

EVALUATION OF CORROSION OF ENGINEERING CERAMICS BY ATOMIC EMISSION SPECTROMETRY IN INDUCTIVELY COUPLED PLASMA

[#]DAGMAR GALUSKOVÁ*, DUŠAN GALUSEK*, PAVOL ŠAJGALÍK**

**Vitrum Laugaricio – Joint Glass Centre of the Institute of Inorganic Chemistry, Slovak Academy of Sciences, Alexander Dubček University of Trenčín, and Faculty of Chemical and Food Technology, Slovak Technical University, Študentská 2, 911 50 Trenčín, Slovak Republic*

***Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 845 36 Bratislava, Slovak Republic*

[#]E-mail: dagmar.galuskova@tuni.sk

Submitted October 23, 2013; accepted March 3, 2014

Keywords: ICP OES, Matrix effect, Ceramics, Corrosion, Alumina, Silicon nitride

An analytical method has been developed and verified, facilitating chemical analysis of saline aqueous solutions from corrosion tests of two types of engineering ceramics, i.e. polycrystalline alumina, and silicon nitride. The method is capable of providing complementary information related to mechanisms of corrosion and kinetics of dissolution of the two main components of the ceramics, i.e. Al in α -Al₂O₃, and Si in Si₃N₄. A radially viewed inductively coupled plasma atomic emission spectroscopy was used, and the operating conditions for the analysis were optimised. The method was validated. Internal standardisation, matrix matching, standard addition technique and direct measurement without matrix correction were applied, and the results were critically discussed. The technique of internal standard was shown to be the most sensitive. The method exhibited satisfactory precision (relative standard deviation up to 5 %), analytical recoveries from 95 to 100 %, and acceptable limits of detection based on 3 σ criterion of 0.095 mg l⁻¹ for Al (measured at 308.215 nm) and 0.099 mg·l⁻¹ for Si (at 251.611 nm).

INTRODUCTION

Advanced ceramics find various applications including their use in destructive environments, e.g. reactor material in supercritical water oxidation units (SCWO reactors) [1], components of devices for hot high salinity solutions (seawater) pumping or parts of car exhaust systems, which are subject to corrosion attack by salt solutions due to winter road maintenance. Salt in mixture with acids (HCl, HNO₃, H₃PO₄, H₂SO₄) creates highly aggressive environment known to accelerate corrosion, and resulting in changes in morphology, and negatively influencing mechanical properties of ceramic materials. In order to study the mechanisms of the corrosion process, two sources of information can be used: (1) study of chemical, phase, and morphological changes of corroded surfaces, and (2) analysis of the corrosion medium itself, both prior, and after the corrosion test, determining the amount of the elements, which were leached from corroded material. In order to achieve comprehensive understanding of corrosion mechanisms, and detailed knowledge of kinetics of the corrosion process the two sources must be complementary. The corrosion solution is analysed on the contents of the elements leached from corroded material. However, in comparison with common metal materials, ceramics, such as aluminium oxide or

silicon nitride, are generally very stable in any corrosive environment, and the concentrations of leached elements are therefore necessarily low. An element, which is leached in sufficiently high concentrations, and can be considered as the most relevant for the study of corrosion mechanisms (so called tracer) is thus often selected and analyzed in the corrosion solution. These often comprise silicon (from silicon nitride), and aluminium (from aluminium oxide).

The low concentrations of the measured elements, together with the presence of high concentrations of other metallic ions in corrosion solutions, e.g. alkali metal ions, represent a serious problem, which can significantly disturb the analysis [2, 3]. Atomic Absorption Spectrometry (AAS) can be adopted for direct analysis of silicates, but the analysis of samples with high concentrations of salts might become rather unreliable, due to interferences from alkali and chloride ions. The Inductively Coupled Plasma Atomic Emission or Mass Spectrometry (ICP-AES or ICP-MS) are commonly applied as sensitive and efficient methods for multi-element analysis of seawater and samples with complex matrices [4]. Determination of low concentrations of metals in salts using the techniques is possible only in strongly diluted salt solutions [3]. On-line separation and pre-concentration can be used prior to analysis of

the trace elements in samples with high contents of dissolved salts [5, 6, 7]. However, these techniques are time-consuming, laborious and costly, and pose a risk of contamination. In addition, dilution of the sample negatively influences the limits of detection.

The presence of easily ionised elements in ICP-AES may also result either in an enhancement or a depression in the analyte signal intensity, accompanied by a shift of the spatial distribution. Romero [8] reported that the effects seemed to be highly dependent on the operating conditions, particularly on the power, the carrier gas flow-rate, and the observation height in radial plasma viewing. A simple procedure, which helps to eliminate any negative influence, is matrix matching: the practical composition of the sample matrix is modelled in calibration standards. Another possibility is internal standardisation: a simple internal standardisation technique was utilised by Krejčová [9, 10] for multi-element analysis of solutions of analytically pure hydroxides and salts by ICP-AES. The common analyte internal standardisation technique, originally developed to correct for drift in ICP-AES measurements can be also applied, as reported by Al-Ammar [11].

The main objective of the present study was the optimisation and verification of the applicability of the internal standardisation technique with beryllium and yttrium as internal standards in the analysis of aluminium and silicon content in a solution containing $0.5 \text{ mol}\cdot\text{l}^{-1}$ of NaCl used in corrosion experiments of alumina and silicon nitride structural ceramics. The results obtained by this technique were compared with the simple matrix matching procedure and the standard addition technique.

EXPERIMENTAL

Samples

Three compositionally different ceramic materials were prepared by sintering [12, 13]. The prepared blocks $50 \times 50 \times 5 \text{ mm}^3$ were cut and ground into rectangular bars $3 \times 4 \times 50 \text{ mm}^3$, their faces polished, and edges chamfered. The bars were then ultrasonically cleaned in acetone for 15 min, rinsed with de-ionized water, and dried in a hot air drying cabinet for 3 h at 110°C . The corrosion tests were carried out in stainless steel pressure reactors. Inner PTFE lining prevented direct contact of corrosion medium with steel.

Denomination of tested ceramics, and the conditions of corrosion experiments applied for verification of the analytical method can be summarized as follows:

- *A* - polycrystalline alumina ceramics (purity 99.995 %) sintered without additives in contact with $0.5 \text{ mol}\cdot\text{l}^{-1}$ NaCl solution for 8 days at 150°C .
- *AH* - polycrystalline alumina prepared in the presence of sintering additives (5 wt. % $\text{CaO}\cdot 5\text{SiO}_2$) and corroded in $0.5 \text{ mol}\cdot\text{l}^{-1}$ NaCl solution at 150°C for 12 days.

- *S* - silicon nitride prepared in the presence of sintering additives (5 wt. % Y_2O_3), and in contact with $0.5 \text{ mol}\cdot\text{l}^{-1}$ NaCl solution at 150°C for 8 days.

Concentrations of Al and Si in the eluates of the ceramic materials were measured applying the internal standardisation with the Be internal standard of two different concentrations ($0.1 \text{ mg}\cdot\text{l}^{-1}$; and $1 \text{ mg}\cdot\text{l}^{-1}$), and the Y internal standard ($1 \text{ mg}\cdot\text{l}^{-1}$), as well as by the standard addition technique (SA).

Instrument

The measurements were carried out with the sequential, radially viewed ICP atomic emission spectrometer Vista MPX (VARIAN), equipped with V-groove nebuliser and MK11 spray chamber. Aluminium was measured at the wavelength of 308.215 nm , silicon at 251.611 nm , Be at 313.107 nm and Y at the wavelength of 371.029 nm . The operating conditions were optimised on the basis of a signal-to-background ratio using a solution containing $5 \text{ mg}\cdot\text{l}^{-1}$ of Al and Si in sodium chloride solution.

Chemicals

All chemicals were of p.a. grade. De-ionised water used for dilution of the chemicals was prepared in the CHEZAR reverse osmosis purification system (Bratislava, Slovak Republic), and the purity verified by measuring electrical conductivity ($25 \pm 5 \mu\text{S}/\text{cm}$).

Leaching solution

$0.5 \text{ mol}\cdot\text{l}^{-1}$ NaCl solution was prepared by dissolving $29.96 \pm 0.03 \text{ g}$ of NaCl (MERCK, Darmstadt, Germany) in 1000 ml of deionised water.

Aqueous calibration solutions

Al and Si multi-element calibration solutions were prepared in the concentrations of 100, 50, 10 and $5 \text{ mg}\cdot\text{l}^{-1}$ by serial dilution of single-element standards $1000 \pm 2 \text{ mg}\cdot\text{l}^{-1}$ Si, Al (ANALYTIKA Prague, Czech Republic) with deionised water and stabilised with 0.25 ml of 65 % w/v HNO_3 (MERCK, Darmstadt, Germany) per 100 ml. A calibration blank was prepared in the same manner omitting the elements.

Matrix-matched calibration solutions

Matrix-matched calibration solutions were prepared in the same manner as the calibration solutions using $0.5 \text{ mol}\cdot\text{l}^{-1}$ NaCl solution instead of deionised water, and applying the rules of the matrix matching technique [2, 5].

Internal standardisation

The internal standards were added as follows: 10 µl Be or 100 µl Be from 1000 ± 2 mg·l⁻¹ Be certified reference material (CRM) (ANALYTIKA Prague, Czech Republic) or 100 µl Y from 1000 ± 2 mg·l⁻¹ Y CRM (ANALYTIKA Prague, Czech Republic) were added per 100 ml of aqueous calibration solutions, matrix-matched calibration solutions and samples, respectively, each of them mixed thoroughly. It corresponded to the internal standard concentration of 0.1 mg·l⁻¹, and 1 mg·l⁻¹ of Be, and 1 mg·l⁻¹ of Y, respectively.

The accuracy of the measurements was verified by the analysis of the CENTMIX4 certified reference material (ANALYTIKA Prague, Czech Republic) containing 1000 ± 5 µg·ml⁻¹ of Al, Si, Zr and 100 ± 0.5 µg·ml⁻¹ Ca, La, Lu, Mg, Nd, Y, Yb. For validation purposes, the certified reference material was diluted 100 times. The CRM was not used when yttrium was utilised as the internal standard.

Determination of corrosion rates

Corrosion rates of the three studied structural ceramics were determined under *quasi*-dynamic conditions. Due to high test temperature (290°C) typical flow-through arrangement with corrosion medium continuously flowing around the tested material could not be used. An alternative arrangement has been therefore used, where every 22 h the reactors were cooled down, the corrosive solution was removed and fresh solution was added to the reactor. The S/V ratio (the specimen surface to corrosion liquid volume ratio) was held constant at 0.7 ± ± 0.03 cm⁻¹, i.e. two bars were placed in one reactor at the same time with 20 ml of the liquid medium. The content of released Si and Al were determined in each eluate by the optimised method described above. Additional static tests at temperatures 150 and 200°C were applied in order to obtain the data for determination of kinetic parameters, and for calculation of the activation energies.

The amount of an element released into solution was expressed in terms of the value NL_i in [g/m²] according to the Equation 1 [14]:

$$NL_i = \frac{c_i}{w_i \cdot (S/V)} \quad (1)$$

where c_i is the concentration of an element i in solution in [mg·l⁻¹], S is the surface of the ceramic material in

contact with corrosive solution in [m²], V is the volume of the corrosive solution in [m³], and w_i is the mass fraction of the element i in the ceramic material. This way the amount of the element released into the solution is normalised with respect to its content in corroded material.

The data acquired from the *quasi* – dynamic tests at the respective time of corrosion t were expressed in terms of the *cumulative* normalised leaching recalculated according to the Equation 2:

$$NL_i^t = \frac{c_i}{w_i \cdot (S/V)} + NL_i^{t-\Delta t} \quad (2)$$

The initial corrosion rates k were calculated by linear fitting of time dependence of the cumulative normalised leaching at various temperatures. The activation energies were obtained from the slope of a plot $\ln k$ vs. $1/T$ using the Arrhenius equation.

RESULTS AND DISCUSSION

The operating conditions for the determination of Al and Si, which were optimised on the basis of the signal-to-background ratio using a solution containing 5 mg·l⁻¹ of Al and Si in 0.5 mol·l⁻¹ NaCl are depicted in Figure 1 and Figure 2. The figures show that the ratio was dependent on the carrier gas pressure, and the viewing height applied, respectively. The carrier gas flow-rate has an influence on the residence time of the aerosol in the plasma. The nebuliser pressure was therefore set to 160 kPa in order to achieve the optimum dwell time for the sample aerosol in plasma. The favourable viewing height of 8 mm was adjusted for the selected analytical wavelengths. The optimum operating conditions are summarised in Table 1.

Limits of detection (LOD) were calculated on the basis of the 3s criterion from the standard deviations of the measurements of ten blank (0.5 mol·l⁻¹ NaCl) replicates measured for each element, as recommended in literature [15]. The LOD achieved for Al at 308.215 nm and Si at 251.611 nm was 0.095 mg·l⁻¹ and 0.099 mg·l⁻¹, respectively.

Figure 3 illustrates the analytical recoveries achieved with the internal standardisation technique using 0.1 mg·l⁻¹ Be, 1 mg·l⁻¹ Be and 1 mg·l⁻¹ Y in comparison with the recoveries obtained from direct measurements without the presence of any internal standard (no IS),

Table 1. Operating conditions of the ICP AES analysis.

Rf power	1.15 kW	Nebuliser pressure	160 kPa
Viewing height	8 mm	Background correction	Fixed point correction
Plasma gas	15.0 l·min ⁻¹	Number of replicates	3
Auxiliary gas	1.5 l·min ⁻¹		
Gas	Argon 99.998 %		

and measured in NaCl matrices. Applied internal standardisation technique (IS) yielded satisfactory recoveries ranging from 95 to 100 % for the determination of both Al and Si.

Comparing to IS method lower average values and poorer precision were achieved for those measurements where no internal standard was used, and the analytical recoveries were only 82 ± 17 % for Si and 84 ± 16 %

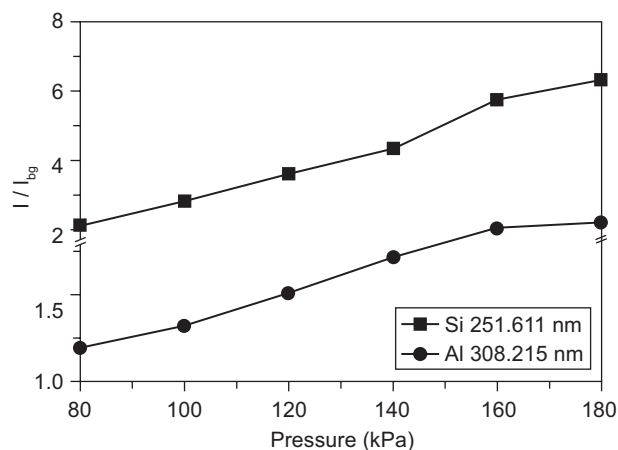


Figure 1. Influence of carrier gas pressure (kPa) on signal to background intensity ratio for Si and Al.

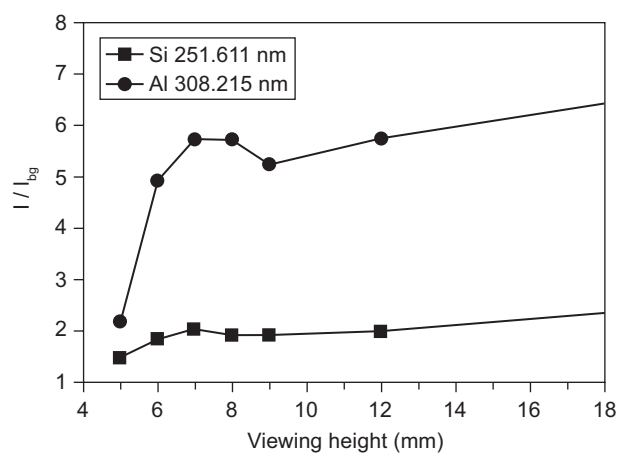


Figure 2. Influence of viewing height on signal to background intensity ratio of Si and Al emission line.

for Al. The IS technique with yttrium as the internal standard appears to be suitable analytical technique for determination of desired elements. Unfortunately, it could not be used in the analysis of silicon nitride corrosion samples since a fraction of yttrium could be leached into the corrosion solution from the amorphous grain boundary phase present in the ceramic material. Yttrium dioxide as a sintering additive can be applied also in preparation of alumina ceramics, in order to achieve required mechanical properties. For our purpose alumina samples used for validation of the internal standardization techniques did not contain Y_2O_3 . Yttrium as the internal standard could be therefore applied for determination of Al in solutions obtained from corrosion tests.

The applied IS technique was verified by measuring the 100-times diluted CENTMIX4 CRM containing $10 \text{ mg}\cdot\text{l}^{-1}$ of both Al and Si. For quantification of the known concentrations of the elements, the calibration solutions prepared in deionised water stabilised with 0.25 mL of 65 % w/v HNO_3 /100 ml and in $0.5 \text{ mol}\cdot\text{l}^{-1}$ NaCl solution were used. The results obtained from these measurements are shown in the Table 2. The matrix matching technique in aqueous calibration solutions were depression of signal was observed in case of silicon determinations in contrary to aluminium, where intensity increased during

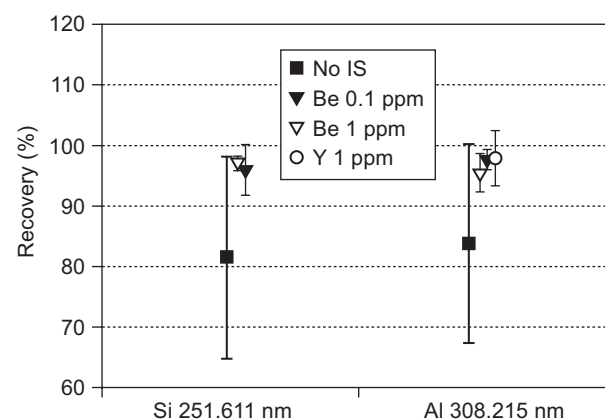


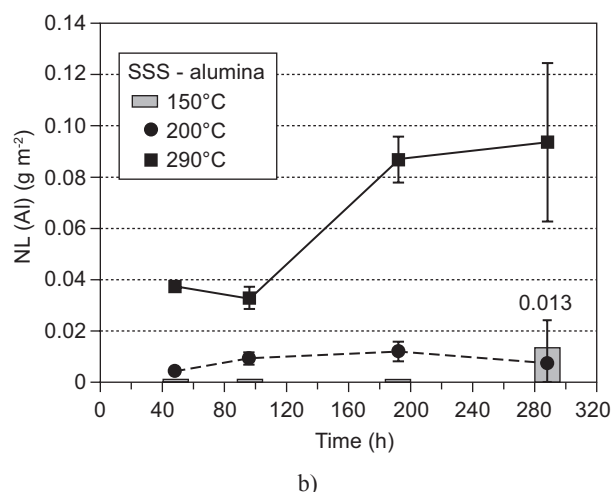
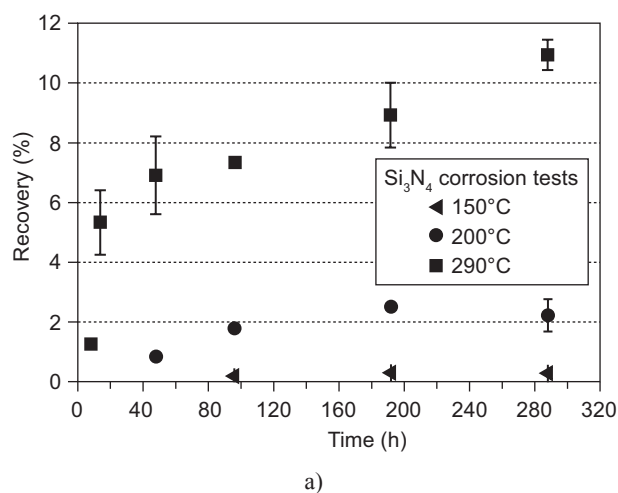
Figure 3. Analytical recoveries acquired using internal standardisation technique with Be and Y compared to direct measurement with no internal standard (no IS).

Table 2. Concentrations of Si and Al in $\text{mg}\cdot\text{l}^{-1}$ measured in 100-fold diluted certified reference material (CRM) CENTMIX4 with certified values $10 \text{ mg}\cdot\text{l}^{-1}$ Al and $10 \text{ mg}\cdot\text{l}^{-1}$ Si.

Internal standard	Aqueous calibration solutions		Calibration solutions in $0.5 \text{ mol}\cdot\text{l}^{-1}$ NaCl	
	$Al_{308.215 \text{ nm}}$ ($\text{mg}\cdot\text{l}^{-1}$) average \pm std n = 6	$Si_{251.611 \text{ nm}}$ ($\text{mg}\cdot\text{l}^{-1}$) average \pm std n = 6	$Al_{308.215 \text{ nm}}$ ($\text{mg}\cdot\text{l}^{-1}$) average \pm std n = 6	$Si_{251.611 \text{ nm}}$ ($\text{mg}\cdot\text{l}^{-1}$) average \pm std n = 6
no	11.6 ± 0.5	7.9 ± 0.2	10.7 ± 0.7	7.6 ± 0.8
$0.1 \text{ mg}\cdot\text{l}^{-1}$ Be	11.2 ± 0.2	9.7 ± 0.3	10.2 ± 0.5	9.8 ± 0.2
$1 \text{ mg}\cdot\text{l}^{-1}$ Be	-	-	10.0 ± 0.3	9.3 ± 0.4
SA technique	10.8 ± 1.6	10.6 ± 0.7	10.2 ± 0.4	10.3 ± 0.3

SA - standard addition; std - standard deviation - not determined

the analysis. The internal standardisation technique combined with matrix matching appear to be the optimal choice for determination of Si and Al in $0.5 \text{ mol}\cdot\text{l}^{-1}$ NaCl, showing good agreement with the certified values, and precision expressed as a relative standard deviation not exceeding 5 %.



The results of the determination of Si and Al in solutions from the corrosion experiment are summarised in Table 3. Si and Al were determined in the eluates of the ceramic materials denoted as S, A, and AH, and containing $0.5 \text{ mol}\cdot\text{l}^{-1}$ of NaCl. The calibration solutions contained the same concentration of NaCl as the samples. In addition, $0.1 \text{ mg}\cdot\text{l}^{-1}$ of Be, $1 \text{ mg}\cdot\text{l}^{-1}$ of Be and $1 \text{ mg}\cdot\text{l}^{-1}$ of Y as the internal standards were added to the calibration solutions and the sample eluates. The measured concentrations of Si and Al obtained by the internal standardisation and standard addition techniques are comparable, and achieve satisfactory precision. The relative standard deviations (RSD in %) vary in the interval from 2 to 5 %. With the use of the matrix matching technique, and without application of the internal standard, enhancement or suppression of the intensity of the analytical signal was observed. Achieved relative standard deviations ranged from 8 to 30 %. The effect of sodium ions in solution on the intensities of ionic lines in ICP-AES was studied by Romero [8] and Mermet [16]. The effect was assigned to both the change in the excitation and ionisation processes in the plasma

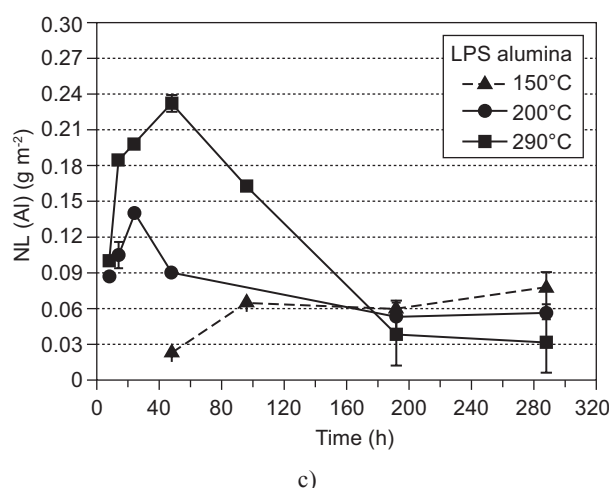


Figure 4. Time dependences of the normalized leaching values of Si and Al from the corrosion tests in 0.5 M NaCl solution of the structural ceramics S (a), A (b) and AH (c).

Table 3. Determination of Al and Si in $0.5 \text{ mol}\cdot\text{l}^{-1}$ NaCl solution originating from the corrosion experiments with discussed ceramic materials (samples A, AH and S).

Sample	A		AH		S	
	$\text{Al}_{308.215 \text{ nm}}$ ($\text{mg}\cdot\text{l}^{-1}$)	$\text{Si}_{251.611 \text{ nm}}$ ($\text{mg}\cdot\text{l}^{-1}$)	$\text{Al}_{308.215 \text{ nm}}$ ($\text{mg}\cdot\text{l}^{-1}$)	$\text{Si}_{251.611 \text{ nm}}$ ($\text{mg}\cdot\text{l}^{-1}$)	$\text{Al}_{308.215 \text{ nm}}$ ($\text{mg}\cdot\text{l}^{-1}$)	$\text{Si}_{251.611 \text{ nm}}$ ($\text{mg}\cdot\text{l}^{-1}$)
Internal standard	ave \pm std n = 3	ave \pm std n = 3	ave \pm std n = 3	ave \pm std n = 3	ave \pm std n = 3	ave \pm std n = 3
no	2.76 ± 0.4	2.01 ± 0.4	0.98 ± 0.1	19.6 ± 0.6	–	12.1 ± 1.0
$0.1 \text{ mg}\cdot\text{l}^{-1}$ Be	3.60 ± 0.3	1.95 ± 0.05	0.90 ± 0.03	20.2 ± 0.6	–	13.6 ± 0.8
$1 \text{ mg}\cdot\text{l}^{-1}$ Be	3.67 ± 0.2	2.11 ± 0.1	0.91 ± 0.04	20.8 ± 0.7	–	14.2 ± 0.4
$1 \text{ mg}\cdot\text{l}^{-1}$ Y	3.65 ± 0.1	–	0.93 ± 0.05	–	–	–
SA technique	3.69 ± 0.1	2.00 ± 0.09	1.1 ± 0.1	21.0 ± 1.0	–	13.7 ± 0.5

SA - standard addition; std - standard deviation - not determined

and to a change in the aerosol formation and transport. Determination of the selected elements without the use of the internal standard did not provide satisfactory results due to low recoveries varying from 60 to 95 % depending on the element analysed.

The optimised matrix matching method combined with internal standardisation was applied for determination of corrosion rates of the three studied structural ceramics at three various temperatures. The time dependences of cumulative normalised leaching values are shown in Figure 4. The calculated initial corrosion rates are summarised in Table 4.

Table 4. The rate constants and activation energies of dissolution of silicon nitride and alumina ceramics corroded at various temperatures in 0.5 M NaCl solution.

Sample		k_c (mmol·m ⁻² ·h ⁻¹)	E_a (kJ·mol ⁻¹)
Si ₃ N ₄ (S)	290°C	20.1 ± 0.7	74 ± 8
	200°C	6.0 ± 0.3	
	150°C	1.0 ± 0.1	
Al ₂ O ₃ (A)	290°C	0.014 ± 0.001	*
	200°C	0.0026 ± 0.0003	
	150°C	*	
Al ₂ O ₃ (AH)	290°C	67 ± 2	49.0 ± 0.1
	200°C	9.7 ± 3	
	150°C	2.1 ± 0.3	

* not determined

In Si₃N₄ ceramics, the severity of corrosion attack increased with time and temperature of corrosion. The Si₃N₄ ceramics corroded preferentially by congruent dissolution of silicon nitride matrix grains in the used corrosion solution, according to the reaction equation (3):



and with initial dissolution rate of 20.0 mmol·m⁻²·h⁻¹, as determined at 290°C. The apparent activation energy of dissolution of Si₃N₄ in the 0.5 M NaCl solution was 69.3 ± 16 kJ/mol, respectively. Similar values of E_a (73 - 110 kJ/mol) were estimated by Sato [17], and Somiya [18], who concluded that dissolution of Si₃N₄ ceramics under hydrothermal conditions (below 300°C) was controlled by surface chemical reactions.

Similarly to silicon nitride-based ceramics, the corrosion rates of both alumina-based ceramics were influenced by the temperature. The rate constants of dissolution at 150°C for the material A could not be determined as the concentrations of aluminium in eluates were close to the limit of detection. Also determination of the activation energy of dissolution of the material A from only two allowable kinetic parameters would be rather questionable, and was therefore not considered. The rate constants of dissolution of the material AH were

determined from the linear parts of the experimental NL (mol·m⁻²) vs time dependences obtained from the analysis of the data acquired respectively from static (at 150 and 200°C), and *quasi*-dynamic (at 290°C) tests. The obtained values are summarized in Table 4.

In the material AH the content of Al leached into the solution grew quickly in the initial period of the corrosion test, followed by flattening of the curve or, at higher temperatures, steep decrease of the NL values at longer dissolution times. The non-linear behavior is attributed to saturation of the solution with respect to aluminum, most likely accompanied by precipitation of hydrated, aluminum containing species at the surface of ceramic material. The rate constants of dissolution of the material A were almost three orders of magnitude lower than the rate constants of the material AH, calculated from the initial, approximately linear part of the NL -time dependence (Figure 4c). The apparent activation energy of dissolution of the AH ceramic material in 0.5 M NaCl solution was 49.0 ± 0.1 kJ/mol. The value of the activation energies reported for dissolution of alumina ceramics with purity 99.8 % corroded by various acids was determined to be 10.68 kJ/mol in HCl and 9.74 kJ/mol in H₂SO₄ [19]. Mikeska [20] determined the activation energies for alumina samples co-doped with MgO and SiO₂ dissolved in aqueous hydrofluoric acid in the range of 30 - 90 kJ/mol depending on composition of the grain boundary glassy phase. They conclude that low activation energies, at the level of 30 kJ/mol in silica doped aluminas is close to that of dissolution of SiO₄ tetrahedra, while high activation energies characteristic for aluminas with Mg/Si ratio ≥ 1 are similar to those of dissolution of AlO₆ octahedra (102 kJ/mol). Therefore, the mechanism of dissolution of silica-doped aluminas in HF is the same that of the fused silica, while the mechanism of dissolution MgO co-doped materials with higher than equimolar Mg/Si ratio is similar to pure sapphire. The values of activation energies obtained in this study for the material AH with Ca/Si ratio 0.2 therefore confirm the results of chemical analysis of eluates, i.e. that the material corrodes by preferential dissolution of the aluminosilicate grain boundary phase, and that the aluminum detected in the eluate originated preferentially from the dissolution of grain boundary phase. This conclusion is in accord also with the results of chemical analysis of eluates from the corrosion of the material A, which revealed extremely slow dissolution of the alumina matrix grains.

CONCLUSIONS

The present work extends the applicability of the method developed for the determination of Al in solutions with high salinity [10] also to the analysis of Si. The applicability of the method was verified by analysis of CRM and real specimens in 0.5 mol·l⁻¹ aqueous solu-

tion of analytically pure NaCl. The simple internal standardisation technique was shown to be sensitive with satisfactory limits of detection: Al (308.215 nm) 0.095 mg·l⁻¹, Si (251.611 nm) 0.099 mg·l⁻¹. Various concentrations of Be internal standard have no significant effect on the accuracy of determination. The method exhibited satisfactory precision (relative standard deviation 3 - 5 %) and high analytical recoveries between 95 and 100 %. A simple matrix matching technique was shown to be inadequate for the elimination of non-spectral interferences that, in the case of Si, led to suppression of the intensity of the analytical signal. Determination of the selected elements with the use of the matrix matching technique did not provide satisfactory results due to low recoveries varying from 65 to 95 % depending on the element analysed. The internal standardization technique with yttrium as the internal standard can be also applied for determination of discussed elements, providing that the ceramic materials do not contain Y₂O₃ as the sintering additive. The optimised analytical method was applied for evaluation of corrosion rates of three types of commonly used oxide and non-oxide structural ceramics corroded under static and *quasi*-dynamic conditions.

Acknowledgement

The financial support of the grants APVV 0500-10, APVV 0218-11, and VEGA 2/0058/14, VEGA 2/0036/10 is gratefully acknowledged. This publication was created in the frame of the project "Centre of excellence for ceramics, glass and silicate materials", ITMS code 26220120056, based on the Operation Program Research and Development funded from the European Regional Development Fund.

References

1. Kritzer P.: J. Supercritical Fluids 29, 1 (2004).
2. Iglesias M., Vaculovic T., Studynkova J., Poussel E., Mermet J. M.: Spectrochim. Acta, 59B, 1841 (2004).
3. Montaser A., Golightly D. W.: *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, VCH Publishers, Inc. New York 1992.
4. Akagi T., Fuwa K., Haraguchi H.: Anal. Chim. Acta 177, 139 (1989).
5. Zhua Y., Umemurab T., Haraguchi H., Inagaki K., Chibaa K.: Talanta 78, 891 (2009).
6. Rahmi D., Yanbei Z., Fujimori E., Umemura T., Haraguchi H.: Talanta 72, 600 (2007).
7. Ferreira S. L. C., de Brito C. F., Dantas A. F., Lopo de Araújo N. M., Spinola Costa A. C.: Talanta 48, 1173 (1999).
8. Romero X., Poussel E., Mermet J. M.: Spectrochim. Acta 52B, 495 (1997).
9. Krejčová A., Černohorský T., Pouzar M.: Microchim. Acta 156, 271 (2006).
10. Krejčová A., Černohorský T., Pouzar M.: Anal. Chim. Acta 582, 208 (2007).
11. Al-Ammar A. S., Barnes R.: Spectrochim. Acta B 53, 1583 (1998).
12. Galusková D., Hnatko M., Galusek D., Šajgalík P.: J. Am. Ceram. Soc. 94, 3035 (2011)
13. Galusková D., Hnatko M., Galusek D., Šajgalík P.: J. Am. Ceram. Soc. 94, 3044 (2011)
14. Helebrant A.: Ceram.-Silikaty 41, 147 (1997).
15. Nölte J.: *ICP Emission Spectroscopy: A Practical Guide*, p. 162, Wiley-VCH Verlag GmbH&Co. KGaA, 2003.
16. Mermet J. M.: J. Anal. At. Spectrom. 13, 419 (1998).
17. Sato T., Tokunaga Y., Endo T., Shimada M.: J. Am. Ceram. Soc. 71, 1074 (1988).
18. Somiya S.: Mater. Chem. Phys. 67, 157 (2001).
19. Curkovic L., Jelača M. F., Kurajica S.: Corr. Sci. 50, 872 (2008).
20. Mikeska K. R., Bennison S. J.: J. Am. Ceram. Soc. 82, 3561 (1999).