

Study of Phosphate Retention on Model of Amorphous Blast Furnace Slags

Studium retence fosfátů na modelových amorfních vysokopecních struskách

Ing. Huczala Radim¹; doc. RNDr. Kostura Bruno, Ph.D.¹; Dr. Ing. Dalibor Matýšek²

¹ VŠB – Technical University of Ostrava, Faculty of Metallurgy and Materials Engineering, Department of Chemistry, 17. listopadu 15/2172, 708 33 Ostrava-Poruba, Czech Republic

² VŠB – Technical University of Ostrava, Institute of Geological Engineering, 17. listopadu 15/2172, 708 33 Ostrava-Poruba, Czech Republic

The sol-gel method was chosen for the preparation of model amorphous blast furnace slag (SG). The amorphous structure of the prepared slag was verified by X-ray diffraction and the specific surface was determined using S^{BET} . Model slag was tested as a sorbent of phosphates from water solutions. The obtained results were compared with the results of the real blast furnace slag of the same composition (BFS). It was found that phosphate retention was accomplished by the same mechanisms as in the case of BFS. The higher value of theoretical adsorption capacity of the model slag, which was 44.05 mg P/g, was caused by a different method of preparation. It turned out that the sol-gel method was suitable for the efficient preparation of model slags of desired composition. The existence of the hydroxyapatite phase (HAp) in the adsorbent product was proven by the FTIR analysis. The main retention mechanism is probably the precipitation of Ca-phosphates. The sections of the phase diagram of the CaO-Al₂O₃-SiO₂ system were prepared by the sol-gel method in order to assess the influence of acid-base properties on the adsorption capacity of slags. Excellent linear dependence of the theoretical adsorption capacity of phosphorus on the optical basicity of model slags was found that enabled an estimation of their sorption capacity.

Key words: Phosphate sorption; sol-gel method; blast furnace slag

Metoda sol-gel byla zvolena pro přípravu modelové amorfní vysokopecní strusky (SG). Amorfní struktura připravené strusky byla ověřena RTG difrakcí, pomocí S^{BET} byl stanoven její specifický povrch. Modelová struska byla testována jako sorbent fosfátů z vodných roztoků. Získané výsledky byly porovnány s výsledky reálné vysokopecní strusky (BFS) stejného složení. Bylo zjištěno, že kinetika sorpce fosforu se u obou strusek řídí modelem pro reakce pseudodruhého řádu a adsorpční data lze proložit Langmuirovou adsorpční izotermou. U obou strusek tedy lze předpokládat stejné retenční mechanismy. Vyšší teoretická adsorpční kapacita strusky SG, která činila 44,05 mg P·g⁻¹, je způsobena rozdílným způsobem výroby. Ukázalo se, že sol-gel metoda je vhodným prostředkem pro rychlou a energeticky méně náročnou přípravu modelových vysokopecních strusek požadovaného složení. Pomocí FTIR analýzy byla v adsorpčním produktu vzorku SG prokázána existence hydroxyapatitové fáze (HAp). Hlavním retenčním mechanismem je zřejmě precipitace Ca-fosfátů. Pro studium vlivu acidobazických vlastností vysokopecních strusek na jejich adsorpční schopnosti byly stejnou metodou připraveny vzorky strusek v řezu CaO:SiO₂ = 1 fázovou soustavou CaO-Al₂O₃-SiO₂. Strusky byly charakterizovány hodnotami optických bazicit a testovány jako sorbenty fosfátů. Pro každý vzorek byla stanovena teoretická adsorpční kapacita. Byla nalezena velmi těsná lineární závislost teoretické adsorpční kapacity fosforu na optické bazicitě modelových strusek, která umožňuje odhad jejich sorpčních schopností.

Klíčová slova: sorpce fosfátů; metoda sol-gel; vysokopecní struska

Human activity leads to a paradoxical phenomenon. Massive use of phosphates in the production of commercial fertilizers, detergents and cleaners causes depletion of their natural resources. On the other hand, increasing the phosphate content in waste waters causes progressive eutrophication of surface waters. These facts lead to search and development of technologies enabling an efficient recycling of the phosphorus. One option of obtaining phosphorus in the form of phosphates is the use of adsorption processes for treatment of industrial wastewaters. Thus, blast furnace slags (BFS) appear as promising sorbents. This is illustrated by the paper [1], according to which the

achieved phosphate removal efficiency from wastewater was 96.15 %. The process of two-stage selective adsorption of Cu (II) and phosphate from aqueous solutions is described in the paper [2].

Slag is an oxide system primarily composed of Ca(II), Mg(II), Al(III) a Si(IV), i.e. elements commonly found in the soil system. Hence, the adsorption product can be used after appropriate treatment as phosphate fertilizer. For this purpose it is necessary to know the mechanisms and forms, in which the phosphates are bound on the slag surface. Findings vary in these cases. For example, sorption mechanisms are described by various types of

isotherms [1 – 6]. For example, physical adsorption and Ca-P precipitation [7 – 9] were reported as the main mechanism of phosphate removal from aqueous solutions. The dominant retention mechanism is usually caused by various factors, such as composition, structure of a slag, duration of adsorption [10] and pH of a solution [11]. In the paper [8], the dependence between the adsorption capacities of crystalline and amorphous slags and equilibrium pH values, and also linear dependence between the adsorption capacities of slags and the ANC_{3,8} (acid neutralizing capacity) values was found.

Preparation of samples of blast furnace slags plays an important role in the research of adsorption capacities of BFS. Model slags of the desired composition can be prepared in conventional manner by melting a mixture of the appropriate oxides or carbonates at temperatures of 1500 – 1600 °C [12]. Disadvantages of these methods are their considerable energy demands and higher requirements to the equipment. The sol-gel method represents an alternative approach. This method is used especially for the preparation of glasses with various content of oxides. In particular, the following glass ceramics are included CaO-B₂O₃-SiO₂ [13], CaO-P₂O₅-SiO₂ [14], SiO₂-CaO-MgO-P₂O₅ [15] or SiO₂-Al₂O₃-CaO-CaF₂ [16]. The papers that deal only with the systems CaO-Al₂O₃-SiO₂ and CaO-MgO-Al₂O₃-SiO₂ are not common. The sections of the phase diagram of the CaO-SiO₂-Al₂O₃ system in the blast furnace slag region were not prepared by this method.

The aims of this work are to verify the usage of sol-gel method for the preparation of the model blast furnace slags, to study the retention mechanisms of phosphates from water solutions using this model of slags prepared as a cross-section of phase diagram of the CaO-Al₂O₃-SiO₂ system.

1. Experimental

1.1 Samples

The model of the blast furnace slag (SG) and several slag samples (SG-01 to SG-05) in the line CaO:SiO₂ = 1 of the phase diagram of CaO-Al₂O₃-SiO₂ system were prepared by the sol-gel method according to the paper [17]. Composition of all slag samples is shown in Tab. 1.

Tab. 1 Composition of prepared sorbents (mol. %)

Tab. 1 Složení připravených sorbentů (mol. %)

Compound	CaO	Al ₂ O ₃	SiO ₂	MgO
SG	34.32	4.69	43.31	17.68
SG01	50.00	00.00	50.00	0.00
SG02	48.00	04.00	48.00	0.00
SG03	42.00	16.00	42.00	0.00
SG04	39.00	22.00	39.00	0.00
SG05	33.33	33.33	33.33	0.00

Corresponding hydrated nitrates were used as sources of CaO, MgO and Al₂O₃, tetraethyl orthosilicate (TEOS) served as a source of SiO₂. All used chemicals were of p.a. purity. The metal salts were dissolved in demineralized water, TEOS in absolute alcohol. TEOS solution was added under stirring to an aqueous solution of salt respecting the ratio of TEOS: ethanol: water 1: 2.5: 5. The resulting solution was stirred for 2 hours at 250 rev / min at room temperature and subsequently evaporated in the oven at 80 °C for 24 hours. The resulting gel was calcined for four hours at temperature of 700 °C. Grain sizes of prepared samples were adjusted by grinding and sieving under 0.1 mm.

1.2 Measurement of the adsorption kinetics

Series of suspensions containing 0.5 g of sorbent and 100 cm³ of phosphate at the concentration of 500 mg (PO₄)/l was prepared in order to determine the adsorption kinetics of phosphates. Suspensions were vigorously shaken, subsequently left unused for an appropriate time (1, 3, 8, 24, 72 and 120 hours) and then filtered. The residual phosphorus contained in the filtrate was determined by spectrophotometry. The obtained data were analyzed using a kinetic model of the pseudo-second order reaction. The mathematical form of the pseudo-second order kinetic equation is

$$\frac{dQ_t}{dt} = k(Q_e - Q_t)^2 \quad (1)$$

where Q_e and Q_t (mmol·g⁻¹) are equilibrium and actual (at time t) amounts of adsorbed phosphorus, respectively.

1.3 Static batch experiments

A series of suspensions containing 0.5 g of sorbent and 100 cm³ of phosphate solution ($c = 100, 300, 500, 750$ and 1000 mg (PO₄)/l) was prepared for the evaluation of the theoretical adsorption capacity of slag samples and construction of their adsorption isotherms. The suspensions were left unused for 5 days and they were vigorously shaken once every 24 hours. The suspensions were then filtered and the residual phosphorus contained in the filtrate was determined by means of spectrophotometry. The acquired data were analyzed using the Freundlich and Langmuir adsorption isotherm model. The theoretical adsorption capacities were calculated for all slag samples.

The Freundlich isotherm equation in the linearized form is

$$\ln Q_e = \ln K_F + (1/n)\ln c_e \quad (2)$$

where K_F is the Freundlich constant and n is the exponent.

The Langmuir isotherm was used in this mathematical form

$$c_e/Q_e = 1/K_L + c_e/Q_m \quad (3)$$

where Q_e ($\text{mg}\cdot\text{g}^{-1}$) is the equilibrium adsorption capacity of phosphorus, c_e is the equilibrium concentration of the adsorbed matter, K_L is the Langmuir constant and Q_m is the Langmuir adsorption maximum.

1.4 Measuring techniques and apparatus

X-ray diffraction analysis of the rehydrated samples was performed by a fully automated diffractometer URD-6 (Rich. Seifert-FPM, Germany) operating at: radiation $\text{CoK}\alpha$, 40 kV, 35 mA. The obtained data were digitalized using the RayfleX Software (RayfleX ScanX a RayfleX Analyze, version 2.289). The specific surface area of the SG sample was measured by S^{BET} method using the instrument Sorptomatic 1990 ThermoFinnigan, Italy. Phosphorus was determined spectro-photometrically as phosphomolybdenum blue on a UV spectrophotometer (UV-1800 Shimadzu, Japan). The pH measurements of the solutions were carried out by a pH meter InoLab pH Level 1, (WTW Weilheim, Germany). The mid-FTIR spectra were recorded using the ATR technique on an FTIR spectrometer (Nicolet NEXUS 470, ThermoScientific USA) in the mid-IR region ($4000 - 400 \text{ cm}^{-1}$) at room temperature with the resolution of 4 cm^{-1} and at 64 scans.

2. Results and discussion

The model of amorphous blast furnace slag (SG) was prepared by the sol-gel method. The amorphous structure of the sample was confirmed by X-ray diffraction (Fig. 1).

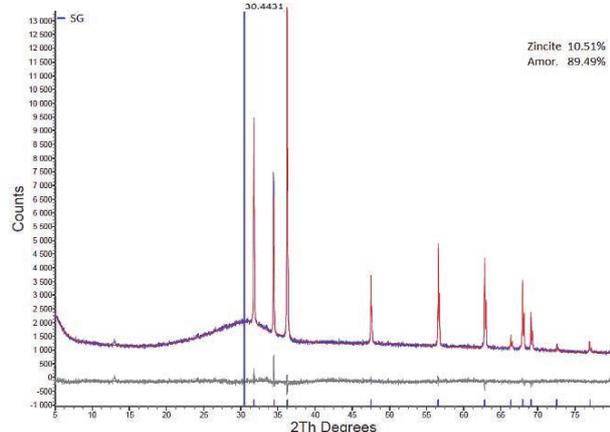


Fig. 1 X-ray diffraction record of the SG sample
Obr. 1 Záznam RTG difrakce vzorku SG

The active surface area was determined using S^{BET} method and the result was compared with the real BFS of the same composition. The active surface area was at the SG sample $40.42 \text{ m}^2\cdot\text{g}^{-1}$, at the BFS only $1.57 \text{ m}^2\cdot\text{g}^{-1}$. Differences in the surface area were caused by the method of preparation.

The SG sample was then tested as a sorbent of phosphates from water solutions. The achieved results were again compared with the results for BFS (Tab. 2).

Tab. 2 Comparison of the results of adsorption experiments with SG and BFS slags

Tab. 2 Srovnání výsledků adsorpčních testů strusek SG a BFS

Sample	Pseudo-second order kinetic			Langmuir isotherm		
	R^2	k ($\text{g}\cdot\text{mmol}^{-1}\cdot\text{h}^{-1}$)	Q_E ($\text{mmol}\cdot\text{g}^{-1}$)	R^2	Q_m ($\text{mg P}\cdot\text{g}^{-1}$)	K_L ($\text{dm}^3\cdot\text{g}^{-1}$)
SG	0.999	2.482	0.908	0.991	44.05	13.85
BFS	0.999	6.593	0.249	0.995	14.90	0.97

It has been found that the phosphate adsorption on SG and BFS is controlled by pseudo-second order kinetics and that it could be characterized by the Langmuir isotherm. It can be assumed that the retention of phosphates on SG is realized by the same mechanisms as in the case of BFS. The adsorption capacity of the model sample SG was $44.05 \text{ mg P}\cdot\text{g}^{-1}$. The higher adsorption capacity of the SG compared to BFS is associated with the larger free surface of the sample SG.

Comparison of the FTIR spectra of the original sample SG and the same sample after adsorption of phosphates (SG-P) was made in order to determine the forms of adsorbed phosphate. Fig. 2 shows the achieved results. A broad adsorption band at the frequency of 989 cm^{-1} was identified in SG sample, which was related to vibrations of Si-O bonds in the SiO_4 tetrahedron and bond vibrations of Si-O-Al in aluminosilicates [18, 19]. A small distinct band at the frequency of 510 cm^{-1} can be attributed to O-Si-O bonds in aluminosilicates [19]. A dominant band at the frequency of 1043 cm^{-1} is apparent from the FTIR record of SG-P, which overlaps the original broad band of silicates and aluminosilicates. This peak can be assigned to calcium phosphates precipitated in the form of hydroxyapatite (HAP) [20]. A small band at the frequency of 557 cm^{-1} also corresponds to the O-P-O bond vibrations in phosphates, which appear in the low frequency region [21]. Bands at the frequencies of 1658 and 1426 cm^{-1} in both records conform to molecular H_2O or CO_3 group in carbonates [22]. Water and CO_2 in the form of carbonates were incorporated into SG slag during preparation.

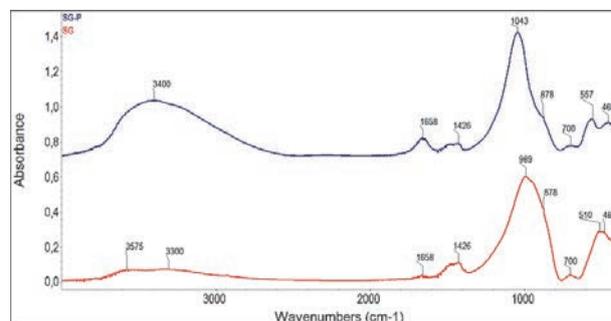


Fig. 2 FTIR spectra of SG and SG-P after phosphate adsorption
Obr. 2 FTIR spektra SG a SG-P po adsorpci fosfátů

A series of samples (SG01 to SG05) corresponding to the line $\text{CaO}:\text{SiO}_2 = 1$ of the phase diagram of the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system was prepared in order to assess

the influence of acid-base properties of model slags on the phosphate retention from aqueous solutions (Fig. 3).

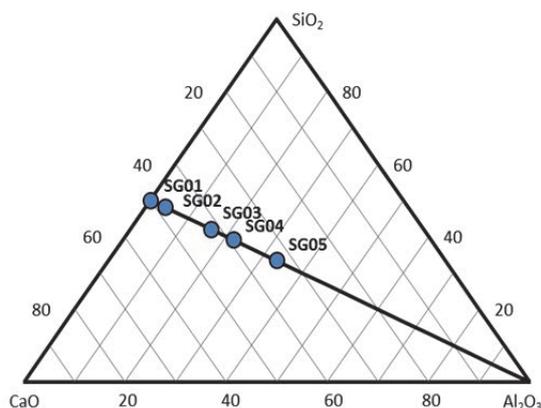


Fig. 3 The phase diagram of the CaO-SiO₂-Al₂O₃ system with marked slag samples

Obr. 3 Fázový diagram soustavy CaO-Al₂O₃-SiO₂ s vyznačenými vzorky strusek

Quantitative scale of the Lewis basicity, i.e. optical basicity Λ , is used for characterization of the acid-base properties in oxide melts. For any oxide system it can be calculated as follows

$$\Lambda = \frac{\sum x_i n_i \Lambda_i}{\sum x_i n_i} \quad (4)$$

where x_i is the mole percentage, n_i is the number of oxygen atoms in the molecule and Λ_i is the optical basicity of appropriate oxide [23]. The optical basicity was used for characterization of prepared sol-gel slag samples. The theoretical adsorption capacity for each sample of the particular section was determined by means of the Langmuir adsorption isotherm. An excellent linear dependence ($R^2 = 0.9794$) was found between the adsorption capacities and optical basicities of slags (Fig. 4). Figure shows that the linear relationship can be applied not only to cross-section points but also for model slag SG. The observed linearity between optical basicities and adsorption capacities enables making of an estimation of the retention capacity of slags having comparable active surface area size.

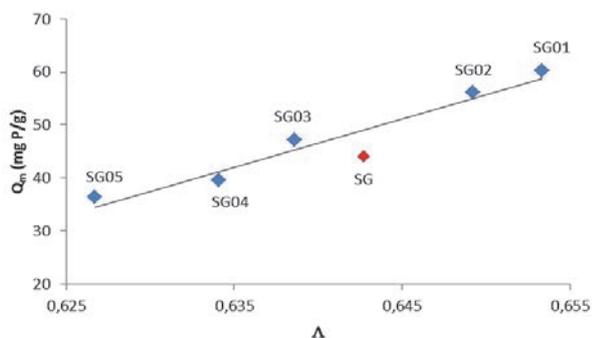


Fig. 4 Dependence of the adsorption capacity of the slag samples on their optical basicity

Obr. 4 Závislost adsorpčních kapacit vzorků strusek na jejich optické bazicitě

Conclusions

The sol-gel method was chosen for the preparation of model samples of amorphous blast furnace slags (SG). The slags prepared by this method were tested as sorbents of phosphates from aqueous solutions. It was found that the sorption kinetics and very sorption of phosphates can be characterized and evaluated by the same model apparatus as in the case of real slags. The phosphates retention on model slags is therefore carried out by the same mechanisms. The sol-gel method showed good results in preparation of model slags of the desired composition. The higher adsorption capacity of model slags is given by their greater active surface area, which is associated with a different preparation method of slag at a significantly lower temperature. Surface precipitation of Ca-phosphates, especially hydroxyapatite appears to be the main retention mechanism. The influence of acid-base properties of blast furnace slags on the phosphate retention was carried out on the model samples prepared according to the line CaO:SiO₂ = 1 of the phase diagram of CaO-Al₂O₃-SiO₂ system. A linear relationship between the adsorption capacities of slags and their optical basicities was found enabling an estimation of the retention abilities of the slags.

Acknowledgement

The work was realized thanks to financial support of specific researches SP 2016/77 and SP 2016/103.

References

- [1] RAGHEB, S. M. Phosphate removal from aqueous solution using slag and fly ash. *HBRC Journal*, 9 (2013), 270–275.
- [2] KOHUTOVÁ, H., KOSTURA, B., KUKUTSCHOVÁ, J., MATÝSEK, D. Oxyhumolite influence on adsorption and desorption of phosphate on blast furnace slag in the process of two-stage selective adsorption of Cu(II) and phosphate. *Chemical Papers*, 68 (2014) 6, 766–773.
- [3] AGYEI, N.M., STRYDOM C.A., POTGIETER J.H. The removal of phosphate ions from aqueous solution by fly ash, slag, ordinary Portland cement and related blends. *Cement and Concrete Research*, 32 (2002), 1889–1897.
- [4] SAKADEVEN K., BAVOR, J. Phosphate adsorption characteristics of soils, slag and zeolite to be used as substrates in constructed wetland systems. *Water research*, 32 (1998), 393–399.
- [5] OGUZ, E. Thermodynamic and kinetic investigations of PO₄³⁻ adsorption on blast furnace slag. *J. Colloid Interface Sci.*, 281 (2005), 62–67.
- [6] LEE, S. H., VIGNESWARAN, S., BAJRACHARYA, K. Phosphorus transport in saturated slag columns. *Water Science and Technology*, 34 (1996), 153.
- [7] JOHANSSON, L., GUSTAFSSON, J.P. Phosphate removal using blast furnace slags and opoka – mechanisms, *Water research*, 34 (2000), 259–265.
- [8] KOSTURA, B., KULVEITOVÁ, H., LEŠKO, J. Blast furnace slags as sorbents of phosphate from water solutions. *Water Research*, 39 (2005), 1795–1802.
- [9] Sheng-gao LU, BAI Shi-qiang, SHAN Hong-dan. Mechanisms of phosphate removal from aqueous solution by blast furnace slag and steel furnace slag. *Journal of Zhejiang University Science A*, 9 (2008) 1, 125–132.

- [10] YANG Jian, WANG Su, LU Zhibo, LOU Shanjie. Converter slag-coal cinder columns for the removal of phosphorous and other pollutants. *Journal of Hazardous Materials*, 168 (2009), 331–337.
- [11] LEE, S. H., VIGNESWARAN, S., CHUNG, Y. A. Detailed Investigation of Phosphorus Removal in Soil and Slag Media. *Environmental Technology*, 18 (1997) 7, 699–709.
- [12] HWA-JUN, L., SANG-WOO, K., SUNG-SOO, R. Sintering behavior of aluminum nitride ceramics with MgO-CaO-Al₂O₃-SiO₂ glass additive. *Int. Journal of Refractory Metals and Hard Materials*, 53 (2015), 46–50.
- [13] WANG, M., ZUO, R., JIN, J., SU, S., ZHAI, J. Investigation of the structure evolution proces in sol-gel derived CaO-B₂O₃-SiO₂ glass ceramics. *Journal of Non-Crystalline Solids*, 357 (2011), 1160–1163.
- [14] CATAURO, M., BOLLINO, F., RENELLA, R.A., PAPALE, F. Sol-gel Synthesis of SiO₂-CaO-P₂O₅ Glasses: Influence of the heat treatment on their bioactivity and biocompatibility. *Ceramics International*, 41 (2015), 12578–12588.
- [15] MA, J., CHEN, C.Z., WANG, D.G., JIAO, Y., SHI, J.Z. Effect of magnesia on the degradability and bioactivity of sol-gel derived SiO₂-CaO-MgO-P₂O₅ system glasses. *Colloids and Surfaces B: Biointerfaces*, 81 (2010), 87–95.
- [16] ZOLOTAR, M.S., ZAVAGLIA, C.A.C. Study of the sol-gel processing of glass-ceramic powders in the SiO₂-Al₂O₃-CaO-CaF₂ system. I. Effect of powder composition on gel time and temperature. *Journal of Non-Crystalline Solids*, 247 (1999), 50–57.
- [17] FU, Y.P., LIN, Ch.H. Synthesis and microwave characterization of 2(MgO, CaO)-2Al₂O₃-5SiO₂ glass ceramic from the sol – gel process. *Journal of Materials Science*, 38 (2003), 3081–3084.
- [18] MARTÍNEZ-ZAPATA, O., MÉNDEZ-VIVAR, J., BOSH, P., LARA, V.H. Synthesis and characterization of amorphous aluminosilicates prepared by sol-gel to encapsulate organic dyes. *J. Non-Cryst. Solids*, 357 (2011), 3480–3485.
- [19] I. SÁEZ del BOSQUE, F., MARTÍNEZ-RAMÍREZ, S., BLANCO-VARELA, M.T. *Construction and Building Materials*, 52 (2014), 314–323.
- [20] MAITZ, M.F., PHAM, M.T., MATZ, W., REUTHER, H., STEINER, G. Promoted calcium-phosphate precipitation from solution on titanium for improved biocompatibility by ion implantation. *Surface and Coating. Technology*, 158–159 (2002), 151–156.
- [21] SZUMERA, M. Structural investigations of silicate-phosphate glasses containing MoO₃ by FTIR, Raman and ³¹P MAS NMR spectroscopies. *Spectrochimica. Acta Part A*, 130 (2014), 1–6.
- [22] MOSTAFA, N.Y., KISHAR, E.A., ABO-EL-ENEIN, A.A. FTIR study and cation exchange capacity of Fe³⁺ and Mg²⁺ substituted calcium silicate hydrates. *J. Alloys Compound*, 473 (2009), 538–542.
- [23] ZHANG G., CHOU K. Model for Evaluating Density of Molten Slag With Optical Basicity, *Journal of Iron and Steel Research, International*, 17 (2010) 4, 1–4.

Podnikům bude i nadále odlehčováno od daní za proud

Stahl Aktuell

12.01.2017

Podniky výrobních odvětví znovu zlepšily svou energetickou efektivitu a obdrží proto i v roce 2017 slevu na dani za proud a energie. Sdělila to spolková vláda na základě monitorovací zprávy Rýnsko-Vestfálského institutu pro výzkum hospodářství (RWI). Podle této zprávy podniky plně dosáhly cílové hodnoty snižování energetické intenzity a obdrží proto tzv. špičkové vyrovnání v plné výši. Tímto tzv. špičkovým vyrovnáním je podnikům odlehčeno od části daně za proud a energii. Od roku 2013 toto vyrovnání podniky obdrží ale jen tehdy, když přinesou svůj podíl na energetických úsporách. Cílová hodnota redukce energetické intenzity byla podle údajů o 3,9 % nižší než průměr let 2007 až 2012.

Levnější než z hliníku: iPhone 8 má být z ušlechtilé oceli

Stahl Aktuell

12.01.2017

Apple se podle údajů z médií rozhodl, že pouzdro iPhone 8 nechá vyrábět z ušlechtilé oceli. Jak dále informuje internetová služba Digitimes, mají být za tímto rozhodnutím cenové důvody. Kování ušlechtilé oceli je o 30 až 50 % levnější než dosavadní způsoby, při kterých je pouzdro frézováno z hliníkového bloku. Kromě toho má být zaručena lepší kontrola kvality, když bude použita nerezová ocel. Digitimes se odvolává na informace z dodavatelského řetězce Applu. iPhone 8 má přijít na trh v tomto roce.

Evraz investuje do nových vysokých pecí

Stahl Aktuell

19.01.2017

Ruský výrobce oceli Evraz Nižnyj Tagil zadal staviteli zařízení Primetals technologies zakázku na dodávku automatizace, elektrotechniky a instrumentalizace nové vysoké pece č. 7. Zásadní automatizace a optimalizace procesů by měly být provedeny jako virtualizovaný automatizační systém na centrálních serverech, čímž by měly být silně redukovány servisní náklady. Objem zakázky reprezentuje několik mil. € Novou procesní automatizací má být také optimalizována spotřeba koksu. Zprovoznění nové vysoké pece je plánováno na konec roku 2017. Pec bude mít výrobní kapacitu 2,5 mil. tun surového železa ročně.