

# UNIT CELL FORMULAS AND FRAMEWORK/EXTRA-FRAMEWORK ALUMINIUM RATIO IN NATURAL AND DEALUMINATED CLINOPTILOLITE

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**Abstract:** Unit cell formulas (UCFs) of clinoptilolite, the main mineral of a rhyolite tuff, were calculated from the chemical analysis, from cation exchange capacity using the method of Barrer et al. (1967), and from the molar cation exchange capacity. The last two methods provided similar results. Exact knowledge of exchangeable cations contents and valency of exchangeable Al-bearing species is needed for correct UCF calculation. A set of dealuminated samples was prepared from  $\text{NH}_4^+$  saturated tuff by its reaction with  $(\text{NH}_4)_2\text{SiF}_6$  for 1 to 24 hr at 95 °C in water suspension of ammonium acetate. Framework (FAI) and extra-framework (EFAI) aluminium were distinguished in the dealuminated samples due to their different dissolution rate in 4 M HCl at room temperature. Unit cell formulas of dealuminated samples calculated using the FAI instead of total Al content are believed to express more correctly the real composition of dealuminated clinoptilolite.

**Key words:** clinoptilolite, dealumination, unit cell formula, acid extraction.

## Introduction

Unit cell formulas (UCFs) provide information on occurrence of individual atoms in different positions in the unit cell. Most frequently, UCFs calculated from the bulk chemical analyses are used (e.g. Alietti 1972). However, this method leads to correct results only for monomineralic samples, presence of admixtures increases their inaccuracy. A combination of chemical and spectral methods, such as IR, MAS NMR and Mössbauer, provides more real information on distribution of atoms in the sample (Čížel & Komadel 1994).

Barrer et al. (1967) calculated UCF of clinoptilolite from the data of cation exchange capacity (CEC) of natural zeolite and from chemical analyses of both natural and Na-forms. CEC of the zeolite phase was calculated from the zeolite content in the sample which was determined by XRD. CEC, volume of unit cell (UC) and density were used to calculate the number of aluminium atoms in UC (Barrer et al. 1967).

UCF of chemically modified zeolites were used to show the degree of zeolite modification in cation exchange and/or dealumination processes (Kozáč & Očenáš 1982). Garralon et al. (1988) used the amount of aluminium atoms removed in the course of dealumination for the dealumination degree determination. Breck et al. (1984) characterized dealuminated zeolites by their Si/Al ratio calculated from the chemical analyses.

The aim of the present work was 1 - to compare the results of three methods for UCF calculation of natural

clinoptilolite and 2 - to determine the UCF of dealuminated clinoptilolite samples.

## Materials and methods

Altered rhyolite tuff from Nižný Hrabovec (East Slovakia) was used. XRD analyses based on comparison of five different combinations of diffraction intensities of the tuff with those of standard clinoptilolite (Hector, California, USA) and cation exchange capacity method (Ming & Dixon 1987) yielded  $75 \pm 5$  mass % of clinoptilolite in the tuff. This is in accordance with the data of Kozáč & Očenáš (1982), who found about 8 mass % labradorite and/or andesite, 6 mass % of cristobalite, 3 mass % of quartz and about 8 mass % of amorphous volcanic glass and/or  $\text{SiO}_2$  in their samples. The tuff was ground and the fraction of 0.8 - 1.6 mm was treated three times for 24 hours with 3 M  $\text{NH}_4\text{Cl}$  at room temperature to prepare  $\text{NH}_4^+$ -form. The product was washed with boiling water until free of chlorides, then dried at 40 °C. The chemical analyses of the natural and  $\text{NH}_4^+$ -saturated forms are given in Tab. 1.

Fifty grams of  $\text{NH}_4^+$ -saturated tuff were heated to 70 °C in 100 ml of 2.5 M ammonium acetate for one hour. After that pH was adjusted to 6 and temperature to 95 °C and the samples were treated with 140 ml of 0.75 M  $(\text{NH}_4)_2\text{SiF}_6$  for different periods of 1 to 24 hours. These samples are subsequently referred to as  $\text{D}_1$  to  $\text{D}_{24}$  together with  $\text{D}_0$  for the untreated  $\text{NH}_4^+$ -saturated tuff.



**Table 1:** Time of dealumination at 95 °C and chemical analyses of untreated and  $\text{NH}_4^+$ -saturated tuff and dealuminated samples.

Sample		$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{TiO}_2$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{Fe}_2\text{O}_3$
[mass %]									
D-untreated tuff		75.19	13.84	3.63	0.74	0.26	1.06	3.38	1.89
D <sub>0</sub> -NH <sub>4</sub> satur. tuff		81.21	14.20	0.60	0.63	0.21	0.62	1.04	1.50
	t [hr]	Dealuminated samples							
D <sub>1</sub>	1	81.66	13.05	0.64	0.71	0.29	0.58	0.99	2.08
D <sub>3</sub>	3	83.06	11.74	0.55	0.78	0.27	0.57	1.00	2.03
D <sub>6</sub>	6	84.42	10.78	0.63	0.78	0.28	0.57	0.99	1.54
D <sub>9</sub>	9	84.82	10.30	0.66	0.90	0.26	0.59	1.02	1.44
D <sub>16</sub>	16	86.58	8.75	0.59	0.70	0.26	0.53	1.02	1.57
D <sub>24</sub>	24	88.66	6.96	0.62	0.63	-	0.53	1.03	1.57

t = time of dealumination at 95 °C,

**Table 2:** Unit cell formulas of clinoptilolite. Methods described in text.

Methods	Coefficients in UCF per 72 O						
	Al	Ca	K	Mg	Na	Al	Si
1	-	1.53	1.69	0.43	0.81	6.42	29.58
2a	0.34	1.96	1.79	0.10	0.51	6.42	29.58
2b	0.43	2.05	1.88	0.10	0.53	8.06	27.92
3a	0.35	1.99	1.82	0.10	0.52	6.52	29.48
3b	0.43	2.08	1.90	0.11	0.54	8.17	27.83

Their dealumination times and chemical analyses are listed in Tab. 1.

Dealuminated samples were washed in 4 M HCl at room temperature for 1, 3, 5 and 8 hours to extract EFAl. Acid treated samples were washed in water until free of chlorides. Residual  $\text{Al}_2\text{O}_3$  content was determined by chemical analysis and is listed in Tab. 1.

## Results and discussion

Low amounts of  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  were omitted in the UCF calculations. Titanium and iron are frequently present as admixtures in clays and zeolites, but 0.26 %  $\text{TiO}_2$  is below the XRD identification limit. Iron is commonly bound in oxides or hydroxides, which due to their microcrystallinity and/or Al substitution escape the detection by XRD. Distribution of iron in the samples can be identified by Mössbauer spectroscopy at low temperatures (liquid nitrogen or even liquid helium, e.g. Vandenberghe et al. 1990).

Three methods were used to calculate UCF of clinoptilolite.

### 1. Calculation from bulk chemical analysis (Alietti 1972)

This is the most frequently used method, though it assumes monomineralic sample free of any admixtures. This assumption is rarely strictly fulfilled. Provided that all Al present in the sample is FAl and Ca, K, Mg and Na

are exchangeable cations, the calculated UCF (Tab. 2) yielded  $\text{Si}/\text{Al} = 4.61$ .

However, chemical analysis of  $\text{NH}_4^+$ -form D<sub>0</sub> (Tab. 1) resulted in  $\text{Si}/\text{Al} = 4.85$ , which leads to tetrahedral Al for Si substitution of 6.15 per 72 O. The difference in  $\text{Si}/\text{Al}$  ratio for samples D and D<sub>0</sub> suggested that 0.75 % of  $\text{Al}_2\text{O}_3$  was removed in course of D<sub>0</sub> preparation. This part of Al was present as EFAl, which is known to occur in zeolites in various forms, such as  $\text{AlO}^+$ ,  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}_2(\text{OH})_6(\text{H}_2\text{O})_4$ ,  $\text{Al}(\text{OH})_2^{2+}$ ,  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ , etc. (Garraón et al. 1988; Wang et al. 1991; Hey et al. 1986; Hunger et al. 1991; Borade et al. 1990). Various valency of these species (0 to 3+) does not allow exact calculation of exchangeable cations in the UCF. Therefore only the extreme cases, i.e. all EFAl bound either in neutral species (e.g.  $\text{Al}_2(\text{OH})_6(\text{H}_2\text{O})_4$ ) or in trivalent cations (e.g.  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ) will be further considered. The calculated values will be distinguished by subscripts 0 and 3, respectively.

### 2. Calculation from CEC, density and UC volume (Barrer et al. 1967)

The degree of Al for Si substitution is calculated from the CEC, thus presence of admixtures of minerals with high CEC (e.g. smectites) would substantially affect the result of this method. However, CECs of all identified admixtures are low, therefore their influence on the calculated UCF is considered to be negligible. Dependence of density on the unit cell composition is neglected in this method.



Equation (1) was used to calculate Al for Si substitution in UCF

$$x = \text{CEC} \cdot N_A \cdot \rho \cdot V \quad (1)$$

where:  $x$  - FAI for Si substitution in UCF,  $N_A$  - Avogadro's constant,  $\rho$  - density,  $2.16 \text{ g/cm}^3$ ,  $V$  - volume of UC (Breck et al. 1974),  $2.1 \times 10^{-21} \text{ cm}^3$ .

CEC of natural clinoptilolite was calculated in two ways, provided that valency of EFAl species is **a** - 0 or **b** - 3+.

**2a** -  $\text{CEC}_0$  was calculated from the difference in Ca, Mg, Na and K contents before and after their exchange for  $\text{NH}_4^+$ . The results yielded  $1.08 \times 10^{-3} \text{ eq/g Ca}^{2+} + 0.05 \times 10^{-3} \text{ eq/g Mg}^{2+} + 0.14 \times 10^{-3} \text{ eq/g Na}^+ + 0.50 \times 10^{-3} \text{ eq/g K}^+ = 1.77 \times 10^{-3} \text{ eq/g}$ . Thus obtained value was divided by the clinoptilolite content in the rhyolite tuff (0.75) to calculate the  $\text{CEC}_0$  of the pure mineral ( $2.36 \times 10^{-3} \text{ eq/g}$ ). Obtained UCF is listed in Tab. 2.

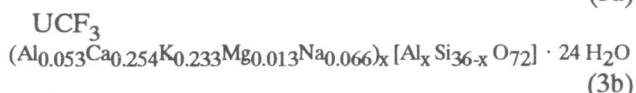
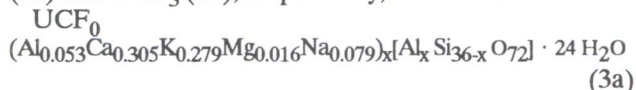
**2b** - 0.75 %  $\text{Al}_2\text{O}_3$  present as EFAl resulted in  $0.44 \times 10^{-3} \text{ eq/g Al}^{3+}$ , which was added to exchangeable cations used in **2a** to calculate  $\text{CEC}_3 = 2.95 \times 10^{-3} \text{ eq/g}$ .  $x = 8.06$  resulted from equation (1) leads to high Al content (Si/Al 3.50). Obtained UCF is listed in Tab. 2.

### 3. Calculation from molar CEC

FAI for Si substitution,  $x$ , was calculated as the product of CEC of clinoptilolite **a** -  $\text{CEC}_0 = 2.36 \times 10^{-3} \text{ eq/g}$ , and **b** -  $\text{CEC}_3 = 2.95 \times 10^{-3} \text{ eq/g}$  and its molar mass,  $M$ , given by (4a) or (4b)

$$x = M \cdot \text{CEC} \quad (2)$$

Contributions of exchangeable cations to CEC were used to calculate their composition in UCF. Provided that valency of EFAl species is **a** - 0 and **b** - 3+ UCF<sub>0</sub> (3a) and UCF<sub>3</sub> (3b), respectively, were obtained.



Substitution for atomic masses in (3a) and (3b) provided for molar mass of clinoptilolite:

$$\text{a) } M_0 = 25.657x + 2595.24 \quad (4a)$$

$$\text{b) } M_3 = 21.443x + 2595.24 \quad (4b)$$

Substitution for  $M$  and CEC led to solution of (2)

$$\text{a) } x_0 = 6.52 \quad (5a)$$

$$\text{b) } x_3 = 8.17 \quad (5b)$$

Resulted UCF are listed in Tab. 2.

Lower values obtained for Mg and Na coefficients from methods 2 and 3 than from method 1 are due to their lower concentration in the exchangeable positions of clinoptilolite compared to their contents in the rhyolite tuff. These cations may be bound also in volcanic glass and/or in feldspar. On the other hand, Ca is bound mainly in clinoptilolite. Calculated Al for Si substitution

is directly dependent on CEC used in methods 2 and 3 (eq. (1) and (2)). Therefore accurate CEC value of pure clinoptilolite would be needed for exact UCF calculation. Methods 2 and 3 provided similar results for the same CEC (compare UCF 2a and 3a or 2b and 3b in Tab. 2). Method 3 is more convenient because it needs no experimental data for correlation of density and UC-volume for various Si/Al ratios, which are needed for method 2 of Barrer et al. (1967).

### UCF determination of dealuminated samples.

The UCF determination of dealuminated zeolites is complicated in distinguishing framework and extra-framework aluminium. EFAl was detected in dealuminated zeolites by  $^{27}\text{Al}$  MAS NMR (Hey et al. 1986; Garalón et al. 1988). Faster dissolution of EFAl than FAI in acids (Alsdorf et al. 1992) was exploited for estimation of EFAl in the dealuminated samples. Acid treatment with 4 M HCl at room temperature caused simultaneous extraction of FAI and EFAl, but the dissolution rate of the latter is much higher. The amounts of FAI in dealuminated samples were obtained as the intercepts of the linear parts of  $\text{Al}_2\text{O}_3$  dissolution curves (Fig. 1). The EFAl contents were calculated from the difference between total Al and FAI. Most EFAl was removed within the first hour of acid extraction of dealuminated samples. Extraction rate of Al was affected not only by various FAI and EFAl contents in the samples, but also by various diffusion paths of reagents and reaction products in the pore system of dealuminated samples, caused by various dealumination degree of the grains. High starting dissolution rate of EFAl was probably connected with its accumulation on the surfaces of dealuminated crystals (Alsdorf et al. 1992). Three processes occur simultaneously in course of dealumination of zeolites. Their rate decreases in order:

1. Extraction of exchangeable cations.
2. Dissolution of EFAl.
3. Dissolution of FAI.

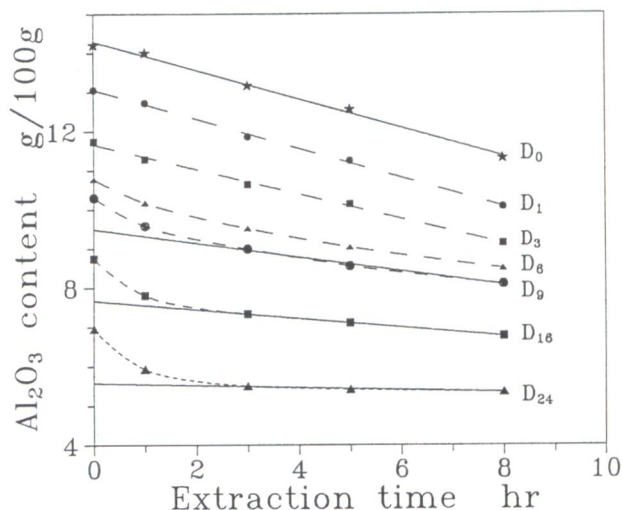


Fig. 1. Dependence of  $\text{Al}_2\text{O}_3$  content on extraction time of dealuminated samples in 4 M HCl.



**Table 3:** EFAl, FAl and Si content per 72 O and Si/Al ratio of untreated and dealuminated samples.

	EFAl	FAl	Si	Si/Al
D <sub>0</sub>	0.00	6.48	29.52	4.56
D <sub>1</sub>	0.00	5.95	30.05	5.05
D <sub>3</sub>	0.00	5.36	30.64	5.72
D <sub>6</sub>	0.20	4.72	31.28	6.63
D <sub>9</sub>	0.26	4.44	31.56	7.11
D <sub>16</sub>	0.30	3.59	32.41	9.03
D <sub>24</sub>	0.57	2.61	33.39	12.79

Distribution of Al in dealuminated samples was calculated from the chemical analyses and acid dissolution data. Obtained FAl values were used to calculate the Si/Al ratios in the samples and Si and Al coefficients in UCFs (Tab. 3). Clearly, the dealumination procedure used was effective and the Si/Al ratio increased from 4.56 in D<sub>0</sub> to 12.79 in D<sub>24</sub>. Negligible content of EFAl was found in the samples D<sub>1</sub> and D<sub>3</sub>. This means that released EFAl has been washed out in the treatment procedure. In more dealuminated samples D<sub>6</sub> to D<sub>24</sub> the amount of EFAl increased with dealumination showing that a part of released Al remained trapped in the solid reaction products. The UCFs based on FAl rather than on the total Al content are believed to express more closely the real composition of dealuminated clinoptilolite.

### Conclusion

Contents of exchangeable cations and valency of exchangeable Al-bearing species are needed for UCF calculation of clinoptilolite containing admixtures. Chemical and quantitative XRD analyses provide sufficient input data for UCF calculation from the molar cation exchange capacity.

Different extraction rates of EFAl and FAl in 4 M HCl at room temperature allow to distinguish between these forms of Al in dealuminated samples.

Applied dealumination procedure was effective in preparation of materials of higher Si/Al ratio. Unit cell formulas of dealuminated clinoptilolite samples based on FAl rather than on total Al are considered to express more closely the real composition of these materials.

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