

## WATER LEACHING OF ALKALINE METALS, Al AND Si FROM SELECTED ALUMINOSILICATES

Zdeněk KLIKA <sup>1)</sup>\*, Zdeněk WEISS <sup>1)</sup> and Marcello MELLINI <sup>2)</sup>

<sup>1)</sup> *Technical University Ostrava, Tr.17.listopadu, 708 33 Ostrava-Poruba, Czech Republic,  
Tel.: (420) 59-6991548, Fax: (420) 59-6991665*

<sup>2)</sup> *Dip.Scienze Terra, Università, Via Laterina 8, 53100, Siena, Italy*

*\*Corresponding author's e-mail: zdenek.klika@vsb.cz*

*(Received March 2005, accepted September 2005)*

### ABSTRACT

Laboratory prepared mica Cs-tetra-ferri-annite, CsAlSiO<sub>4</sub>, Cs-montmorillonite and Cs-zeolite 13X together with natural phyllosilicates (biotite, muscovite, illite, and Na-montmorillonite), orthoclase, analcime, and zeolites (NaY-Z, Na4A-Z) were tested on leaching of alkaline metals, Al, and Si with water at 100 °C. There was found good potential for leaching of alkali elements. Cesium is better leachable from Cs-minerals (mica, aluminosilicate and zeolite) than K or Na from related K- and Na- mineral analogues. From all samples except zeolites silicon leaches more easily than aluminium. Iron and/or aluminium bonded in octahedral positions in micas and montmorillonites are the least leached elements almost from all samples except zeolites. From tetrahedral position of zeolites the aluminum leaches out easily due to rich pore texture of zeolites. The leaching of alkali elements and aluminium increases with increasing ratio of Al/Si in related solid samples. The structural considerations that led to the hypothesis about very high structural stability and limited leachability of micas have been fully confirmed. The micas are most leach-resistant materials and therefore Cs-tetra-ferri-annite can be considered as a waste form for the fixation of Cs from radioactive Cs waste. Cs-montmorillonite bonds Cs<sup>+</sup> more strongly than Na<sup>+</sup> ion so that Na-montmorillonite can be considered for an outer barrier capable of buffering the possible escape of Cs.

**KEYWORDS:** cesium, leaching, Cs-tetra-ferri-annite, CsAlSiO<sub>4</sub>, Cs-zeolite, Cs-montmorillonite

### 1. INTRODUCTION

The problem of radioactive cesium waste disposal is getting more important. In fact, cesium can be usually leached out easily with water from most of the Cs-containing materials; subsequently, cesium may be transported through the water ecosystem and adsorbed on soils (Gutierrez and Fuentes, 1996; Hsu and Chang, 1994; Dumat et al., 2000). For the safe disposal of the radioactive waste, deep underground deposits are usually proposed. They are composed of three zones (Jurček et al., 1996). In zone (1), the radioactive waste is transformed into an immobilized form, from which the dangerous components cannot be easily leached out. The immobilized waste should have not only chemical but also mechanical resistance. Zone (2), an engineered barrier, secures long-time retardation of radionuclides escape and host rocks, zone (3), then protect the penetration of underground water from zones (1) and (2).

Some radioactive waste strategies use for immobilization of radioactive isotopes (<sup>137</sup>Cs and <sup>135</sup>Cs) Cs-aluminosilicates (zone 1). Particularly the phases CsAlSiO<sub>4</sub>, CsAlSi<sub>5</sub>O<sub>12</sub> and CsAlSi<sub>2</sub>O<sub>6</sub> (pollucite) have been discussed. Gallagher et al. (1977) and by Ito (1976) described the preparation of CsAlSiO<sub>4</sub> and CsAlSi<sub>5</sub>O<sub>12</sub> phases, respectively. Recently, two new mica phases (Cs-annite and Cs-tetra-ferri-annite) were synthesized and characterized

(Mellini et al., 1996; Drábek et al., 1998; Comodi et al., 1999). These mineral analogues offer one more potential way to deal with the efficient immobilization of radioactive cesium. Cs-tetra-ferri-annite, in particular, can be easily synthesized under hydrothermal conditions attainable even within a real, industrial-scale immobilizing plant. Furthermore, its formation conditions do not contrast with the expected working conditions in the waste depository. Finally, from the structural point of view, Cs-tetra-ferri-annite appears extremely stable, with limited internal strain (Mellini et al., 1996; Comodi et al., 1999).

Zeolites and clay minerals are typical materials for engineered barriers (zone 2). Natural zeolites, e.g., ferrierite (Mimura et al., 1992) and clinoptilolite (Arcoya et al., 1996), as well as synthesized zeolites (usually obtained from fly ash) were studied for sorption of cesium from water solutions (e.g. Alastuey et al., 1997; Weiping et al., 1996). Clay minerals and clays are probably the most frequently tested for cesium adsorption. These phases occur in sediments and therefore they control immobilization and transport of <sup>137</sup>Cs and <sup>135</sup>Cs isotopes in water solutions (Smith and Comans, 1996; Kim and Kirkpatrick, 1997 and 1998; Hsu et al., 1994; Hsu and Chang, 1994).

For the case of catastrophic scenario at which the zone 1 will be dislocated the leaching and adsorption ability of materials considered for zone 1 and zone 2,

respectively will be of the first priority. The adsorption of Cs on zeolites and clay minerals were described anywhere (e.g. Gutierrez and Fuentes, 1996; Oscarson et al., 1994; Miyahara et al., 1991; Cho et al., 1993; Khan et al., 1994) but the studies focused on the leaching/dissolution of Cs together with other material forming elements (Si, Al, etc) in water are less numerous (e.g. Haynes, 1978 and Berger et al., 1988). The sequence and intensity of major elements leaching from poorly leachable/soluble minerals is rather more studied using acid solutions than water. From these studies result that exchangeable cations from mineral interlayer dissolve the first. Leached cations are replaced by protons forming H mineral forms (Komadel, 2003). Then the process continues by removing central atoms from octahedral and Al also from tetrahedral sites. Protons from solutions attack not only margins of the grain particles but also interlayer of the mineral structure. Trioctahedral minerals are more easily dissolved than dioctahedral ones (Rodríguez, 1994; Jozefaciuk and Bowanko 2002). Using the NMR and Mossbauer spectroscopy it was found that dissolution velocities of  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  from octahedrons and tetrahedrons of smectites are similar but with increasing replacement of Al for Mg and/or Fe the dissolution velocity from octahedrons increases (Novák and Čičel, 1978). Final product of clay mineral dissolution in acid solutions is partly protonated microcrystalline  $\text{SiO}_2 \cdot x\text{H}_2\text{O}$  (Tkáč et al., 1994; Bickmore et al., 2001).

We now report the actual leachability of Cs-tetra-ferri-annite and compare it with leachability of biotite, muscovite and illite. The leachability of  $\text{CsAlSiO}_4$  is then compared with leachability of natural orthoclase and analcime. Both Cs-tetra-ferri-annite and  $\text{CsAlSiO}_4$  were obtained by laboratory synthesis and can be used for the immobilization of radioactive isotope of  $^{137}\text{Cs}$  in zone 1. In contrast, Na-montmorillonite and Na-zeolite are the most frequently proposed materials for engineered barriers (zone 2). The Cs doped montmorillonite and zeolite 13X were laboratory prepared by full saturation with Cs solution and their leaching was performed. The leachability of the Cs-montmorillonite is compared with leachability of natural Na-montmorillonite and leachability of Cs-zeolite 13X with Na-zeolite Y as well as with Na4A-zeolite, both use in commerce.

## 2. EXPERIMENTAL

### ANALYTICAL METHODS

X-ray fluorescence (SpectroLab) was used for bulk chemical analyses of solid samples. Cesium, Na, K, Mg and Ca in solids and leachates were determined by atomic absorption spectrometry (AAS, Unicam 969). Dissolved Si, Al and Fe concentrations in leachates were determined by ICP (Jobin Yvon 24). An INEL X-ray powder diffractometer with a PSD 120 position sensitive detector, Ge monochromator and  $\text{CuK}_\alpha$  radiation was used to record X-ray patterns.

The specific surface area of samples and pore size distribution were determined by Sorptomatic 1990 (TermoQuest). The cation exchange capacity (CEC) of Na-montmorillonite and Na-zeolite was determined from  $\text{Cs}^+ \leftrightarrow \text{Na}^+$  ion exchange (Zachara et al., 2002). Loss of ignition (L.O.I.) was determined by gravimetry at  $1000^\circ\text{C}$ .

### SAMPLES

Four groups of minerals containing alkaline metal (Cs or Na and /or K) were selected for water leaching test. The minerals ranged into groups I (micas) and II (tectosilicates) contain alkaline metals strongly bonded in the mineral structure while in minerals ranged into groups III (smectites) and IV (zeolites) the alkaline metals are weakly bonded in the interlayer and in the structure channels, respectively. The following aluminosilicates are included in the individual groups:

#### Group I:

1. Cs-tetra-ferri-annite (Cs-TFA) with the chemical formula  $\text{Cs Fe}^{2+}_3 (\text{Fe}^{3+} \text{Si}_3) \text{O}_{10} (\text{OH})_2$ , was synthesized from a mixture of  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{CsOH}$  at  $600^\circ\text{C}$  (Drábek et al., 1998). The specific area and CEC of powdered sample used for leaching tests are less than the limits of detection,  $0.4 \text{ m}^2 \cdot \text{g}^{-1}$  and  $0.03 \text{ m-equiv} \cdot \text{g}^{-1}$ , respectively, for the techniques used in this study.

2. Biotite (BIO) with the chemical formula  $(\text{K}_{0.90}\text{Na}_{0.10}(\text{Al}_{1.17}\text{Fe(III)}_{0.30}\text{Mg}_{1.20}\text{Fe(II)}_{1.20}\text{Ti}_{0.10})[\text{Al}_{1.01}\text{Si}_{3.00}]) \text{O}_{10}(\text{OH})_2$  was collected from pegmatite at Dolní Bory (Czech Republic) and the specific area of powdered sample used for leaching tests is equal to  $8.0 \text{ m}^2 \cdot \text{g}^{-1}$ .

3. Muscovite (MUS), with the chemical formula  $(\text{K}_{0.79}\text{Na}_{0.09}(\text{Al}_{1.88}\text{Fe(III)}_{0.01} \text{Mg}_{0.05}\text{Fe(II)}_{0.07} \text{Ti}_{0.004})[\text{Al}_{0.60}\text{Si}_{3.40}]) \text{O}_{10}(\text{OH})_2$  was also collected at Dolní Bory (Czech Republic) and the specific area of powdered sample used for leaching tests is equal to  $6.2 \text{ m}^2 \cdot \text{g}^{-1}$ .

4. Illite (ILL) with the chemical composition  $(\text{K}_{0.38}\text{Na}_{0.11}(\text{Al}_{1.60}\text{Fe(III)}_{0.05}\text{Mg}_{0.10} \text{Fe(II)}_{0.20}\text{Ti}_{0.10})[\text{Al}_{0.45}\text{Si}_{3.55}])\text{O}_{10}(\text{OH})_2$  was obtained from Illinois (USA) and its specific area is  $53.3 \text{ m}^2 \cdot \text{g}^{-1}$ .

#### Group II:

5. CsAlSiO<sub>4</sub> (Cs-AS) was synthesized from a mixture of  $\text{Cs}_2\text{CO}_3$  and kaolinite at  $1100^\circ\text{C}$ . The specific area of powdered sample used for leaching tests is equal to  $11.2 \text{ m}^2 \cdot \text{g}^{-1}$  and CEC to  $0.10 \text{ m-equiv} \cdot \text{g}^{-1}$ .

6. Orthoclase (ORT) with the composition  $\text{K}_{0.92}\text{Na}_{0.08}\text{Al}_{0.97}\text{Si}_{3.05}\text{O}_8$  was sampled at Kunštát (Czech Republic) and specific area of powdered sample used for leaching tests is equal  $5.3 \text{ m}^2 \cdot \text{g}^{-1}$ .

7. Analcime (ANALC) with the composition  $\text{Na}_{0.90}\text{K}_{0.10}\text{Al}_{0.97} (\text{SiO}_3)_2 \cdot \text{H}_2\text{O}$  was also sampled at Kunštát (Czech Republic) and specific area of powdered sample is  $5.3 \text{ m}^2 \cdot \text{g}^{-1}$ .

**Table 1** Bulk chemical analyses of Cs-tetra-ferri-annite (Cs-TFA), CsAlSiO<sub>4</sub> (Cs-AS), Na-montmorillonite (Na-MMT), Cs-montmorillonite (Cs-MMT), Na-zeolite 13X (Na-Z) and Cs-zeolite 13X (Cs-Z).

	Cs-TFA (%)	Cs-AS (%)	Cs-MMT (%)	Cs-Z (%)
SiO <sub>2</sub>	29.94	25.27	53.44	37.27
TiO <sub>2</sub>	<0.02	<0.02	0.16	0.02
Al <sub>2</sub> O <sub>3</sub>	0.21	19.85	18.87	21.79
Fe <sub>2</sub> O <sub>3</sub>	12.10	<0.01	4.54	<0.01
FeO	34.52	<0.02	<0.02	<0.02
CaO	<0.05	<0.05	0.32	0.06
MgO	<0.24	<0.24	2.20	<0.24
Na <sub>2</sub> O	<0.05	<0.05	<0.05	3.84
K <sub>2</sub> O	<0.02	<0.02	0.59	0.03
Cs <sub>2</sub> O (Cs)	20.32 (19.17)	54.87 (51.7)	9.36 (8.83)	24.84 (23.43)
L.O.I.	2.92	<0.05	10.53	12.05
TOTAL	100.01	99.99	100.01	99.87

**Table 2** Bulk chemical analyses of Na and K analogues to Cs-TFA, Cs-AS, Cs-MMT and Cs-Z.

	MUS (%)	BIO (%)	ILL (%)	ORT (%)	ANAL (%)	Na-MMT (%)	NaY-Z (%)	Na4A-Z (%)
SiO <sub>2</sub>	52.38	38.11	53.70	65.70	54.56	57.80	53.61	33.67
TiO <sub>2</sub>	0.08	1.58	2.00	0.05	<0.03	0.16	0.04	0.01
Al <sub>2</sub> O <sub>3</sub>	31.38	12.83	29.07	17.70	22.45	20.25	16.61	28.06
Fe <sub>2</sub> O <sub>3</sub>	0.19	5.14	0.95	0.05	<0.04	4.89	0.11	0.03
FeO	1.26	18.42	4.06	-	-	<0.02	-	-
CaO	0.01	0.04	0.10	<0.05	<0.04	0.35	0.06	0.02
MgO	0.50	10.11	0.94	<0.10	<0.10	2.40	<0.06	<0.06
Na <sub>2</sub> O	0.70	0.70	0.81	0.89	12.66	2.05	8.36	14.72
(Na)	(0.52)	(0.52)	(0.60)	(0.66)	(9.39)	(1.52)	(6.20)	(10.94)
K <sub>2</sub> O	9.37	9.11	4.17	15.56	1.89	0.70	0.03	0.04
(K)	(7.78)	(7.56)	(3.46)	(12.92)	(1.57)	(0.58)	(0.03)	(0.03)
L.O.I.	4.52	3.87	4.50	0.10	8.18	11.35	21.00	23.01
TOTAL	100.39	99.91	100.30	100.05	99.74	99.95	99.82	99.56

**Group III:**

8. Na-montmorillonite (Na-MMT) with the chemical formula Na<sub>0.41</sub>K<sub>0.11</sub>Ca<sub>0.05</sub>(Mg<sub>0.47</sub>Fe(III)<sub>0.49</sub>Al<sub>3.05</sub>) [Si<sub>7.78</sub>Ti<sub>0.02</sub>Al<sub>0.21</sub>] O<sub>20</sub>(OH)<sub>4</sub>, was obtained from Wyoming (U.S.A). Its specific area and CEC are equal to 136 m<sup>2</sup>.g<sup>-1</sup>, and 0.71 m-equiv.g<sup>-1</sup>, respectively.

9. Cs-montmorillonite (Cs-MMT) was prepared from previously described Na-MMT using cation-exchange procedure (Klika et al., 2005).

**Group IV:**

10. Cs-zeolite 13X (Cs-Z) with the composition 0.088Cs<sub>2</sub>O . 0.062Na<sub>2</sub>O . 0.214Al<sub>2</sub>O<sub>3</sub> . 0.620SiO<sub>2</sub> . 0.670H<sub>2</sub>O was prepared (Klika et al., 2005) from commercially available Na-form of zeolite 13X (Na-Z) produced by Linde Air Products Company, USA

and its specific area is 465 m<sup>2</sup>.g<sup>-1</sup> and CEC is equal to 2.13 m-equiv.g<sup>-1</sup>.

11. NaY-zeolite (NaY-Z), with the composition 0.135Na<sub>2</sub>O. 0.163Al<sub>2</sub>O<sub>3</sub>. 0.896SiO<sub>2</sub>. 1.17H<sub>2</sub>O is commercially available and it is produced by VURUP, Bratislava (Slovakia). Its specific surface area is 641 m<sup>2</sup>.g<sup>-1</sup>.

12. Na4A-zeolite (Na4A-Z) with the composition 0.238Na<sub>2</sub>O. 0.275Al<sub>2</sub>O<sub>3</sub>. 0.557SiO<sub>2</sub>. 1.28H<sub>2</sub>O is commercially available and it is produced by VURUP, Bratislava (Slovakia). Its specific surface area is 150 m<sup>2</sup>.g<sup>-1</sup>.

The bulk chemical analyses of all samples are given in Tables 1 and 2. All samples were ground and milled using an agate rotary mill. The ground materials were then sieved to obtain the size fraction below 0.04 mm, which was used for the water leaching study.

**Table 3** Na, Cs, Al, Fe<sub>tot</sub> and Si leached from samples at 100 °C after 80 hours.

Mineral groups	Samples	$w_i$ (mg/g)						Alk (wt %)
		Cs	K	Na	Al	Fe <sub>tot</sub>	Si	
micas	Cs-TFA	6.52	-	-	-	0.05	4.50	3.40
	BIO	-	1.16	-	<0.02	-	5.28	1.58
	ILL	-	1.44	-	<0.02	-	1.98	4.04
	MUS	-	1.56	-	0.22	-	1.60	2.05
alumosilicates	Cs-AS	104	-	-	1.60	-	13.0	20.1
	ORT	-	0.84	-	0.22	-	5.56	0.62
	ANALC	-	-	2.92	0.35	-	3.16	3.823
montmorillonites	Cs-MMT	11.6	-	0.80	0.05	-	8.20	13.1
	Na-MMT	-	-	8.72	2.8	-	36.4	57.2
zeolites	Cs-Z	37.7	-	2.0	9.30	-	6.20	16.1
	NaY-Z	-	-	7.76	10.0	-	14.0	12.58
	Na4A-Z	-	0.20	8.80	5.44	-	3.4	8.04

#### BATCH LEACHING OF SAMPLES UNDER REFLUX

The sample (100 mg in weight) was kept boiling (100 °C) with 100 cm<sup>3</sup> of deionized water in a boiling flask equipped with a water cooler. After a boiling period of 80 hours, the suspension was cooled to the laboratory temperature, and the solid phase was separated by centrifugation at 5000 rpm for 30 min. The supernatant was filtered through the micro filter Pragopor 5 (0.60 μm), pH was measured and the Cs, K and Na concentrations were determined by AAS. Al, Si and total Fe were also determined using the ICP or photometric methods.

### 3. RESULTS AND DISCUSSION

The 12 solid samples were tested for alkali (Alk) and next metal (Al, Fe and Si) removal by water leaching. The weight fractions of leached metals from solid samples,  $w_i$  (mg.g<sup>-1</sup>), were calculated from the formula

$$w_i = \frac{c_i \cdot V}{m} \quad (1)$$

where  $c_i$  is the concentration of the  $i$ -th metal in solution after leaching (mg.cm<sup>-3</sup>),  $V$  the volume of water solution added (cm<sup>3</sup>), and  $m$  the weight of the Cs-form sample before leaching (g).

The percentages of leached alkali metal (Alk %) with respect to total alkali metal in the original sample,  $w_s$  (mg.g<sup>-1</sup>), can be calculated from the formula

$$Alk \text{ (wt \%)} = 10^2 \frac{w_{Alk}}{w_s} \quad (2)$$

where  $w_{Alk}$  is calculated from eq. (1)

Alkali metals might be extracted from the solid sample either by partial dissolution of the sample,

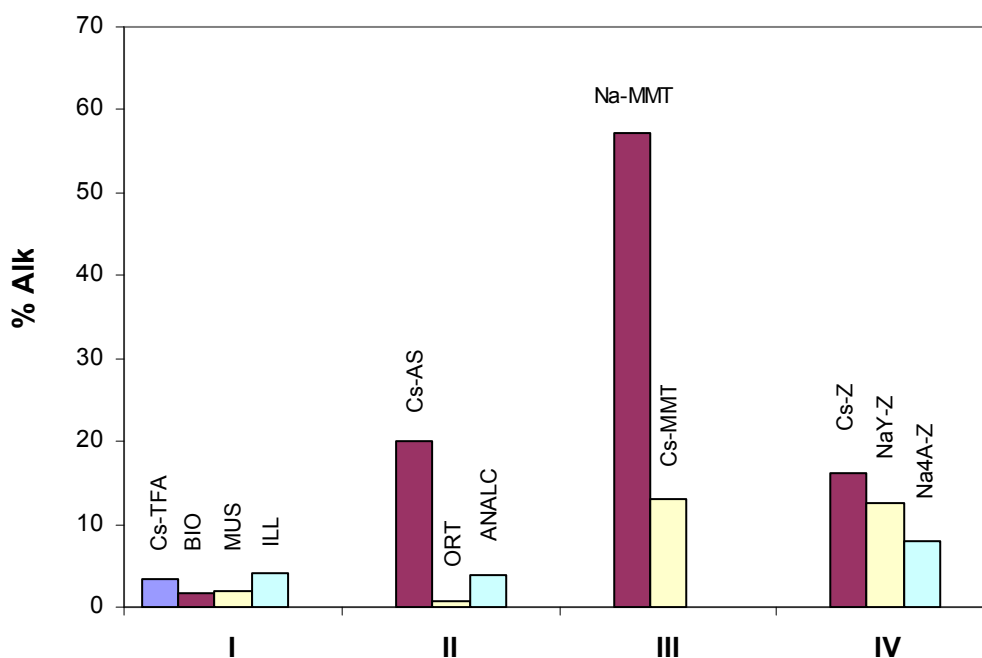
and/or by selective leaching from the material. To investigate these alternatives the solid samples were extracted with water using the above method described in paragraph 2. Batch leaching at the boiling point of water gives greater alkali and next metal removal and therefore it was preferred before leaching at ambient temperature.

X-ray diffraction patterns of 80-hours leached solid samples were recorded and the patterns matched exactly with those ones related to original samples. No other diffraction patterns belonging to new crystalline phases were observed in the leached samples by Berger et al. (1988) who studied zeolite, chlorite and smectite in connection with leaching of glasses at temperatures from 50 to 300 °C. They found the diffraction patterns of newly formed phases not until 100°C, at lower temperatures the new phases were present in a very poor crystallized forms.

The 80-hours leachates were analyzed for Cs, Na, K, Al, Fe and Si. The weight fractions

of leached elements from the all samples ( $w_i$ ) are reported in Table 3. In the same table percentages of alkali metal related to total alkali metal content in the minerals (*Alk wt. %*) were calculated using the eq. (2); the values  $w_s$  were recalculated from data given in Tables 1 and 2.

As the alkali element cesium was selected for Cs-TFA, Cs-AS, Cs-MMT, Cs-Z, potassium for MUS, BIO, ILL, ORT, and sodium for ANALC, Na-MMT, NaY-Z, Na4A-Z. The percentages of leached alkali metals are plotted in Fig.1. Minerals from group I (mica) are the most resistant against the alkali metals dissolution. Next minerals follow them from groups II, III and IV. The extreme leaching of Cs from Cs-AS suggests that the advantages of preparing the phase at high temperatures has almost disappeared when Cs-AS is leached with water at 100 °C. Komarneni and Roy (1978) found that by heating Cs saturated illites



**Fig. 1** Percentages of leached alkali elements (wt%) into water solutions at 100 °C after 80 hours of leaching

to temperatures exceeding 750 °C drastically reduced de-sorption of Cs by factors of between about 8 and 1.4. These findings are in agreement with the results obtained for Cs-AS prepared at temperature 1100 °C. The Cs leached from Cs-AS at ambient temperature (Klika et al., 2005) is much lower (3.3%) than that leached at 100 °C (20.1%). Also Na from Na-MMT leaches much easier than Cs from Cs-MMT. The bond of Na in interlayer of MMT is very poor comparing it with other alkali elements (Weiss et al, 1998). The higher leaching of alkali elements from mineral group III and IV is given by character of their bonds. In montmorillonites the alkali elements are situated in interlayer and in zeolites in micro pores while in micas and aluminosilicates they are strongly bonded in aluminosilicate structure.

The percentages of the samples that had dissolved were estimated by summing the leached elements (Table 3). In mineral group I (micas) the percentages of leached samples are about: 1.1% for Cs-TFA, 0.65 % for BIO, 0.32 % MUS and 0.35 % of ILL. In mineral group II (tectosilicates) the percentages of leached samples are about: 12 % for Cs-AS, 0.67 % for ORT and 0.65 % of ANALC. Similarly in-group III (smectites) the percentages of leached samples are about: 4.8 % for Na-MMT and 2.1 % for Cs-MMT; in-group IV (zeolites) the percentages of leached samples are about: 5.3 % for Cs-Z, 3.2 % for NaY-Z and 1.8 % for Na4A-Z.

In order to compare the proportion of elements extracted from solid to leachate, solution molar ratios (SMR =  $w_i/w_{Si}$ ) between these elements and silicon were calculated (Table 4). Berger et al. (1988) used similar approach. The data in Table 4 were

recalculated from data presented in Table 3. The molar ratio of elements in the original solid samples (formula molar ratio, FMR =  $w_i/w_{Si}$ ) was calculated from the bulk chemical analyses of Tables 1 and 2, the  $Fe_{total}$  content was calculated from percentages of FeO and Fe<sub>2</sub>O<sub>3</sub> oxides. Calculated FMR and SMR values for all samples elements under the study are reported in Table 4.

Results from *micas* leaching (Cs-TFA, BIO, MUS, and ILL) showed that alkali metals but also Si, Al and/or Fe dissolve least from all tested 12 samples (Table 3). Moreover, except Cs-TFA and biotite not congruent leaching of Cs (SMR > FMR) is observed for ILL and MUS. The dissolution of Al and/or Fe is much less than dissolution of alkali metals; compare SMR data for Cs/Si, K/Si and Al/Si (or Fe/Si for Cs/TFA) in Table 4. In micas Al and/or Fe atoms are mostly bonded in octahedral layer enclosed between two tetrahedral layers (containing Si atoms), forming together three layered structure; alkali metals (Cs, K, Na) are then tightly bonded between these 2:1 layers. From this structural order much less leaching of Al and/or Fe atoms in contrast with alkali elements (and Si) can be anticipated. In Fig. 2 the molar ratios SMR (Alk/Si and Al/Si) versus FMR (Al/Si) are plotted. Increasing trend of Al and K solubility with increasing Al content in BIO, ILL and MUS samples is observed. Different leaching behaviour of Cs from Cs-TFA can be evocated by much higher diameter of Cs cation between 2:1 layers and by fact that the Cs-TFA was prepared synthetically in laboratory and therefore its somewhat different leachability can be expected.

Structure of *tectosilicates* is formed from tetrahedrons mutually linked by all their oxygen

**Table 4** Molar ratios of major elements to Si in samples (FMR) and in their leachates (SMR) after leaching at 100° C for 80 hours

Mineral groups	Samples	$w_i/w_{Si}$ (mmol/mmol)						
		Mass ratios	Cs/Si	K/Si	Na/Si	Al/Si	Fe <sub>total</sub> /Si	
micas	Cs-TFA	<b>FMR</b>	0.30	-	-	-	1.26	
		<b>SMR</b>	0.30	-	-	-	0.01	
	BIO	<b>FMR</b>	-	0.30	-	0.39	0.50	
		<b>SMR</b>	-	0.16	-	<0.004	0.02	
	ILL	<b>FMR</b>	-	0.11	-	0.58	-	
		<b>SMR</b>	-	0.54	-	<0.01	-	
	MUS	<b>FMR</b>	-	0.23	-	0.73	-	
		<b>SMR</b>	-	0.70	-	0.19	-	
	alumosilicates	Cs-AS	<b>FMR</b>	0.93	-	-	0.93-	-
			<b>SMR</b>	1.69	-	-	0.12	-
ORT		<b>FMR</b>	-	0.30	-	0.32	-	
		<b>SMR</b>	-	0.11	-	0.04	-	
ANALC		<b>FMR</b>	-	-	0.45	0.49	-	
		<b>SMR</b>	-	-	1.12	0.11	-	
montmorillonites	Cs-MMT	<b>FMR</b>	0.074	-	<0.002	0.42	-	
		<b>SMR</b>	0.30	-	0.12	0.006	-	
	Na-MMT	<b>FMR</b>	-	0.01	0.05	0.42	-	
		<b>SMR</b>	-	-	0.25	0.08	-	
zeolites	Cs-Z	<b>FMR</b>	0.27	-	0.20	0.69	-	
		<b>SMR</b>	1.29	-	0.39	1.6	-	
	NaY-Z	<b>FMR</b>	-	-	0.30	0.36	-	
		<b>SMR</b>	-	-	0.67	0.74	-	
	Na4A-Z	<b>FMR</b>	-	-	0.85	0.99	-	
		<b>SMR</b>	-	0.04	3.14	1.66	-	

Notes: FMR  $[(w_i/w_{Si})_s]$ , formula molar ratio, calculated from chemical analysis of solid sample (calculated from data in Tables 1 and 2)

SMR  $[(w_i/w_{Si})_l]$ , molar ratio of elements in water leachates after leaching at 100° C for 80 hours (calculated from data in Table 3)

atoms. The presence of Al in tetrahedrons enables the presence of alkali metals bonded in cavities of tetrahedral system. From this aspect the alkali metals can be relatively easily leached (not ORT) while Al and Si dissolve much poorly. Leaching tests with  $K_{0.92}Na_{0.08}Al_{0.97}Si_{3.05}O_8$  (ORT),  $Na_{0.90}K_{0.10}Al_{0.97}(SiO_3)_2 \cdot H_2O$  (ANALC) and  $CsAlSiO_4$  (Cs-AS) validate that with increasing proportion of Al/Si in mineral formula (FMR) the SMR of alkali elements (Alk/Si) and Al/Si in water leachates increase (Table 4). The trend of SMR for Alk/Si and Al/Si are also plotted in (Fig. 3).

Structure of *smectites* is similar to mica structure, however, the hydrated alkali metal cations are weakly bonded in the interlayer. Coulombic, Van der Waals and interactive energy (e.g., Grauer et al, 1987; Tahani et al., 1999) participate on the bonding of hydrated cations and therefore the alkali metals bonds are much inferior to their covalent bond in micas. It results in somewhat easier leaching of alkali elements from smectites than that from micas (Fig. 1 and Table 4). The ratio Al/Si in leachates remains very low as was already discussed for micas.

Alkali metals leaches from all tested *zeolites* very easy (SMR of Cs/Si or Na/Si are much higher than their FMR, see Table 4). In contrast to previous minerals aluminium is more easily removed (Table 4). Easy removal of aluminium from zeolites was also reported by Haynes (1978) for higher temperatures and acid solutions. The zeolite minerals belong also to tectosilicates but in contrast with Cs-AS, ANALC and ORT they form complicated structure with relative big cavities among their tetrahedrons. The maximal occurrence of the pore width is less than 7-8 Å (detection limit of the method) as is shown in Fig. 4 for Cs-Z sample. Very large specific surface area and numerous pores enable relatively good leaching of alkali metals and aluminium from zeolites. In Fig. 5 SMR ratios of Al/Si and Alk/Si in water leachates from three zeolite samples (NA4-Z, Cs-Z and NaY-Z) are plotted. The increasing trends of both curves show more intensive leaching of Al and alkaline cations from zeolites with higher content of Al. In tested zeolites the leaching of elements (Cs and/or Na, Al and Si) is more influenced by composition (and probably structure) of zeolites than by their surface

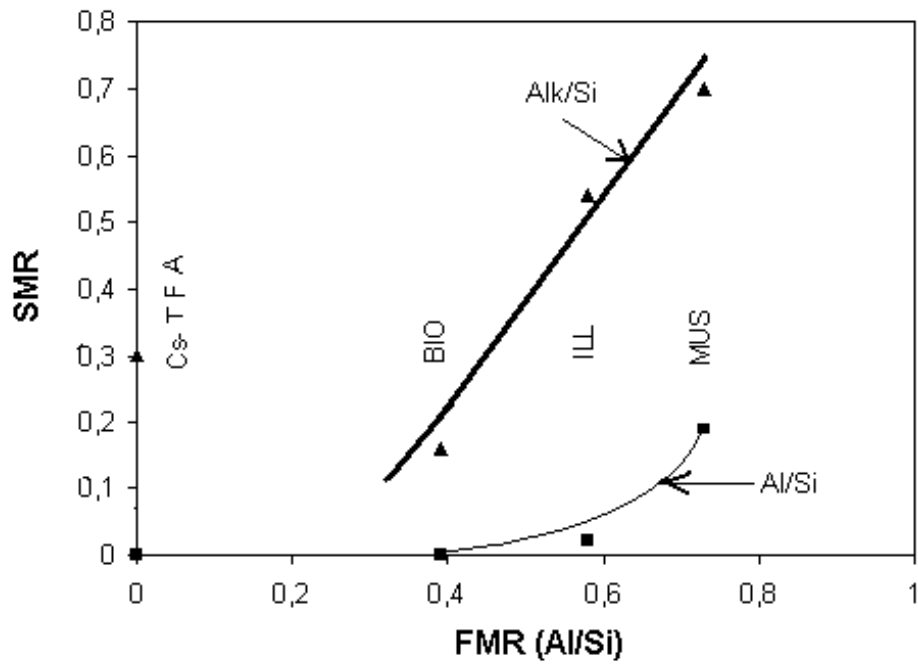


Fig. 2 SMS ratios of Alk/Si and Al/Si in water solutions after 80 hours of leaching at 100 °C with Al/Si ratio in solid mica samples

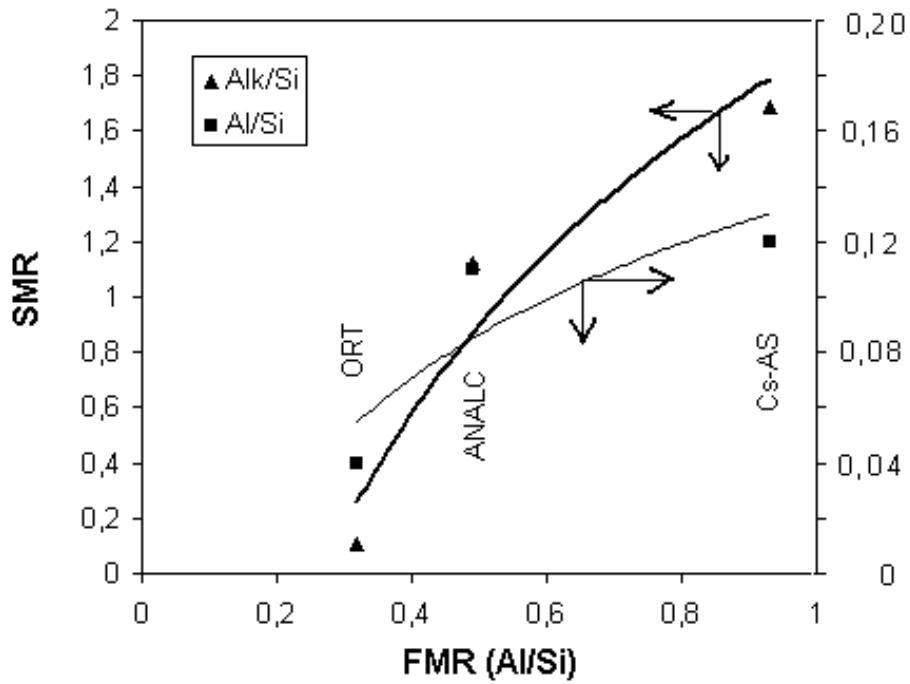


Fig. 3 SMS ratios of Alk/Si and Al/Si in water solutions after 80 hours of leaching at 100 °C with Al/Si ratio in solid aluminosilicate samples

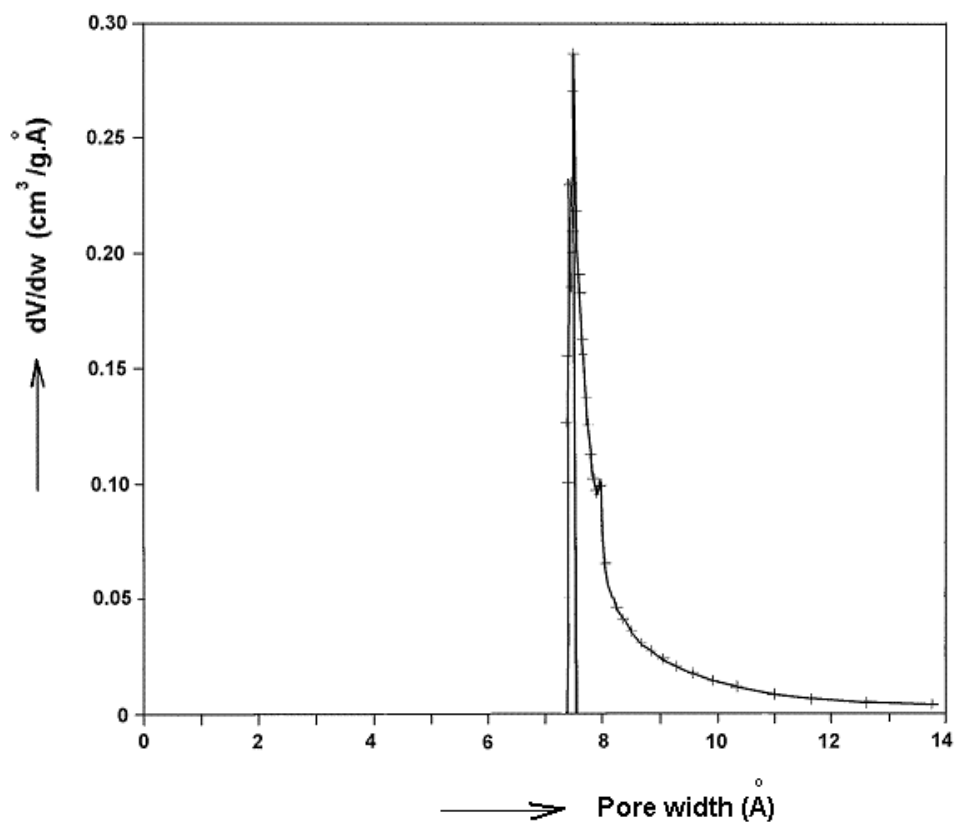


Fig. 4 Horvath-Kawazoe differential pore volume plot for Cs-Z sample

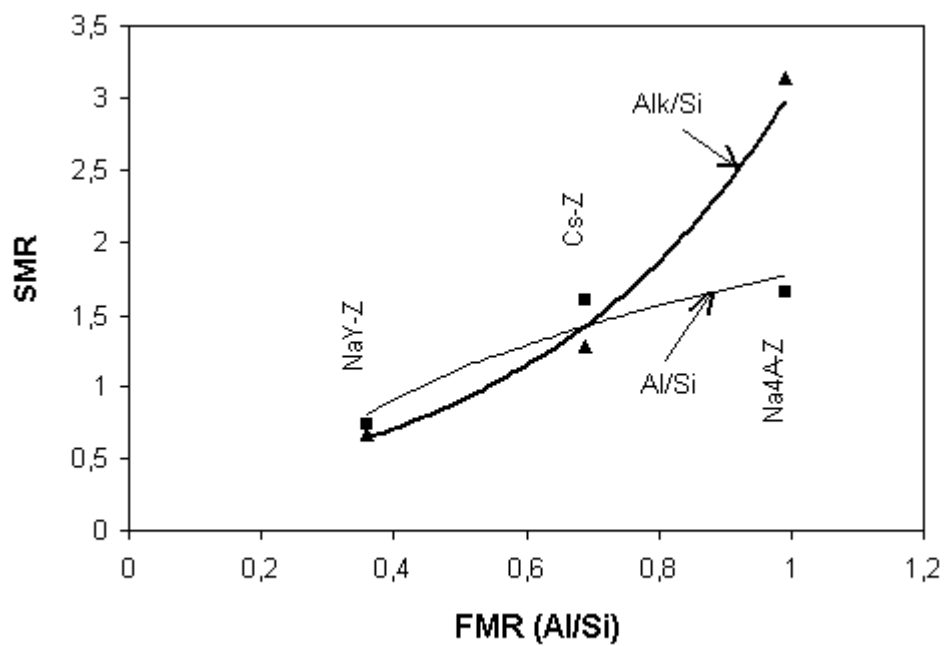


Fig. 5 SMS ratios of Alk/Si and Al/Si in water solutions after 80 hours of leaching at 100 °C with Al/Si ratio in solid zeolite samples



area. The increasing sequence of zeolite solubility is: NaY-Z, Cs-Z and Na4A-Z while the increasing sequence of zeolite surface area is quite opposite: 150 m<sup>2</sup>.g<sup>-1</sup> for Na4A-Z, 465 m<sup>2</sup>.g<sup>-1</sup> for Cs-Z and 641 m<sup>2</sup>.g<sup>-1</sup> for NaY-Z.

#### 4. CONCLUSIONS

Batch leaching at 100 °C indicates that the most leach-resistant materials are micas (Cs-tetra-ferri-annite, biotite, muscovite and illite) followed by tectosilicates (orthoclase, analcime and CsAlSiO<sub>4</sub>), montmorillonites and zeolites. Cesium is better leachable from all Cs-analogues (micas, CsAlSiO<sub>4</sub> and zeolites) than K or Na from relating K- and Na-mineral analogues. Only exception is Cs-montmorillonite where Cs<sup>+</sup> more strongly bonded than Na<sup>+</sup> ion. We therefore envisage a possible scenario for the treatment of Cs wastes involving the coupled use of tetra-ferri-annite and montmorillonite. On the one hand, Cs-tetra-ferri-annite might be suited to fix Cs from Cs-rich or intermediate waste streams within a crystalline, solid matrix and on the other hand, Na-montmorillonite might be used as an outer, barrier capable of buffering the possible escape of Cs.

Iron and/or aluminium bonded in octahedral positions in micas and montmorillonites are the least leached elements almost from all samples except zeolites. From tetrahedral position of zeolites the aluminum is easily leached out. Easy Al leaching is due to rich pore texture of zeolites. Except zeolites from all samples silicon bonded in tetrahedrons leaches more easily than aluminium.

In micas, tectosilicates and zeolites the ratio between leached alkali elements and silicon (Alk/Si) and between leached aluminium and silicon (Al/Si) increases with increasing ratio of Al/Si in related solid samples. In zeolites even ratio of Al/Si in solid samples influences the leaching of alkali metal more than their specific surface area (SMR of Alk/Si and Al/Si with increasing specific surface area decreases).

#### ACKNOWLEDGEMENTS

Research activities and international cooperation was possible due to grants GACR 104/02/1464 and MSM 6198910016. One of us (MM) received financial support from the Italian MURST.

#### REFERENCES

- Alastuey, A., Querol, X., Plana, F. and Lopez-Soler, A.: 1997, A fast method for recycling fly ash: Microwave-assisted zeolite synthesis. *Environmental Science of Technology*, 2527-2533.
- Arcoya, A., Gonzales, A.J., Llabre, G., Seoane, L.X. and Travieso, N.: 1996, Role of the counter-cations on the molecular sieve properties of a clinoptilolite. *Microporous Materials* 7, 1-13.
- Berger, G., Schott, J. and Guy, C.: 1988, Behavior of [Li, Rb and Cs during basalt glass and olivine dissolution and chlorites, smectite and zeolite precipitation from seawater: Experimental investigations and modelization between 50 °C and 300 °C. *Chem.Geol.* 71, 297-312.
- Bickmore, B.R., Bosbach, D.M., Hochella, F., Charlet, L. and Rufe, E.: 2001, In situ atomic force microscopy study of hectorite and nontronite dissolution: Implications for phyllosilicate edge surface structures and dissolution mechanisms. *Am. Mineral.* 86, 411 – 423.
- Cho, W.J., Oscarson, D.W., Gray, M.N. and Cheung, S.C.H.: 1993, Influence of diffusant concentration on diffusion coefficients in clay. *Radiochemica Acta* 60, 159-163.
- Comodi, P., Zanazzi, P.F., Weiss, Z., Rieder, M. and Drábek, M.: 1999, "Cs-tetra-ferri-annite." High-pressure and high-temperature behavior of a potential nuclear waste disposal phase. *Amer. Mineral.* 84, 325-332.
- Drábek, M., Rieder, M., Viti, C., Weiss, Z. and Fryda, J.: 1998, Hydrothermal synthesis of Cs ferruginous trioctahedral mica. *Canad. Mineralogist* 36, 755-761.
- Dumat, C., Quiquampoix, H. and Staunton, S.: 2000, Adsorption of caesium by synthetic clay-organic matter complexes"effect of the nature of organic polymers. *Environ. Sci. Technol.*, 34, 2985-2989.
- Gallagher, S.A., Mc Carthy, G.J. and Smith, K.D.: 1977, Preparation and X-ray characterization of CsAlSiO<sub>4</sub>. *Mat. Res. Bull.* 12, 1183-1190.
- Grauer, Z., Malter, A.B., Yariv, S. and Avnir, D.: 1987, Sorption of Rhodamine B by Montmorillonite and Laponite. *Colloids and Surfaces*, 25, 41-85.
- Gutierrez, M. and Fuentez, R.H.: 1996, A mechanistic modelling of montmorillonite contamination by cesium sorption. *Applied Clay Science* 11, 11-24.
- Haynes, H.Y.J.: 1978, Chemical, physical, and catalytic properties of large pore acidic zeolites. *Catal.- Rev.- Sci. Eng.*, 17, 273-336.
- Hsu, C.N. and Chang, K.P.: 1994, Sorption and desorption behaviour on soil components. *Appl. Radiat. Isot.*, Vol. 45, No.4, 433-437.
- Hsu, C.N., Liu, D.C. and Chang, K.P.: 1994, Equilibrium and kinetic sorption behaviors of cesium and strontium in soils. *Appl. Radiat. Isot.*, Vol. 45, No.10, 981-985.
- Ito, J.: 1976, Crystal synthesis of a new cesium aluminosilicate CsAlSi<sub>5</sub>O<sub>12</sub>. *Am. Mineralogist*, 61, 170-171.
- Jozefaciuk, G. and Bowanko, G.: 2002, Effect of acid and alkali treatments on surface areas and adsorption energies of selected minerals. *Clays Clay Miner.* 50, 771 – 783.
- Jurček, P., Jedináková-Křížová, V. and Vanová, P.: 1996, Migration of <sup>134</sup>Cs and <sup>85</sup>Sr in clay minerals. *Journal of Radioanalytical and Nuclear Chemistry* 208, 519-527.

- Khan, S.A., Riaz-ur Rehman and Khan, M. A.: 1994, Sorption of cesium on bentonite. *Waste Management* 14 (7) 629-642.
- Kim, Y. and Kirkpatrick, R.J.: 1997,  $^{23}\text{Na}$  and  $^{133}\text{Cs}$  NMR study of cation adsorption on mineral surfaces: local environments, dynamics, and effects of mixed cations. *Geoch. Cosmoch. Acta* 61, 5199-5208.
- Kim, Y. and Kirkpatrick, R.J.: 1998, NMR  $T_1$  relaxation study of  $^{133}\text{Cs}$  and  $^{23}\text{Na}$  adsorbed on illite. *Amer. Mineral.* 83, 661-665.
- Klika, Z., Weiss, Z., Mellini, M. and Drábek, M.: Water leaching of cesium from selected cesium mineral analogues. *J. Appl. Geochem.* (submitted to *Jour. Appl. Geochem.*).
- Komadel, P.: 2003, Chemically modified smectites. *Clay Miner.* 38, 127 – 138.
- Komarneni, S. and Roy, D. M.: 1978, Effect of layer charge and heat treatment on Cs fixation by layer silicate minerals. *J. Inorg. Nucl. Chem.*, 40, 893-896.
- Mellini, M., Weiss, Z., Rieder, M. and Drábek, M.: 1996, Cs-ferriannite as possible host for waste cesium. *Eur. J. Mineral.* 8, 1265-1271.
- Mimura, H., Tachibana, F. and Akiba, K.: 1992, Ion-exchange selectivity for cesium in ferrierites. *Journ. Nucl. Sci. and Technology* 29, 184-186.
- Miyahara, B., Ashida, T., Kohara, Y., Yusa, Y. and Sasaki, N.: 1991, Effect of bulk density on diffusion for cesium on compacted sodium bentonite. *Radiochimica Acta* 52/53, 293-297.
- Novák, I. and Čičel, B.: 1878, Dissolution of smectites in hydrochloric acid: II. Dissolution rate as a function of crystallochemical composition. *Clays Clay Miner.* 26, 341 – 344.
- Oscarson, D.W., Hume, H.B. and King, F.: 1994, Sorption of cesium on compacted bentonite. *Clays and Clay Minerals*, 42, 731-736.
- Rodríguez, M.A.V., Barrios, M.S., Gonzalez, J.D.L and Muñoz, M.A.B., 1994. Acid activation of a ferrous saponite (griffithite): Physico-chemical characterization and surface area of the products obtained. *Clays Clay Miner.* 42, 724 – 730.
- Smith, J.T. and Comans, R.N.J.: 1996, Modelling the diffusive transport and remobilisation of  $^{137}\text{Cs}$  in sediments. The effects of sorption kinetics and reversibility. *Geoch. Cosmoch. Acta*, 60, 995-1004.
- Tahani, A., Karroua, M., Van Damme, H., Levitz, P. and Bergaya, F.: 1999, Adsorption of Cationic Surfactant on Na-montmorillonite. *Journal of Colloid and Interface Science*, 216, 242-249.
- Tkáč, I., Komadel, P. and Müller, D.: 1994, Acid-treated montmorillonites – a study by  $^{29}\text{Si}$  and  $^{27}\text{Al}$ , MAS – NMR. *Clay Miner.* 29, 11 - 19.
- Weiping, M.A., Brown, P.W. and Komarneni, S.: 1996, Sequestration of cesium and strontium by tobermorite synthesized from fly ashes. *J. Am. Ceram. Soc.* 79,1707-1710.
- Zachara, M., Smith, S.C., Liu, Ch., McKinley, J.P., Serne, R.J., and Gassman, P.L.: 2002, Sorption of  $\text{Cs}^+$  to micaceous subsurface sediments from the Hanford site, USA. *Geoch. Cosmoch. Acta*, 66, 193-211.
- Weiss, Z., Klika, Z., Čaková, P., Janeba, D. and Kozubová, S.: 1998, Sodium - cadmium and sodium - zinc exchangeability in montmorillonite. *Phys.Chem. Minerals*, 25, 534-540.