRATION DETERMINATION

Linearity $10 - 60 \mu\text{g}\cdot\text{L}^{-1}$	a	0.0028
	b	0.0072
	R	0.9839
Precision-repeatability, R.S.D.	n	5 (at $20 \mu\text{g/L}$)
	%	9.74
Precision- reproducibility, R.S.D.	n	12 (at $20 \mu\text{g/L}$)
	%	6.11
Trueness ("bias")	n	12 (at $20 \mu\text{g/L}$)
	%	6.58
Recovery	%	93.90–100.8

Note: linearity expressed as $y = ax+b$; R– correlation coefficient;
R.S.D. – relative standard deviation; n – no. of repetitive analyses

Table 3
CHEMICAL COMPOSITION OF THE ANALYSED GROUNDWATER SAMPLES

Sample No.	Source	Aquifer	t (°C)	pH	Eh (mV)	TDS (g/L)	ELEMENT	
							Na (mg/L)	K (mg/L)
1	Well B7	Berriasian	13.7	7.52	104	1.07	144.8	1.5
2	Drilling FS9	Quaternary	16.6	7.48	-141	1.29	85.2	5.9
3	Drilling FS8	Berriasian	14.7	7.48	-113	0.39	63.3	1.5
4	Drilling FS27	Berriasian	14.5	8.02	172	0.63	67.3	5.3
5	Pump group North (F2)	Berriasian	15.2	7.40	63	0.75	67.0	2.0
6	Pump group East (FS21)	mixture	14.6	9.22	124	0.21	43.5	19.5
7	Pump group Center(Fc)	Berriasian	13.6	7.27	172	0.70	65.3	1.1
8	Pump group South (F3)	Berriasian	13.0	7.25	158	0.77	75.2	2.1
9	Pump group West (F1)	Berriasian	13.2	7.32	167	0.72	71.8	1.7
10	Drilling FS18	mixture	13.0	10.60	22	0.11	30.4	6.7
11	Drilling FS24	mixture	13.2	9.72	105	0.10	17.7	11.9
12	Drilling Apt2	Aptian	12.9	7.28	206	2.26	347.9	33.4
13	Well Valea Cismeiei	Eocene	15.2	7.48	119	1.32	199.5	0.5
14	Drilling FC22	Berriasian	13.7	7.30	n.d.	0.47	18.5	0.4
15	Drilling FC17	Aptian	14.5	8.66	n.d.	0.14	55.5	1.8

Sample No.	ELEMENT				HCO ₃ ⁻ (mg/L)	Si (mg/L)	ION NO ₃ ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	F ⁻ (mg/L)	Cl ⁻ (mg/L)
	Mg (mg/L)	Ca (mg/L)	Fe (mg/L)	Al (µg/L)						
1	61.4	137.2	-	13.3	308.1	8.0	23.8	389.4	0.11	156.1
2	88.5	118.5	9.11	10.4	951.4	8.3	5.2	4.6	0.05	62.0
3	37.5	37.0	0.71	14.2	170.7	1.1	0.9	81.5	0.09	112.7
4	37.8	99.8	-	8.3	195.7	2.4	21.1	196.0	0.02	113.9
5	42.8	109.7	0.05	5.5	315.9	6.8	7.5	199.8	0.21	99.3
6	3.5	5.1	0.03	164.9	129.3	0.6	2.9	7.5	0.13	25.2
7	39.3	102.7	-	0.4	320.7	6.6	6.8	157.8	0.17	86.7
8	45.5	113.5	0.01	1.3	321.4	6.5	9.5	195.3	0.21	117.8
9	42.1	104.5	0.04	1.2	304.3	6.3	10.2	179.0	0.18	99.6
10	0.4	1.9	-	4.7	62.3	0.3	1.2	1.7	0.27	22.2
11	2.8	6.5	1.40	24.0	56.7	0.2	1.7	2.0	0.09	28.5
12	198.4	176.3	-	4.5	442.6	8.0	46.0	1011.2	0.33	451.9
13	88.4	108.1	-	2.9	443.6	7.2	28.5	447.9	0.09	135.0
14	27.4	90.2	-	27.2	267.1	8.4	6.4	48.4	0.01	71.6
15	11.2	32.6	-	124.5	25.3	0.3	3.8	7.4	0.01	153.3

Notes: TDS – total dissolved solids; Eh – redox potential; n.d. – value not determined

the "thermo.com.V8.R6.230" database from the EQ3/6 software package converted to PHREEQC format. The database LLNL was used because it includes thermodynamic data for a large number of aluminium species. The latter are addressed in more detail in this database, as compared to other computer-based models (WATEQ4F, MINTEQ, MINEQL, etc.). Yet a much larger number of species, generated under various conditions by aluminium in natural waters (prevalently groundwater), have been identified and further described in terms of their thermodynamic properties.

The list of the aqueous aluminium species considered in the present study is indicated in table 4. The formation equilibria for the chemical species that the LLNL data base did not include have been rewritten in a PHREEQC code format; all the data were referenced to infinite dilution.

The most important chemical species occurring in an aqueous solution as a result of the aluminium hydrolysis is the tetrahydroxoaluminate ion, [Al(OH)₄]⁻. The temperature dependence of its stability constant has been derived by means of observations concerning the gibbsite solubility [44]. The AlO₂⁻ species is, from this perspective, redundant, since it represents in fact a conventional re-writing of the aluminate anion [26]. That convention has been imposed by the necessity to find a way of avoiding interpretation confusions which might arise in relationship with certain diverging results obtained by various authors who investigated the gibbsite solubility in an acid environment. The hydroxide complexes generation has been documented experimentally by means of ²⁷Al NMR spectroscopy [51, 52] or by means of potentiometry and dynamic light scattering [52], whereas the generation of the di-, tri- or polymeric species was proven to be controlled by the hydrolysis ratio values.

The constants associated to the formation of the silica-hydroxide complex AlH₃SiO₄²⁺ have been derived by potentiometric measurements, either against the glass electrode, over the temperature range 25–150°C [45], or, more recently, by means of potentiometric titration against the hydrogen electrode [53]. For the silica-aluminate ion-pair, the thermodynamic constant of stability and the temperature dependence of the latter have been derived by means of observations concerning the boehmite solubility [54]. Similarly, by relying on solubility measurements conducted on the corundum+kyanite (Al₂O₃+Al₂SiO₅) system under analogous crustal fluids conditions, there has been inferred the generation of the ion-pair AlHSiO₄ [55].

For aluminium, the fluoride anion behaves as an outstandingly strong complexing agent. The generation of ionic associations of the AlF_n³⁻ⁿ (1 ≤ n ≤ 6) type is a well-known process and the corresponding stability constants have been derived by a certain number of investigators. The modeling approach adopted by the present study has outlined that the ionic strength of groundwater exerted a certain control on the generation of those species. The generation of the fluoride-hydroxide complexes of aluminium has been documented by means of NMR spectroscopy [49].

The sulfate anion forms a series of ion-pairs with Al³⁺, the corresponding thermodynamic constants of stability being derived by means of potentiometric titration over a wide range of temperatures [56]. Despite the fact that both ions carry large charges, which in principle should warrant to the corresponding ion-pair significant percentages of occurrence, our modeling has shown that hydrolysis-related equilibria are actually much more competitive. For the ion-pair sodium cation – aluminate anion, NaAl(OH)₄, the

stoichiometry and the thermodynamic constant of stability have been derived both through boehmite solubility measurements, and by potentiometric determinations [57]. Gibbsite solubility measurements, conducted in the $\text{Na}^+ \text{K}^+ \text{Cl}^- \text{HO}^- [\text{Al}(\text{OH})_4]^-$ system, at temperatures ranging between 6–80°C and for molal ionic strengths in the 0.01–5.00 range, have been interpreted through the ion specific interaction model introduced by Pitzer, by taking into account the interaction parameters for $\text{Na}^+ \text{[Al}(\text{OH})_4]^-$ and $\text{K}^+ \text{[Al}(\text{OH})_4]^-$ [58].

As a general rule, the $\text{Al}^{3+} \text{Na}^+ (\text{K}^+) \text{HO}^-$ type species percentage has to be taken into consideration for groundwater with very high concentrations of Na^+ and K^+ , like some of the water samples analyzed in this paper. The present study did not consider a series of chemical species which aluminium can form in natural aqueous systems, like for instance the AlCO_3^+ ion-pair with thermodynamic stability constant, $\lg \beta_{298} = 6.54$, which is characteristic to the sea water [40], and aluminium complexes with humic acids (conditional constants of stability derived by means of ^{27}Al nuclear magnetic resonance [59]).

In figure 2 the relative distributions of the aluminium chemical species calculated as probably presents in the analyzed groundwater samples there are indicated. The obtained average mean values are: hidroxo-aluminium species, Al-OH – 42.23%, aluminium species containing silicium, Al-Si – 57.44%, aluminium species with Na^+ and K^+ ions, Al-M – 0.26%, aluminium free ions, Al^{3+} – 0.04%, aluminium species with F ions, Al-F – 0.03%, aluminium species with SO_4^{2-} ions, Al- SO_4 – 0.0001%. There has been noticed that aluminium hydroxide complexes and silica-hydroxide complexes are the prevalent species.

Chemical analysis by themselves reveal little about processes that change the chemical character of groundwater as it moves through the aquifer systems. One

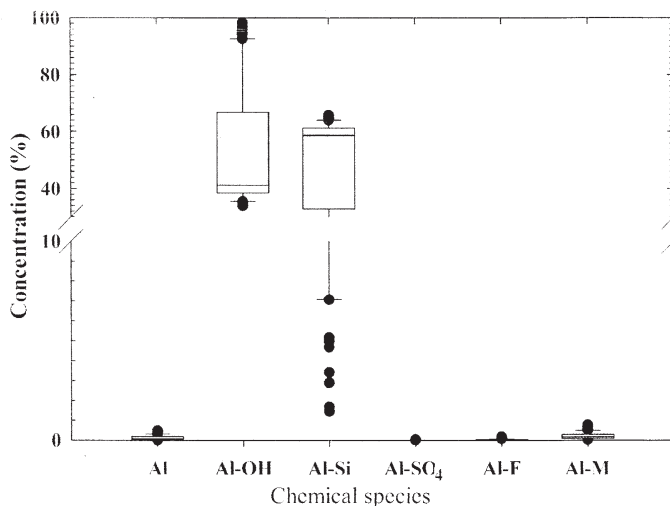


Fig. 2. Calculated distribution of aluminium species for the groundwater samples from FWMAWR Saligny.

Al – Al^{3+} free ions; Al-OH – hidroxo-aluminium species; Al-Si – aluminium species containing silicium; Al- SO_4 – aluminium species with SO_4^{2-} ions; Al-F – aluminium species with F ions; Al-M – aluminium species with Na^+ and K^+ ions

of the principal methods of interpreting natural groundwater geochemistry is to assume that all dissolved species are at equilibrium. This assumption permits the use of thermodynamic models of aqueous solutions to calculate the distribution of dissolved species, a technique adopted for this study. Once the species activities are calculated, the saturation state of the groundwater with respect to mineral and gases can be tested. Additional computations can also be made that quantitatively predict the evolution of an initial solution into a final solution by mixing and reaction with other solutions, gases, or solids. PHREEQC

Specie	Reaction	$\log \beta_{298}^{\circ}$	ΔH°	Ref.
Al^{3+}	–	–	–	–
$\text{Al}(\text{OH})_4^-$	$\text{Al}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_4^- + 4\text{H}^+$	-22.87	42.30	[44]
AlOH^{2+}	$\text{Al}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{AlOH}^{2+} + \text{H}^+$	-4.96	49.80	LLNL
AlO^+	$\text{Al}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{AlO}^+ + 2\text{H}^+$	-10.34	–	[26]
AlO_2^-	$\text{Al}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{AlO}_2^- + 4\text{H}^+$	-22.88	180.90	LLNL
AlHO_2	$\text{Al}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{AlHO}_2 + 3\text{H}^+$	-16.43	144.70	LLNL
$\text{Al}(\text{OH})_2^+$	$\text{Al}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_2^+ + 2\text{H}^+$	-10.60	98.28	LLNL
$\text{Al}_2(\text{OH})_2^{4+}$	$2\text{Al}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Al}_2(\text{OH})_2^{4+} + 2\text{H}^+$	-7.69	–	LLNL
$\text{Al}_3(\text{OH})_4^{5+}$	$3\text{Al}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Al}_3(\text{OH})_4^{5+} + 4\text{H}^+$	-13.88	–	LLNL
$\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$	$13\text{Al}^{3+} + 28\text{H}_2\text{O} \rightleftharpoons \text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+} + 32\text{H}^+$	-98.73	–	LLNL
$\text{AlH}_3\text{SiO}_4^{2+}$	$\text{Al}^{3+} + \text{SiO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{AlH}_3\text{SiO}_4^{2+} + \text{H}^+$	-2.39	77.38	[45]
$\text{Al}(\text{OH})_3\text{H}_3\text{SiO}_4^-$	$\text{Al}^{3+} + \text{SiO}_2 + 5\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_3\text{H}_3\text{SiO}_4^- + 4\text{H}^+$	-19.04	–	[46]
AlHSO_4^{2+}	$\text{Al}^{3+} + \text{H}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{AlHSO}_4^{2+}$	2.44	–	[47]
AlSO_4^+	$\text{Al}^{3+} + \text{SO}_4^{2-} \rightleftharpoons \text{AlSO}_4^+$	3.01	2.15	LLNL
$\text{Al}(\text{SO}_4)_2^-$	$\text{Al}^{3+} + 2\text{SO}_4^{2-} \rightleftharpoons \text{Al}(\text{SO}_4)_2^-$	4.9	3.84	LLNL
AlF^{2+}	$\text{Al}^{3+} + \text{F}^- \rightleftharpoons \text{AlF}^{2+}$	7.00	5.63	LLNL
AlF_2^+	$\text{Al}^{3+} + 2\text{F}^- \rightleftharpoons \text{AlF}_2^+$	12.60	11.00	LLNL
AlF_3	$\text{Al}^{3+} + 3\text{F}^- \rightleftharpoons \text{AlF}_3$	16.70	13.30	LLNL
AlF_4^-	$\text{Al}^{3+} + 4\text{F}^- \rightleftharpoons \text{AlF}_4^-$	19.10	15.08	LLNL
AlF_5^{2-}	$\text{Al}^{3+} + 5\text{F}^- \rightleftharpoons \text{AlF}_5^{2-}$	20.79	15.20	[48]
AlF_6^{3-}	$\text{Al}^{3+} + 6\text{F}^- \rightleftharpoons \text{AlF}_6^{3-}$	21.69	10.40	[48]
$\text{AlF}(\text{OH})^+$	$\text{Al}^{3+} + \text{F}^- + \text{H}_2\text{O} \rightleftharpoons \text{AlF}(\text{OH})^+ + \text{H}^+$	0.74	37.35	[49]
$\text{AlF}(\text{OH})_2$	$\text{Al}^{3+} + \text{F}^- + 2\text{H}_2\text{O} \rightleftharpoons \text{AlF}(\text{OH})_2 + 2\text{H}^+$	-5.70	98.85	[49]
$\text{AlF}(\text{OH})_3^-$	$\text{Al}^{3+} + \text{F}^- + 3\text{H}_2\text{O} \rightleftharpoons \text{AlF}(\text{OH})_3^- + 3\text{H}^+$	-12.77	170.25	[49]
$\text{AlF}_2(\text{OH})$	$\text{Al}^{3+} + 2\text{F}^- + \text{H}_2\text{O} \rightleftharpoons \text{AlF}_2(\text{OH}) + \text{H}^+$	5.22	20.3	[49]
$\text{AlF}_2(\text{OH})_2^-$	$\text{Al}^{3+} + 2\text{F}^- + 2\text{H}_2\text{O} \rightleftharpoons \text{AlF}_2(\text{OH})_2^- + 2\text{H}^+$	-1.66	–	[49]
NaAlO_2	$\text{Al}^{3+} + \text{Na}^+ + 2\text{H}_2\text{O} \rightleftharpoons \text{NaAlO}_2 + 4\text{H}^+$	-23.63	190.33	LLNL
$\text{NaAl}(\text{OH})_4$	$\text{Al}^{3+} + \text{Na}^+ + 4\text{H}_2\text{O} \rightleftharpoons \text{NaAl}(\text{OH})_4 + 4\text{H}^+$	-22.91	–	[46]
$\text{NaAl}(\text{OH})_2\text{F}_2$	$\text{Al}^{3+} + \text{Na}^+ + 2\text{F}^- + 2\text{H}_2\text{O} \rightleftharpoons \text{NaAl}(\text{OH})_2\text{F}_2 + 2\text{H}^+$	-17.28	309.33	[50]
$\text{NaAl}(\text{OH})_3\text{F}$	$\text{Al}^{3+} + \text{Na}^+ + \text{F}^- + 3\text{H}_2\text{O} \rightleftharpoons \text{NaAl}(\text{OH})_3\text{F} + 3\text{H}^+$	-12.89	187.77	[50]
KAIO_2	$\text{Al}^{3+} + \text{K}^+ + 2\text{H}_2\text{O} \rightleftharpoons \text{KAIO}_2 + 4\text{H}^+$	-20.34	211.68	[50]

Table 4
THERMODYNAMIC STABILITY
CONSTANTS AND STANDARD MOLAL
ENTHALPY VALUES (kJ/mol) for
ALUMINIUM CHEMICAL SPECIES
FORMATION EQUILIBRIA
CONSIDERED IN THIS STUDY

Table 5
SATURATION INDEX VALUES OF THE ALUMINIUM MINERALS CALCULATED
FOR THE ANALYZED GROUNDWATER SAMPLES

Mineral	Formula	Source								
		FS9	FS8	FS27	PG-N	PG-E	VC	PG-S	PG-W	Apt2
Albite	NaAlSi ₃ O ₈	0.29	-2.17	-1.32	-0.23	-2.14	0.02	-0.72	-0.82	0.71
Alunite	KAl ₃ (OH) ₆ (SO ₄) ₂	-7.09	-4.08	-6.68	-4.23	-11.76	-5.61	-4.93	-5.62	-1.28
Amesite	Mg ₄ Al ₄ Si ₂ O ₁₀ (OH) ₈	1.09	-1.37	0.46	-1.82	5.60	-1.63	-5.14	-5.09	-0.85
Analcime	Na _{0.9} Al _{0.96} Si _{2.04} O ₆ ·H ₂ O	-0.13	-1.78	-1.25	-0.58	-1.48	-0.36	-1.07	-1.16	0.22
Andalusite	Al ₂ SiO ₅	-1.35	-1.78	-2.91	-1.73	-3.30	-2.43	-2.61	-2.84	-1.53
Anorthite	CaAl ₂ (SiO ₄) ₂	-4.01	-5.82	-5.15	-4.69	-5.03	-5.29	-5.97	-6.09	-4.71
Beidellite-Ca	Ca _{0.165} Al _{2.33} Si _{3.67} O ₁₀ (OH) ₂	4.41	1.74	1.54	3.82	-0.39	3.08	2.86	2.57	4.38
Beidellite-Mg	Mg _{0.165} Al _{2.33} Si _{3.67} O ₁₀ (OH) ₂	4.45	1.80	1.53	3.81	-0.36	3.12	2.85	2.55	4.44
Beidellite-Na	Na _{0.33} Al _{2.33} Si _{3.67} O ₁₀ (OH) ₂	4.02	1.40	1.14	3.41	-0.64	2.84	2.47	2.18	4.19
Boehmite	AlOOH	1.67	1.89	1.16	1.52	1.30	1.16	1.09	0.99	1.59
Celadonite	KMgAlSi ₄ O ₁₀ (OH) ₂	2.52	-1.61	1.12	1.06	1.87	0.67	0.22	0.14	2.82
Corundum	Al ₂ O ₃	-0.01	0.41	-1.05	-0.32	-0.78	-1.05	-1.22	-1.43	-0.23
Dawsonite	NaAlCO ₃ (OH) ₂	0.74	0.20	-0.47	0.08	-0.71	0.30	-0.24	-0.39	0.98
Diaspore	AlOOH	2.08	2.31	1.59	1.94	1.72	1.58	1.52	1.41	2.01
Epidote	Ca ₂ FeAl ₂ Si ₃ O ₁₂ OH	-0.48	-3.80	-	-0.11	3.02	-	-1.26	-0.40	-
Gibbsite	Al(OH) ₃	1.53	1.77	1.04	1.40	1.18	1.03	0.98	0.87	1.48
Gismondine	Ca ₂ Al ₄ Si ₄ O ₁₆ ·H ₂ O	6.27	3.35	4.76	5.42	4.97	4.24	3.69	3.38	6.26
Grossular	Ca ₃ Al ₂ (SiO ₄) ₃	-9.55	-13.23	-9.32	-10.76	-7.51	-11.16	-12.81	-12.70	-11.26
Illite	K _{0.6} Mg _{0.25} Al _{1.8} Al _{0.5} Si _{3.5} O ₁₀ (OH) ₂	4.50	1.62	2.03	3.50	1.47	2.54	2.44	2.15	4.76
Jadeite	NaAl(SiO ₃) ₂	-1.68	-3.29	-2.78	-2.14	-2.94	-1.91	-2.66	-2.75	-1.32
K-Feldspar	KAlSi ₃ O ₈	2.08	-0.80	0.56	1.22	0.50	0.41	0.73	0.55	2.71
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	4.39	3.16	2.39	3.99	1.33	3.32	3.21	2.96	4.39
Kyanite	Al ₂ SiO ₅	-1.05	-1.49	-2.61	-1.43	-3.00	-2.13	-2.31	-2.54	-1.23
Laumontite	CaAl ₂ Si ₄ O ₁₂ ·4H ₂ O	1.86	-1.59	-0.23	1.10	-1.44	0.56	-0.05	-0.21	1.41
Lawsonite	KAl ₂ Si ₂ O ₇ (OH) ₂ ·H ₂ O	0.65	-1.09	-0.42	0.02	-0.30	-0.58	-1.18	-1.31	0.09
Margarite	CaAl ₂ Si ₂ O ₁₀ (OH) ₂	0.01	-1.34	-2.13	-0.96	-1.74	-2.28	-3.09	-3.42	-0.83
Montmorillonite-Ca	Ca _{0.165} Mg _{0.33} Al _{1.67} Si ₄ O ₁₀ (OH) ₂	4.13	0.91	1.64	3.44	-0.11	3.09	2.65	2.47	4.05
Montmorillonite-Mg	Mg _{0.495} Al _{1.67} Si ₄ O ₁₀ (OH) ₂	4.25	1.04	1.70	3.50	-0.00	3.20	2.72	2.53	4.19
Montmorillonite-Na	Na _{0.33} Mg _{0.33} Al _{1.67} Si ₄ O ₁₀ (OH) ₂	3.82	0.64	1.31	3.11	-0.29	2.92	2.34	2.15	3.94
Mordenite	Ca _{0.2895} Na _{0.361} Al _{0.94} Si _{5.06} O ₁₂ ·3.468H ₂ O	0.46	-3.81	-2.14	-0.11	-4.67	-0.10	-0.53	-0.67	0.67
Muscovite	KAl ₃ Si ₃ O ₁₀ (OH) ₂	6.72	4.30	4.21	5.58	4.42	4.04	4.24	3.85	7.21
Nontronite-Ca	Ca _{0.165} Fe ₂ Al _{0.33} Si _{3.67} H ₂ O ₁₂	6.58	3.11	-	8.94	9.60	-	9.78	11.46	-
Nontronite-Mg	Mg _{0.165} Fe ₂ Al _{0.33} Si _{3.67} H ₂ O ₁₂	6.62	3.17	-	8.93	9.64	-	9.77	11.45	-
Nontronite-Na	Na _{0.33} Fe ₂ Al _{0.33} Si _{3.67} H ₂ O ₁₂	6.20	2.77	-	8.53	9.35	-	9.40	11.07	-
Paragonite	NaAl ₃ Si ₃ O ₁₀ (OH) ₂	4.01	2.01	1.41	3.20	0.86	2.73	1.86	1.55	4.29
Phlogopite	KAlMg ₃ Si ₃ O ₁₀ (OH) ₂	-0.33	-4.45	-0.04	-2.84	4.35	-2.46	-4.55	-4.35	-0.98
Prehnite	Ca ₂ Al ₂ Si ₃ O ₁₀ (OH) ₂	-2.09	-5.21	-2.75	-3.03	-2.11	-3.52	-4.62	-4.64	-3.17
Pyrophyllite	Al ₂ Si ₄ O ₁₀ (OH) ₂	3.37	0.43	0.34	2.84	-2.05	2.22	2.10	1.82	3.47
Sanidine	KAlSi ₃ O ₈	0.83	-2.07	-0.71	-0.05	-0.77	-0.86	-0.54	-0.72	1.43
Saponite-Ca	Ca _{0.165} Mg ₃ Al _{0.33} Si _{3.67} O ₁₀ (OH) ₂	0.62	-3.72	0.59	-1.32	2.83	-0.13	-2.62	-2.32	-0.50
Saponite-Mg	Mg _{3.165} Al _{0.33} Si _{3.67} O ₁₀ (OH) ₂	0.67	-3.66	0.58	-1.33	2.87	-0.09	-2.63	-2.33	-0.44
Saponite-Na	Na _{0.33} Mg ₃ Al _{0.33} Si _{3.67} O ₁₀ (OH) ₂	0.24	-4.06	0.19	-1.73	2.58	-0.38	-3.00	-2.71	-0.68
Scolecite	CaAl ₂ Si ₃ O ₁₀ ·3H ₂ O	3.37	0.78	1.80	2.68	1.25	2.11	1.52	1.37	2.88
Spinel	Al ₂ MgO ₄	-7.80	-7.85	-8.30	-8.71	-6.54	-9.04	-10.08	-10.15	-8.56
Wairakite	CaAl ₂ Si ₄ O ₁₀ (OH) ₄	-2.82	-6.33	-4.98	-3.62	-6.18	-4.16	-4.84	-5.00	-3.38
Zoisite	Ca ₂ Al ₃ (SiO ₄) ₃ OH	-3.39	-6.32	-4.60	-4.51	-3.82	-5.36	-6.58	-6.70	-4.63

calculates both activities of aqueous species and departure from equilibrium (saturation index, SI_{min} [60]) for many heterogeneous systems containing a solid phase (minerals) and gases that might be in contact with the aqueous phase. The SI_{min} is expressed as:

$$SI_{min} = \lg \frac{Q}{K_{sp}}$$

where Q – the activities product of the ions belonging to the solid or to the gaseous phase compounds, and K_s – the solubility coefficient of the concerned solid or gaseous phase, for the specified temperature.

When SI_{min} is equal to 0, the solid is in equilibrium with the aqueous phase. When SI_{min} is less than 0, the solution is inferred to be under-saturated with respect to the concerned phases and therefore the latter are liable to be further dissolved. When SI_{min} is greater than 0, the solution is subject to oversaturation states and the mineral species dissolved are liable to get out of the system, by

precipitation. If present in the aquifer system, minerals characterized by calculated negative saturation indices probably are dissolving, although the dissolution rates may be extremely low.

The values of the saturation indexes, SI_{min} of some representative analyzed groundwater samples, with respect to computed mineral species of aluminium are presented in table 5. The chosen samples include a group of five monitoring wells installed to determine water content variation with depth. These wells, named "Pump groups" are very close together: about 4–10 m. As the red clay was considered the most important hydro geologic barrier, they were only drilled to the bottom of this horizon.

The obtained data shows that the groundwater proceeding from a singular aquifer system is strongly oversaturated with respect to clay mineral species (montmorillonite, beidellite, illite, nontronite, kaolinite etc.). When this groundwater is mixed with a weakly mineralized surface water, the SI_{min} values decrease and the water becomes under-saturated with respect to some mineral

species. This is the case of the Pump Group East (PGE) well, as well as for FS18 and FS24 drilling respectively (table 5). This is an important observation because it makes the possibility of the solubilization of the red clay horizons, considered as natural barriers for the radionuclides migration.

Conclusions

In order to evaluate the distribution of inorganic species of aluminium in groundwater from Saligny area where the low and intermediate level radioactive wastes generated at Cernavodă Nuclear Power Plant are planned to be disposed into a future new repository, water samples have been collected from aquifers with distinct hydrogeological features. The atomic absorption spectrometric method with electrothermal atomization in a graphite furnace, GF-AAS has been employed for directly assessing the aluminium content in all the samples.

The aluminium speciation modelling for the investigated water types, has been conducted by means of the PHREEQC computer code, with the required database supplied by the Lawrence Livermore National Laboratory (LLNL) as version "thermo.com.V8.R6.230"; additionally supplemented with thermodynamic data were necessary in order to provide assessments for other ionic associations that aluminium generated with Si species, SO_4^{2-} , F^- , Na^+ and K^+ in natural aqueous systems.

For groundwater derived from low permeability reservoir rocks of Saligny area the prevalent inorganic species of aluminium were the hydroxide complexes, among which the largest percentage was displayed by the tetrahydroxoaluminate ion. Moreover, significant concentrations of ion-pairs were formed by the aluminate ion with dissolved silica. The chemical-analytical data were interpreted by means of groundwater saturation state calculation, as SI_{min} values, toward some mineral species of the aluminium. This evaluation makes an oversaturated state of the groundwater in clay mineral species, but when this groundwater is mixed with a weakly mineralized surface water, it becomes under-saturated with respect to some mineral species. The possible solubilization of the red clay horizons, diminishes the role of the natural red clay layers as natural barriers for the radionuclides migration.

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