

Influence of sodium molybdate(VI) on the corrosion of S235 carbon steel

Joanna TRELA*, Milena CHAT, Mieczysław SCENDO – Institute of Chemistry, Jan Kochanowski University in Kielce, Poland

Please cite as: CHEMIK 2015, 69, 9, 592–599

Introduction

Carbon steel (CS), thanks to the good mechanical properties and low production costs is wide use in different fields of industry [1–2]. Unfortunately, CS undergoes corrosion in aggressive solutions [3]. The use of inhibitors is one of the most widely practical methods for protection of metals against corrosion. Corrosion inhibitors are compounds which even small concentration considerably reduce the rate of corrosion. Most of the well-known organic inhibitors are heterocyclic compounds containing π -electrons, heteroatoms like nitrogen, oxygen or sulphur and aromatic rings [4 – 7]. Inorganic inhibitors are not so popular. The cost of inorganic inhibitors is low, but most of them are toxic, for example: chromates, nitrites, arsenates [8]. Molybdate compounds are not toxic [9]. Most studies concerning the inhibitory properties of molybdates was carried out in a neutral solutions [10 – 12]. Corrosion inhibition effect in a weakly acidic solution of hydrochloric acid by molybdenum compounds have been examined by Mu et al. [10]. In the literature, there are few reports on the protective properties of molybdate salts in acid solution. Therefore, the aim of this study was to investigate the effect of the concentration of sodium molybdate(VI) (Na_2MoO_4) on the corrosion of S235 carbon steel in a solution of chloride and nitrate(V) ions. For the research was used linear sweep voltammetry (LSV).

Experimental methods

Electrodes

The working electrode was prepared from S235 carbon steel. The elements compositions at weight percentages (wt. %) of the investigated steel is show in Table I.

Table I

Chemical composition of S235 carbon steel

Element	C	S	P	Si	Mn	Cr	Ni	Cu	Fe
Wt (%)	<0.22	<0.050	<0.050	0.10-0.35	<1.10	<0.30	<0.30	<0.30	rest

The geometric area of electrode was 0.22 cm². The working electrode was mechanically abraded with a series of emery papers (800, 1200 and 2500 grade). Than it was rinsed in acetone and double distilled water before their immersion in solution.

Electrode potentials were measured and reported against the saturated calomel electrode (SCE) connected with solution via an salt - bridge.

A platinum wire (99.99% Pt) was used as an auxiliary electrode.

Apparatus. All voltammetric experiments were performed using a potentiostat/galvanostat PGSTAT 128N, AutoLab, Netherlands with NOVA 1.7 software the same firm. Moreover, experiments were carried out at suitably well-chosen temperature ($25 \pm 0.5^\circ\text{C}$) in an air thermostat with the forced air circulation.

Potentiodynamic experiments. The electrochemical behavior of S235 carbon steel sample in uninhibited and inhibited solutions were studied by recording cathodic and anodic potentiodynamic polarization curves. The electrode potential was changed from -800 to -300 mV vs. SCE, at a scan rate of 1 mV s⁻¹. The linear Tafel segments of cathodic and anodic curves were extrapolated to corrosion potential (E_{corr}) to obtain corrosion current densities (j_{corr}) and the Tafel slopes the cathodic (b_c) and anodic (b_a). The corrosion inhibition efficiency and the rate of corrosion were calculated from the equations:

$$IE(\%) = \frac{j_{\text{corr}} - j_{\text{corr(inh)}}}{j_{\text{corr}}} \times 100 \quad (1)$$

and:

$$k_{\text{corr}} = 3.268 \frac{j_{\text{corr}} M_e}{\rho n} \quad (2)$$

where j_{corr} is the corrosion current density in the absence of sodium molybdate(VI), $j_{\text{corr(inh)}}$ is the corrosion current density in the presence of Na_2MoO_4 , M_e is the molar mass of iron, ρ is the density of iron and n is the number of electrons transferred in the corrosion reaction.

Results and discussion

The electrochemical behaviour of S235 carbon steel sample in corrosive solution in the absence and presence of sodium molybdate(VI) are shown in Figure 1, as polarization curves.

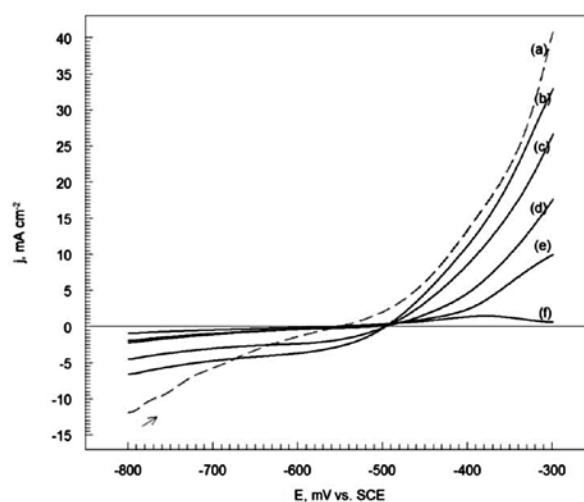


Fig. 1. Polarization curves for S235 carbon steel in solutions containing 0.5 M NaCl, 0.5 M NaNO₃, 0.1 M HCl and: (a) 0, (b) 20, (c) 40, (d) 60, (e) 80 and (f) 100 mM Na₂MoO₄, dE/dt 1 mV s⁻¹, at temperature 25°C

The cathodic hydrogen evolution mechanism is [13 – 14]:



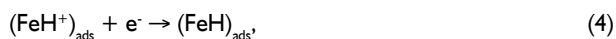
Corresponding author:

Joanna TRELA – M.Sc., e-mail: joanna.trela@ujk.edu.pl

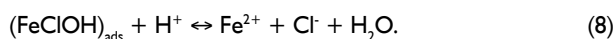
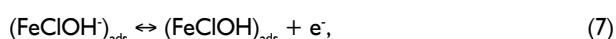
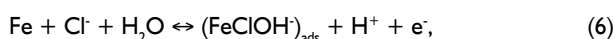
Table 2

Corrosion parameters of S235 carbon steel in Cl⁻ and NO₃⁻ solutions in the absence and presence sodium molybdate(VI), at temperature 25°C

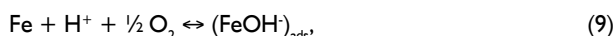
Concentration Na ₂ MoO ₄ mM	E _{corr} mV	-b _c	b _a	i _{corr} mA cm ⁻²
		mV dec ⁻¹		
0	-549	-	230	3.10
20	-495	-	170	2.70
40	-497	-	150	1.90
60	-507	-	140	0.90
80	-538	250	140	0.35
100	-552	240	140	0.17



The dissolution of iron is [15]:



The tested solution electrolyte was not deoxygenated, therefore at more anodic potential the reactions take place according to the mechanism:



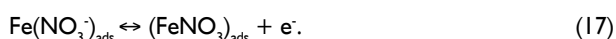
and:



In the presence of Cl⁻ and NO₃⁻ ions the reactions take place according to the mechanisms [16]:



and:



The iron(II) chloride and iron(II) nitrate(V) (reactions (16) and (17)) which was probably form on the steel surface, undergoes adsorption on the electrode, reducing of the corrosion processes. In the more positive potential the adsorbed (FeCl)_{ads} and (FeNO₃)_{ads} layers are dissolved:



and:



Therefore, film (FeCl)_{ads} and (FeNO₃)_{ads} don't protect the steel surface, against oxidation and dissolution.

Both the cathodic and anodic currents density were decreased with the addition sodium molybdate(VI) which suggested that the Na₂MoO₄ reduced the hydrogen evaluation, and also retarded anodic dissolution of carbon steel. The inhibition of the steel corrosion was probably due by the adsorption of the tested compound on the electrode surface. Corrosion parameters are given in Table 2.

Moreover, should be noted that E_{corr} shifted imperceptibly towards more negative values with an increase in the concentration of sodium molybdate(VI). The imperceptibly negative shifts of corrosion potential is characteristic for mixed inhibitors. The cathodic (b_c) Tafel slope able to designate only to the solution containing the electrolyte in addition to the sodium molybdate(VI) with concentration of 80 and 100 mM. The cathodic (b_c) Tafel slope decrease with increase concentration of the tested compound. Decrease anodic (b_a) Tafel slope indicated that increased concentration of Na₂MoO₄ change the mechanism corrosion of steel. The corrosion current density (i_{corr}) decreased when the concentration of sodium molybdate(VI) was increased (Tab. 2) which indicates the inhibiting effect of Na₂MoO₄. Then has appointed values of corrosion inhibition efficiency to the solutions containing different concentrations of investigated compound. The values IE are presented in Figure 2.

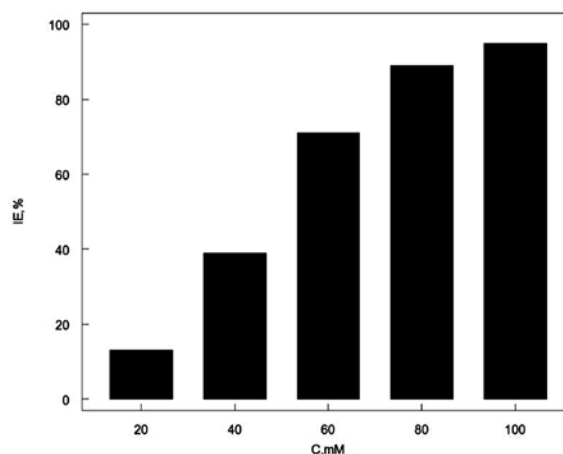


Fig. 2. Corrosion inhibition efficiency of S235 carbon steel in a solution containing different concentrations of sodium molybdate(VI), at temperature 25°C

The increase in the concentration of sodium molybdate(VI) causes increase the inhibition efficiency values. For the highest concentration of the inhibitor, IE reaches about 95%.

Then has appointed corrosion rate for solutions containing different concentration of inhibitor. The obtained results are shown in Figure 3.

With the increase of the concentration of sodium molybdate(VI) the corrosion rate decreases (Fig. 3). For the highest concentration of Na₂MoO₄, the corrosion rate decreases about 18 times compared to a solution without inhibitor. This result reveals the capability of sodium molybdate(VI) to act as a corrosion protective layer on S235 carbon steel surface in solution containing Cl⁻ and NO₃⁻ ions.

Adsorption isotherm shows as a function of the relative excess adsorbent on the surface of the electrode of the activity or concentration in the bulk solution. The adsorption isotherm of sodium molybdate(VI) on the S235 carbon steel surface is show in Figure 4.

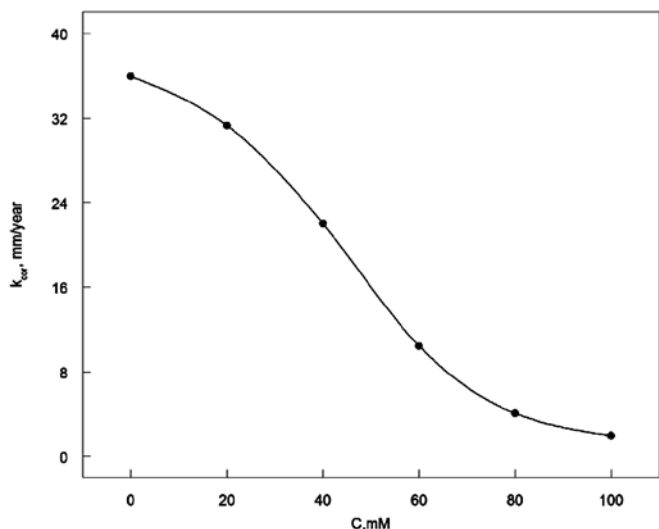


Fig. 3. The corrosion rate of S235 carbon steel in a solution containing 0.5 M NaCl, 0.5 M NaNO₃, 0.1 M HCl and different concentrations of sodium molybdate(VI), at temperature 25°C

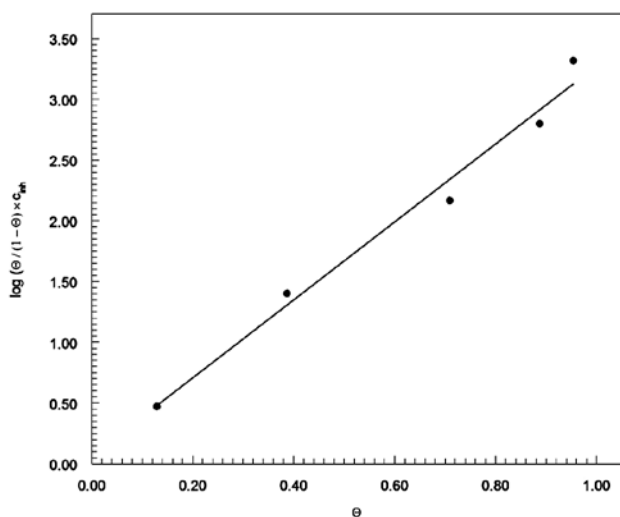


Fig. 4. Adsorption isotherms of sodium molybdate(VI) on the S235 carbon steel surface in a solution containing 0.5 M NaCl, 0.5 M NaNO₃, 0.1 M HCl, at temperature 25°C

It has been found that the adsorption of the tested inhibitor is in accordance with the Frumkin isotherm [17], which is described by the following equation:

$$\log(\Theta/(1-\Theta)c) = \log K_{ads} + 2g\Theta \quad (22)$$

where c is the inhibitor concentration, Θ is the surface coverage, K_{ads} is the equilibrium constant for the adsorption/desorption process and g is the adsorbate parameter.

Parameters of adsorption are shown in Table 3.

Table 3

Linear correlation coefficient, adsorbate parameter, equilibrium constant adsorption/desorption and standard free energy of the adsorption for S235 carbon steel in the solution containing 0.5 M NaCl, 0.5 M NaNO₃ in the presence of sodium molybdate(VI), at temperature 25°C

Inhibitor	R ²	g	K _{ads} M ⁻¹	-ΔG ^o _{ads} kJ mol ⁻¹
Na ₂ MoO ₄	0.9912	3.21	1.16 × 10 ³	27.43

Generally the standard free energy of adsorption values of 20 kJ mol⁻¹ or less negative are associated with an electrostatic interaction between charged metal surface (*physical adsorption*), those of 40 kJ mol⁻¹ or more negative involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate covalent bond (*chemical adsorption*). Obtained results indicated, that the adsorption of Na₂MoO₄ onto the steel surface takes place through both physical and chemical adsorption, namely mixed type with predominant chemical one. The parameter g is an effect lateral interaction between the inhibitor molecules. The positive value an adsorbate parameter indicates that the sodium molybdate(VI) particles attract each other.

Protective layer model

The effectiveness of protection against corrosion of the metal surface depends on the construction of the protective layer. Obtained results helped to propose a model of protective layer, which may be formed on the surface of carbon steel see, Figure 5.

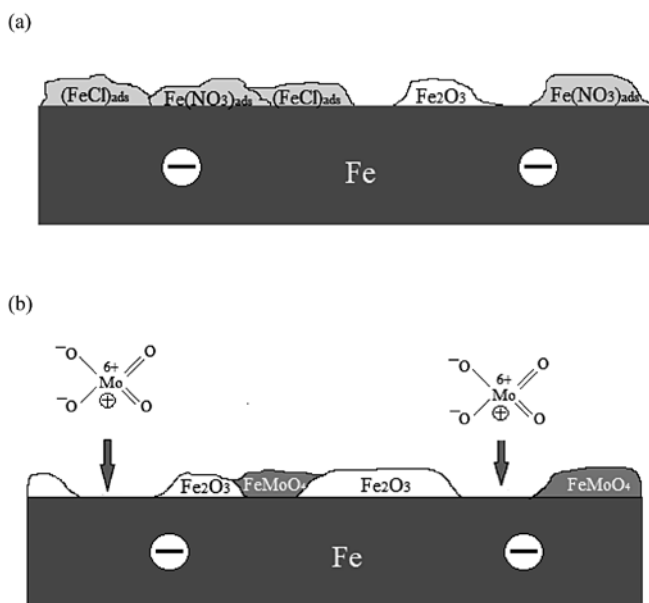
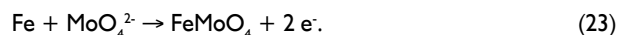


Fig. 5. Proposal of models of protective layer on surface S235 carbon steel (a) with absence (b) with presence of inhibitor

In the presence of chloride and nitrate(V) ions, the protective layer on the surface steel was formed. The protective layer consists of (FeCl)_{ads} and (FeNO₃)_{ads}. The formed film will dissolve at a more positive potential (Fig. 5(a)). As a result of the oxidation of iron oxide layer Fe₂O₃ was formed, which acts as a passive layer. After adding the inhibitor to the basic electrolyte solution following the disappearance of the layer of iron oxide(III). The protective layer iron(II) molybdate(VI) was formed (Figure 5(b)):



Iron(II) molybdate(VI) formed by the interaction of the inhibitor with the surface of the steel. The effectiveness of the protective layer depends on the orientation of molybdate ions, relative to the steel surface. The donor centers are probably atoms of molybdenum.

Thanks to the regular arrangement of iron(II) molybdate(VI) relative to the steel surface was formed quite tight protective layer.

Conclusion

From the data obtained the following points can be emphasized:

1. The sodium molybdate(VI) has good inhibition effect for the corrosion of S235 carbon steel in investigated solution.
2. The inhibition efficiency corrosion of S235 increases with increase of concentration of inhibitor.

- The corrosion rate decrease with an increase concentration of sodium molybdate(VI).
- Sodium molybdate(VI) in acidic solutions of chloride and nitrate(V) ions forms a protective layer on the steel surface.
- The Frumkin adsorption isotherm exhibited the best fit to the experimental data.
- Obtained ΔG°_{ads} value indicated, that the Na_2MoO_4 undergoes mixed adsorption creating protective layer on surface S235 carbon steel.
- Virtanen S., Surber B., Nylund P.: Influence of MoO_4^{2-} anion in the electrolyte on passivity breakdown of iron. *Corrosion Science* 2001, **43**, 1165-1177.
- Yurt A., Balaban A., Kandemir S. U.: Investigation on some Schiff bases as HCl corrosion inhibitors for carbon steel. *Materials Chemistry and Physics* 2004, **85**, 420-426.
- Quraishi M. A., Rafique M. Z. A., Khan S., Saxena N.: Corrosion inhibition of aluminium in acid solutions by some imidazoline derivatives. *Journal of Applied Electrochemistry* 2007, **37**, 1153-1162.
- Chin R. J., Nobe K.: Electrodeposition kinetics of iron in chloride solutions. *Journal of the Electrochemical Society* 1972, **119**, 1457-1461.
- Scendo M., Trela J.: Corrosion Inhibition of Carbon Steel in Acid Chloride Solution by Schiff Base of *N*-(2-chlorobenzylidene)-4-acetylaniline. *International Journal of Electrochemical Science* 2013, **8**, 8329 – 8347.
- Hussin M. H., Kassim M. J.: The corrosion inhibition and adsorption behavior of *Uncaria gambir* extract on mild steel in 1 M HCl. *Materials Chemistry and Physics* 2011, **125**, 461-468.
- Musa A. V., Kadhum A. A. H., Mohamad A. B., Takriff M. S., Daud A. R., Kamarudin S. K.: On the inhibition of mild steel corrosion by 4-amino-5-phenyl-4H-1, 2, 4-triazole-3-thiol. *Corrosion Science* 2010, **52**, 526- 533.

Literature

- Badr G. E.: The role of some thiosemicarbazide derivatives as corrosion inhibitors for C-steel in acidic media. *Corrosion Science* 2009, **51**, 2529-2536.
- Alsabagh A. M., Migahed M. A., Awad H. S.: Reactivity of polyester aliphatic amine surfactants as corrosion inhibitors for carbon steel in formation water (deep well water). *Corrosion Science* 2006, **48**, 813-828.
- Ghareba S., Omanovic S.: Interaction of 12-aminododecanoic acid with a carbon steel surface: Towards the development of "green" corrosion inhibitors. *Corrosion Science* 2010, **52**, 2104-2113.
- El-Maskoud S. A.: The influence of some Arylazobenzoyl acetonitrile derivatives on the behaviour of carbon steel in acidic media. *Applied Surface* 2003, **206**, 129-136.
- Lebrini M., Bentiss F., Vezin H., Lagrene 'e M.: The inhibition of mild steel corrosion in acidic solutions by 2,5-bis(4-pyridyl)-1,3,4-thiadiazole: Structure-activity correlation. *Corrosion Science* 2006, **48**, 1279-1291.
- Trela J., Scendo M.: Wybrane zasady purynowe jako inhibitory korozji stali węglowej. *Ochrona przed korozją* 2012, **55**, 220-224.
- Lebrini M., Lagrene 'e M., Vezin H., Traisnel M., Bentiss F.: Experimental and theoretical study for corrosion inhibition of mild steel in normal hydrochloric acid solution by some new macrocyclic polyether compounds. *Corrosion Science* 2007, **49**, 2254-2269.
- Hinton B. R. W.: Corrosion Prevention and Chromates, the End of an Era? *Metal Finishing* 1991, **89**, 55-61.
- Jefferies J., Bucher B.: New look at molybdate. *Materials Performance* 1992, **31**, 50-53.
- Mu G., Li X., Qu Q., Zhou J.: Molybdate and tungstate as corrosion inhibitors for cold rolling steel in hydrochloric acid solution. *Corrosion Science* 2006, **48**, 445-459.
- Cansever N., Cakir A. F., Urgan M.: Inhibition of stress corrosion cracking of AISI 293 stainless steel by molybdate ions at elevated temperatures under salt crust. *Corrosion Science* 1999, **4**, 1289-1303.

*Joanna TRELA – M.Sc., is a Ph.D. student at Jan Kochanowski University (UJK) in Kielce (Poland) at Institute of Chemistry. Her interests are on scientific investigations relating to influence of chosen of organic (mainly heterocyclic) and inorganic compounds on corrosion of some steels in water acid solution of salts.
e-mail: joanna.trela@ujk.edu.pl

Milena CHAT – M.Sc., is a Ph.D. student at Jan Kochanowski University (UJK) in Kielce (Poland) at Institute of Chemistry. She conducts research on the inhibitory action of protective coatings, eg. diamond like carbon (DLC).

Mieczysław SCENDO – Ph.D., D.Sc., is an Associate Professor at Jan Kochanowski University (UJK), Institute of Chemistry in Kielce, Poland. His principal of scientific investigation concerns the influence of organic compounds (mainly heterocyclic) on the kinetic electrode processes of copper, and the inhibition of corrosion of some steels in water acid solution of salts. He has published over 50 scientific articles in international journals. The majority of his investigative results have been presented at national and international conferences.

- Stowarzyszenie Inżynierów i Techników Przemysłu Chemicznego - Zarząd Oddziału Gliwice, Zarząd Główny Warszawa
 - Polska Izba Przemysłu Chemicznego, Warszawa
 - Federacja SNT NOT Rada Miejska, Gliwice
- zapraszają na

XXI Ogólnopolską Konferencję Naukowo-Techniczną

pod honorowym patronatem Wiceprezesa Rady Ministrów, Ministra Gospodarki Pana Janusza Piechocińskiego

PRZEMYSŁ CHEMICZNY – WYZWANIA I BARIERY

z cyklu

restrukturyzacja przemysłu chemicznego w Polsce

25-27 listopada 2015 r. Ustroń-Jaszowiec

Komitet programowo-organizacyjny

Jacek KIJENSKI – Przewodniczący, Instytut Chemii Przemysłowej, Zarząd Główny SITPChem Warszawa; Anna CZUMAK-BIENIECKA – Zarząd Główny SITPChem Warszawa, Redakcja Miesięcznika CHEMIK nauka-technika-rynek; Elżbieta JARGUZ – SITPChem Zarząd Oddziału Gliwice; Bożenna KA-WALEC-PIETRENKO – Politechnika Gdańska, ZG SITPChem; Jerzy KROPIWNIKI – SITPChem Zarząd Oddziału Gliwice, ZG SITPChem; Grażyna KRÓL - SITPChem Zarząd Oddziału Gliwice, ZG SITPChem; Jerzy PAPROCKI - Zarząd Główny SITPChem Warszawa; Erwin SROKA – FSNT NOT Rada Miejska Gliwice; Zbigniew ŚLĘZAK – Zarząd Główny SITPChem, Warszawa; Tomasz ZIELIŃSKI – Polska Izba Przemysłu Chemicznego, Warszawa

Tematy wiodące

Przemysł chemiczny w świecie • Reindustrializacja w Unii Europejskiej • Nauka a przemysł • Polskie osiągnięcia w ostatnim dziesięcioleciu
• Narzędzia restrukturyzacji, innowacji i konsolidacji przemysłu chemicznego • Polska gospodarka, a ograniczenia emisji CO₂ • Problemy społeczno-gospodarcze i przemysł chemiczny w statystyce

Kontakt

Elżbieta Jarguz – 32 231 27 26 lub 664 421 351

Grażyna Król – 664 421 349