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Adsorption of fission products on stainless steel and zirconium

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Abstract Contamination of the structural materials of nuclear reactors is a crucial question in view of radiation protection, especially, if due to some leakage, uranium and its fission products appear in the cooling water. Since it is rather difficult to obtain in situ experimental data on the actual amount of adsorbed radioactive species, the surface contamination may be quantified by measuring bulk activity concentrations of the cooling water and by calculating the amount of adsorbed material on the surfaces by using a partition coefficient. To do this, the knowledge of an appropriate adsorption isotherm is needed. Thus, our paper presents results, based on electrochemical measurements, about the extent and effect of the adsorption of certain fission products—caesium and iodide—in their ionic forms on the surface of some alloys used in the nuclear industry. Our findings allow the conclusion that the adsorption of these ions can be described by a Langmuir-type isotherm, where the saturation values correspond to surface monolayers.

Keywords Electrochemical quartz crystal microbalance · Fission products

1 Introduction

Contamination of the structural materials of nuclear reactors is crucial question in view of radiation protection, especially, if due to some leakage, uranium and its fission products appear in the cooling water. Additionally, the adsorption of these products can modify the corrosion behavior of the alloys, which can be found in the primary circuit. Thus, the knowledge of the extent of adsorption may be of significant importance in case of malfunctions. Such situation took place a couple of years ago in the Paks NPP (Hungary) when fission material and fission products were released into the cooling water of the spent fuel storage pool due to a non-nuclear incident. Although some estimations could have been given to the extent of surface contamination (Nagy et al. 2007), the results pointed out the necessity of the knowledge of adsorption isotherms.

Thus, the aim of this work is to determine the extent of the adsorption of certain fission products (caesium and iodide) and of uranium on metals, modeling the alloys from the primary circuit of a VVER reactor. Although the release of fission material under severe accident conditions has thoroughly been studied, much less is known about the adsorption of fission products on solid surfaces under room temperature. There are only a few papers dealing with uranyl adsorption on reactor materials and even less is known about the adsorption of the fission products. Room temperature adsorption of fission products from aqueous solutions on zirconium and stainless steel surfaces were investigated (Hirschberg et al. 1999; Varga et al. 2001; Fujii et al. 2002; Vajda et al. 2004). Similar experiments were done also at higher temperatures up to about 300 °C (Lister 1975, 1976, 1993; Lister et al. 1983; Pattison and Walton 1961). Dombovári et al. (2007) examined the accumulation of uranium and its species on several types of stainless steels. They presented some information about uranyl chemistry in boric acid solution including the pH dependence of uranyl adsorption and of the maximum coverage. The role of pH on UO_2 solubility was studied by Casas et al. (1998).

The literature on adsorption of fission product in soils or single minerals is extensive (see for example Takamiya et al. 2006; Farley et al. 1985; Hsi and Langmuir 1985;

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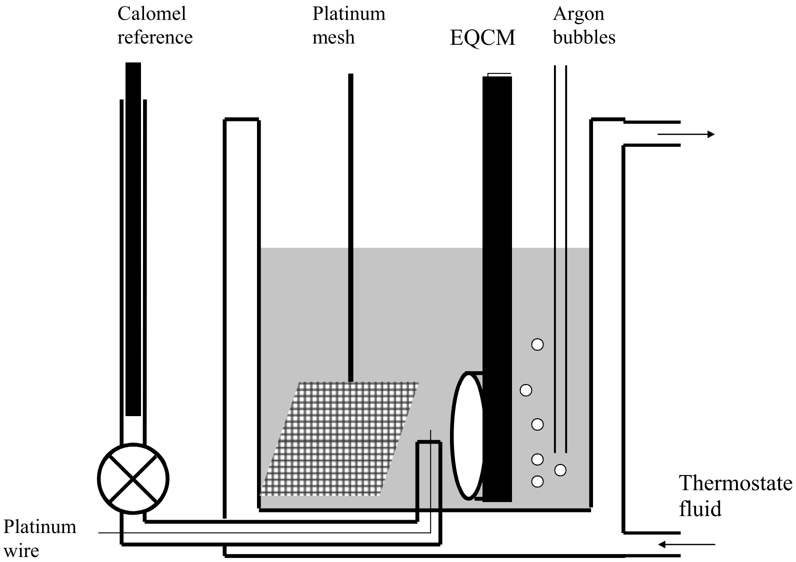

Fig. 1 Sketch of the experimental setup

Waite et al. 1994). Iron oxide and hydroxide suspensions are usually effective adsorbents which can greatly influence the fate of the dissolved ions; a good number of data could have been found also about these processes, see e.g. Lister (1980), Rommel (1978), Musić and Ristić (1988), Stén et al. (2003), Farley et al. (1985), Missana et al. (2003a, 2003b), Liger et al. (1999), Hsi and Langmuir (1985) and Waite et al. (1994).

2 Experimental

Fission product adsorption was determined by electrochemical quartz crystal microbalance (EQCM). This method is based on a mass-change generated frequency shift measurement of a piezoelectric quartz crystal. Mass-change, caused by ion adsorption, causes a measurable frequency shift. The extent of this shift is proportional with the adsorbed mass following the Sauerbrey (1959) equation:

$$\Delta f = -C_f \Delta m \tag{1}$$

where Δf is the observed frequency change, Δm is the change in mass per unit area and C_f the sensitivity factor for the crystal. For the experiments a QCM200 equipment was used with a 1 inch diameter 5 MHz AT-cut quartz crystal ($C_f = 56.6$ Hz µg^{-1}cm^2). The accuracy of the equipment is 10^{-1} Hz ~1 ng/cm^2. Chronopotentiometry (Bard and Faulkner 1980) was used for measuring the potential between the studied metal and a reference electrode to follow open circuit potential, and the pH was also monitored continuously. Three electrodes—the sample, calomel reference and platinum mesh counter electrodes—were inserted into a double wall glass cell, which was connected to a precision thermostat to provide constant temperature during the measurements. A platinum wire in the Luggin-capillary serves as a high frequency reference was connected to the reference input through a 4 µF capacitor to reduce the high frequency noise. The electrochemical cell is shown in Fig. 1.

The stainless steel film was prepared by sputtering with argon bombardment, zirconium was vacuum deposited, while iron was electrodeposited onto the quartz crystal surface. Surface morphology was checked by scanning tunneling microscopy. The chemicals used in the experiment were of analytical purity, the water was of Millipore grade (pH of the water is 6.7). The fundamental solution contained boric acid (8 g/l) and potassium hydroxide (5 mg/l) modeling the composition of the primary circuit cooling water of the Paks NPP. The liquid was degassed and mixed by argon bubbling through the system. After immersing the sample into the base solution and the initial stabilization of the mass signal a well known amount of the solution of the investigated ions was injected into the cell. During injection mass, potential and pH changes were recorded. This procedure was repeated several times. When the maximal coverage was reached (i.e. the frequency did not change upon renewed addition) the experiment was terminated and a cyclic voltammogram was taken.

EQCM is sensitive not only to mass changes at the crystal-solution interface, but also to density, ρ_L and viscosity, η_L changes, and surface roughness may cause a frequency shift, as well. As the effects are additive the overall frequency change is expressed as (Tsionsky et al. 1996)

$$\Delta f = \Delta f_m + \Delta f_p + \Delta f_\eta + \Delta f_r \tag{2}$$

where Δf_m is the mass effect caused by the added mass which is attached to the surface, Δf_p is the compression effect caused by changes of pressure of the fluid in contact with the quartz, Δf_η is the viscosity effect, Δf_r is the roughness effect. The pressure and the roughness effects are negligible in this system, but the viscosity and the density of the interfacial layer can change significantly. Concentration near to the crystal (in the double-layer) may become much higher than it is in the bulk. The addition of the investigated ions can increase not only the bulk concentration, but also the concentration in the double-layer. The increasing of the viscosity and density causes increasing dissipation of oscillation energy. The Butterworth-Van Dyke model describes the quartz crystal by a serial LCR electronic oscillator circuit. The Butterworth-Van Dyke equation (Martin et al. 1991) predicts linear relationship between the change in series resistance ($\Delta_{\mathrm{U}}^{\mathrm{L}} R$)—due to the transfer of the crystal from the unloaded state (contacted with air) to the liquid—and $(\rho_L \eta_L)^{1/2}$ where ρ_L and η_L are the density and the viscosity of the liquid in contact with the crystal.

$$\Delta_{\mathrm{U}}^{\mathrm{L}} R = \left(\frac{n\omega_s L_U}{\pi}\right) \cdot \left(\frac{2\omega_s \rho_L \eta_L}{\rho_q \mu_q}\right)^{1/2} \tag{3}$$

In this equation n is the number of sides in contact with liquid, ω_S is the angular frequency, L_U is the inductance for the unperturbed resonator (30 mH for our system), ρ_q is the density of the quartz (2.648 g/cm^3), μ_q is the shear modulus of the quartz (2.947$\cdot 10^{11}$ g/cm s^2).

The frequency change caused by the viscosity effect—again between the loaded and the unloaded case—can be calculated by the equation of Kanazawa and Gordon (1985):

$$\Delta_{\mathrm{U}}^{\mathrm{L}} f_\eta = -f_U^{3/2} \left(\frac{\rho_L \eta_L}{\pi \rho_q \mu_q}\right)^{1/2} \tag{4}$$

where f_U is frequency of oscillation of unloaded crystal.

The change of serial resistance (ΔR)—relative to the state in the solution without examined adsorbing ions—can be measured parallel with the resonance frequency during adsorption process. The frequency change caused by viscosity effect can be calculated on the base of the (3) and (4) using the following relations:

$$\Delta(\rho_L \eta_L)^{1/2} = \left(\frac{n\omega_s L_U}{\pi}\right)^{-1} \left(\frac{2\omega_s}{\rho_q \mu_q}\right)^{-1/2} \Delta R$$

$$\Delta f_\eta = -f_U^{3/2} (\pi \rho_q \mu_q)^{-1/2} \Delta(\rho_L \eta_L)^{1/2}$$

The mass change was calculated from measured frequency change corrected by Δf_η using (1).

3 Results and discussion

One example of the experimental results is iodide adsorption on stainless steel, presented in Fig. 2. As the steps on the curves indicate there is a rapid change after addition and both the resistance and the frequency signal stabilize rather soon, due to vigorous stirring. By adding more and more iodide into the solution staircase-type curves obtained. It was striking to observe that the frequency change was not always monotonic as it would have been expected if Δf corresponded to the mass change through the Sauerbrey equation (1). As our example shows in Fig. 2, the frequency curve often went through a minimum when the ion concentration reached the mmol/dm^3 range. Such behavior was observed for the I$^-$ ion, but never for the Cs$^+$ ions. This effect cannot be attributed to changes in the pH or in the electrode potential. As it is seen in Fig. 3 the electrode potential of the stainless steel shifts monotonically to less positive values, while the pH changes only 0.15 units in the beginning of the iodide addition, while it stabilizes around 5.1 at higher concentrations.

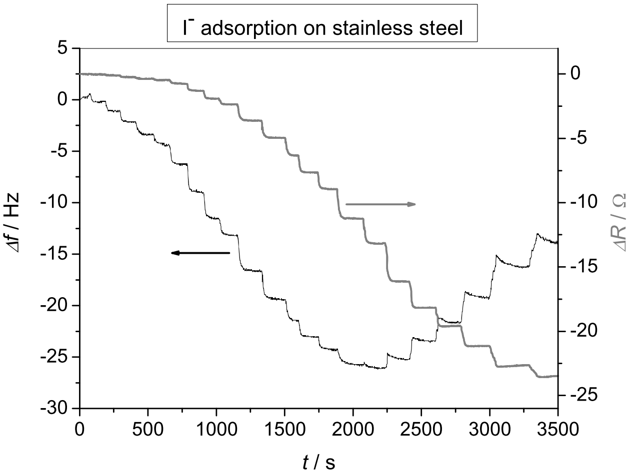

Fig. 2 Changes of the EQCM frequency (Δf) and of series resistance (ΔR) as a function of time due to stepwise addition of small amounts of 100 mmol/dm^3 iodide ion solution

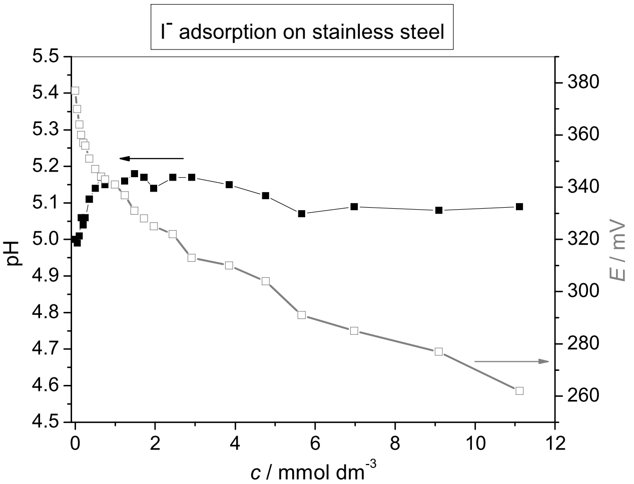

Fig. 3 Changes of the pH of the solution and the potential of the stainless steel electrode as a function of iodide ion concentration

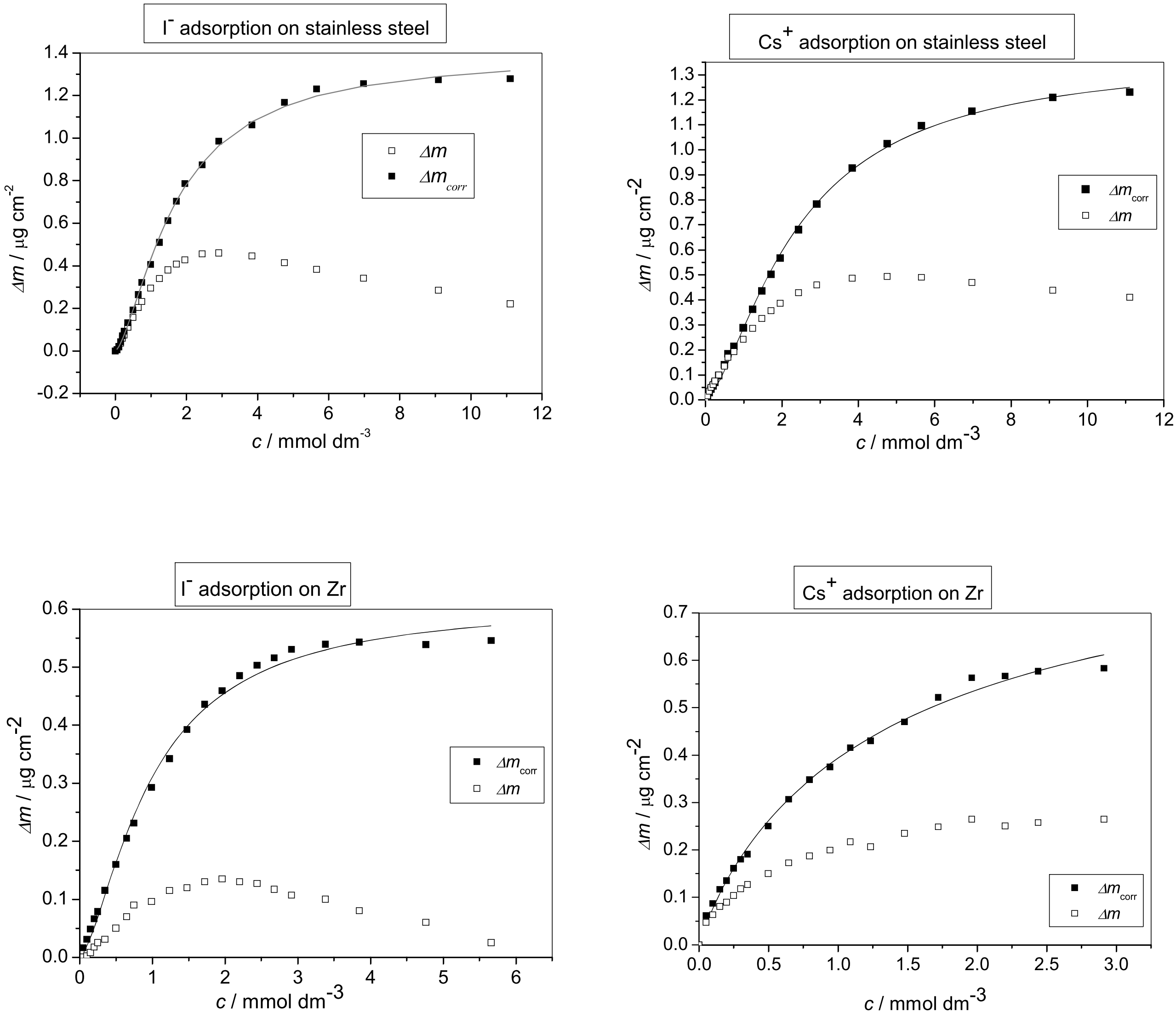

Fig. 4 Adsorption isotherm of the fission products on stainless steel and zirconium calculated from the data in Fig. 2. Δm is obtained directly from (1), while Δm_{corr} is calculated by (2), (3) and (4). The *line* is obtained by fitting (5)

Our results may be understood by taking into account that the overall frequency shift is influenced not only by the mass change but also by other factors, as it is expressed by (2). The changes in the density and viscosity of the liquid in the interfacial region can be corrected by using (2) and (3). As it is seen in Fig. 4, the corrected mass change, Δm_{corr}, shows asymptotic behavior.

The shape of the Δm_{corr} vs. concentration curves are similar for all the systems investigated. At small bulk concentrations Δm_{corr} increases quasi linearly, and it approaches a limiting value at higher concentrations. Although certain methods exist (Marczewski et al. 1989), it is difficult to select the most appropriate adsorption isotherm from the rather large number of the existing models (Toth 2002; http://adsorption.org) for our results. Thus, we decided to use an extended Langmuir isotherm for comparison, since it has a simple analytical form and only three free parameters:

$$\Delta m_{corr} = (a + b \cdot c^{n})^{-1} \tag{5}$$

In this equation a is the reciprocal of $\Delta m_{\max}$ and b is the reciprocal of the initial slope, while n is an empirical exponent. By fitting (5) we could describe the Δm_{corr} vs. concentration curves consistently and the different systems could be compared unambiguously. The results of fits are given in Table 1.

The change in the mass due to an ion in the diffuse double layer may be expressed as (Waite et al. 1994)

$$\Delta m = n \cdot (M_{ion} - M_W \nu_w - M_I \nu_I) \tag{6}$$

Table 1 Characteristic parameters of the adsorption process for the different systems. $\Delta m_{\max}$ is calculated from a. The best fits were obtained with $n \approx -1.5$ for all the investigated systems. In some case strong correlation was found between n and b, and same mechanism can be supposed for all the system, thus n was fixed as -1.5

Metal	Ion	Langmuir parameters			$\Delta m_{\max}$
		a	b	n (fixed)	μg/cm^2
Zr	I^-	1.6 ± 0.3	1.8 ± 1.1	-1.5	0.63
	Cs^+	1.8 ± 0.2	0.3 ± 0.2	-1.5	0.55
Steel	I^-	0.7	1.6	-1.5	1.4
	Cs^+	0.76 ± 0.10	2.5 ± 0.2	-1.5	1.3
Iron	I^-	1.4	0.7	-1.5	0.71
	Cs^+	1.3 ± 0.2	0.44 ± 0.04	-1.5	0.77

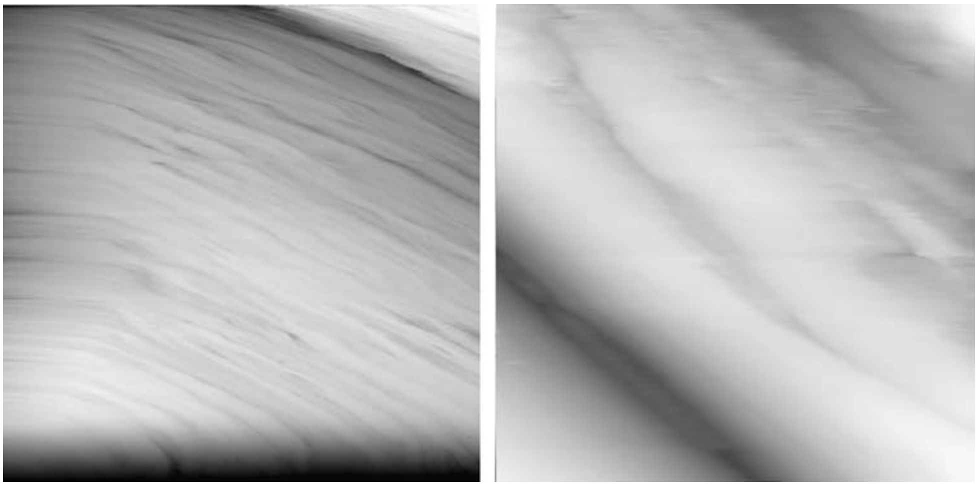

Fig. 5 250 nm × 250 nm topographic STM images of zirconium (*left*) and stainless steel (*right*)

where n is number of ions to adsorb, M_{ion}, M_I and M_w are the molecular weights of the ion to adsorb, of another ion to desorb, and of water, respectively. The replacement coefficients ν_w, ν_I, reflect the number of water molecules and ions replaced by the respective ion. Equation (6) clearly shows that it is difficult to assess the surface coverage only by knowing Δm.

The mass change due to the adsorption and desorption processes are inseparably coupled. On the basis of the hard sphere model we can analyze the simplest cases: (a) adsorption on empty surface, (b) replacement of one species.

For iodide ions it may be assumed that contact adsorption may happen similarly to the case of iodide adsorption on gold and platinum—although in earlier investigations (Bayri et al. 2001) iodide adsorption was not found on stainless steels. If we consider a close packed quadratic arrangement of the adsorbed iodide ions—which is an overestimation since a $\sqrt{3} \times \sqrt{3}$ arrangement was found on gold and platinum—a maximum coverage of $\sim$0.5 μg/cm^2 may be calculated from the ionic radius. Since our results gave a higher limit of Δm_{corr} we should attribute the difference to the surface roughness.

To have a reasonable estimation we measured the surfaces with STM in different resolutions and calculated roughness (r_{STM}) from the topographic images. The results are shown for zirconium and stainless steel in Fig. 5.

The surfaces showed marked differences which may be attributed to the different preparation methods. The Zirconium surface shows step-like features while the stainless steel surface shows hills and valleys which are typical for polycrystalline surfaces. The surface roughness was found to be rather large: 7 ± 6 for Zr, while 15 ± 6 for the 08H18N10T steel. The high uncertainty indicates that the surfaces are not morphologically homogeneous.

If we calculate the surface roughness from the maximal Δm_{corr} and the close packed monolayer coverage supposing no replacement we obtain r_{EQCM} to be 1.3 for the Zr surface, 2.8 for the 08H18N10T steel surface, and 1.4 for the iron surface. These values are a factor of 5 smaller than the roughness from the STM experiments, but the ratio between the values calculated from the STM and the EQCM data are similar: the steel surface is twice as rough as the zirconium surface.

If we assume that iodide ion replaces solely the borate ions on the surface we may calculate the number of borates, ν, replaced by iodide by using (6) and the roughness factor, r_{STM}, from the STM experiments. The calculations show that, irrespective of the substrate quality, the number of replaced borate is $\sim$1.7.

Caesium ions cannot be regarded as being contact adsorbed because of the hydration shell (Hsi and Langmuir 1985). If we consider, however, a hypothetic close packed

Table 2 Calculated roughness values and ion replacement coefficients. For details see text

Metal	Roughness r_{STM}	Ion	Roughness r_{EQCM}	Replacement coefficient ν
Zr	7 ± 6	I^-	1.3	1.7
		Cs^+	0.9	3.0
Steel	15 ± 6	I^-	2.8	1.7
		Cs^+	2.1	2.9
Iron	–	I^-	1.4	1.7[a]
		Cs^+	1.2	3.0p[a]

[a] With $r_{STM} = 7$

quadratic monolayer, a maximum coverage of ~0.63 μg/cm^2 may be calculated. Thus, with the data in Table 2, a roughness (r_{EQCM}) of 0.87 for Zr, 2.1 for the 08H18N10T steel, and 1.2 for iron is obtained, which is fairly closed to the values obtained from the results of the iodide adsorption EQCM experiments. If we assume that Cs^+ replaces only K^+ during adsorption, we find the number of replaced ions (ν) to be ~3 by using (6) and r_{STM}.

As the number of replaced ions seems to be reasonable for both cases, and the surface roughness from the STM experiments is not unrealistically high, we may conclude that both Cs^+ and I^- do adsorb on the surfaces of zirconium, the 08H18N10T steel, and iron. The maximal coverage is close to be a monolayer. The adsorption process takes place by ion replacement.

4 Conclusion

The extent of the adsorption of certain fission products—caesium and iodide—in their ionic forms on some alloys used in the nuclear industry are presented based on electrochemical quartz crystal measurements. We found that all investigated ions do adsorb on all investigated metals: iron, 08H18N10T steel and zirconium. The maximum coverage is close to be a monolayer. According to our experimental data and our model the adsorption process takes place by ion replacement, during iodide adsorption the number of replaced borate is 1.7, while it is 3 for the number of replaced potassium ions during caesium adsorption. Further investigations are planned with cerium and uranyl ions.

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