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COMBINING NANOFILTRATION AND OTHER SEPARATION METHODS (REVIEW)

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ABSTRACT

The potential implementation of membrane separation to bioactive compounds like soluble phenolics from aqueous and organic solvent solutions is gaining increasing interest in the recent years. The scope of this investigation is the concentration and fractionation of polyphenols from plant extracts by nanofiltration and its combination with other separation techniques (adsorption, precipitation, crystallization) in order to increase the selectivity of the process. The aim of the study is to review the observed tendencies in membrane processes applications for separation of polyphenols derived from natural products, as well as to present own results of such combination schemes on the example of extracts from several natural sources (Sideritis, grape seeds, propolis etc.). Organic solvent nanofiltration (OSN) is in the focus, applied for concentrating and fractionating polyphenolics from plant extracts. Own results using nanomembranes with different molecular weight cut-off Starmem (200 and 400 Da) and Duramem (200 to 900 Da) are included.

Keywords: organic solvent nanofiltration, polyphenols, antioxidants.

INTRODUCTION

In recent years organic solvent nanofiltration (OSN) is successfully applied for concentration of polyphenols from different plant extracts [1-10] and recovery of the residual solvent. Compared to the traditional methods used for concentrating biologically active compounds, the membrane filtration has the advantages of operating at ordinary temperatures, absence of phase transition and low energy consumption. Laboratory scale OSN is performed in one of the two modes: dead-end filtration, where the entire solution is directed normal to the membrane area under applied pressure, or cross-flow (tangential) filtration, where the direction of the flow is parallel to the surface of the membrane. The latter provides flux and rejection data more consistent with the industrial scale. Larger scale membrane filtration is performed in tangential mode. For a number of industrially important applications integrated membrane processes are proposed in the recent years. Despite this increasing popularity of membrane technologies, the main problem for their large scale application remains the membrane fouling, which remains in the focus of a number of publications. Another problem is the low selectivity, especially pronounced in complex systems such as natural extracts with large number of compounds, including the groups of polyphenols and flavonoids with biological activity, which are gaining increasing interest in the recent years. To solve this problem multistage processing is considered, coupling membrane filtration with other separation methods.

OSN for concentrating and fractionating polyphenolics from plant extracts

UF [11-15] and UF-NF [2, 10] processes, coupled with solid-liquid extraction, are tested for a variety of materials with application in the pharmaceutical industry (Table 1) [25]. Possibilities for extraction intensification for liberating polyphenols from the solid material are also discussed [7, 9, 16, 17]. Regarding the solvent recovery (in permeates), as well as the preservation of high biological activity in the obtained retentates, the results are fully encouraging [4-8]. The concentration polarization effect and pronounced flux decline remains the major difficulty for larger-scale operations [6, 11,
the methodology for its control being in the focus of a great number of publications concerning polyphenols [19-21]. Change of running modes may be very practical for the membrane fouling control in the pilot-scale or large-scale applications [11, 18]. In the case of nanofiltration of ethanolic extracts of Sideritis the transfer from dead-end to cross-flow mode of filtration [6], as well as intermediate washing and transmembrane pressure increase (Fig. 1) encouraged the larger-scale application of the process of concentration by nanofiltration.

Most of the reported investigations are laboratory scale UF, NF or RO [9], but few examples on industrial scale are also available, especially for concentrating aqueous extracts [11,18, 22]. Forward osmosis (FO) [23] and osmotic distillation (OD) [24] have also been considered for large-scale concentrations (roselle extracts, anthocyanins from kokum extracts, etc.).

Nanofiltration can also be successful in applications involving fractionation and purification. The latter is rather hindered by the similar molecular masses (MM)

Table 1. Concentration of plant extracts by multistage membrane separation.

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Solvent, Process</th>
<th>Membr. Process</th>
<th>Material (Manufacturer)</th>
<th>Operatio n mode</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Almond skins [12]</td>
<td>acetone/ H2O, 50:50;</td>
<td>UF (as preparation technique)</td>
<td>Semipermeable, not specified, (Millipore, Bedford, USA)</td>
<td>centrifugal UF membranes, diafiltration</td>
<td>11 low MW phenolics: benzoic acids, flavan-3-ols mono-, oligomers, flavanol and flavanone glycosides; High MW proanthocyanins: di-, decamers</td>
</tr>
<tr>
<td>Ginko biloba [1]</td>
<td>50% EtOH</td>
<td>NF</td>
<td>Not specified</td>
<td>flat-sheet cross flow</td>
<td>Flavone glycosides, derivatives of quercetin, kaempferol andisorhamnetin.</td>
</tr>
<tr>
<td>Persimmon [13]</td>
<td>MeOH</td>
<td>UF</td>
<td>Polysulfone (Tianjin, China)</td>
<td>hollow fiber</td>
<td>polyphenols, including condensed tannin</td>
</tr>
<tr>
<td>Sideritis</td>
<td>EtOH</td>
<td>NF</td>
<td>Crosslinked polyimide Duramem (Evonik, UK)</td>
<td>Dead-end [5] flat sheet,</td>
<td>Chlorogenic acid, lavandulifolioside, verbascone,</td>
</tr>
</tbody>
</table>
of various compounds in the feed. In particular, nanofiltration (NF) has been intensively investigated [1-11, 18, 27-29] for fractionation of complex solutions by selecting a sequence of membranes with suitable molecular weight cut-off (MWCO) in the range of 150–1000 Da. Natural antioxidants from winemaking by-products [30] were successfully treated by UF, NF and RO. Separation and concentration of polyphenols in the bergamot juice [31] was achieved by a multistep filtration, including two UF(MWCO 100 and 1 kDa) and two NF modules (MWCO 750 and 450 Da). Extract from propolis was fractionated by a sequence of nanomembranes Duramem with MWCO 900, 500 and 300 [4]. Rejections and obtained fluxes are given on Fig. 2.

Polyphenols from grape seeds extract were fractionated by nanofiltration. The comparison between measured rejections and fluxes during individual and sequential filtration (Duramem MWCO 900 and 500) are given on Figs. 3 and 4. As can be seen, increased flux and lower rejection is obtained when the Duramem 500 membrane is used for sequential filtration of the permeate from Duramem 900 in comparison to the data for the individual nanofiltration of the raw extract. In all examples the fractions were characterized by their different antioxidant activity [4,31].

Diafiltration is a perspective approach for successful fractionation and following concentration of multicomponent solutions such as plant extracts. For instance the dual membrane diafiltration [32] is a promising method for membrane separation and concentration. It comprises a separation step, where lower MM compound is separated from higher MM compound, followed by a solvent recovery step, where the lower MM compound is retained by the membrane, allowing the solvent to be recycled into the first stage. Diafiltration was used to separate caffeic from rosemarinic acid, extracted from rosemary [8]. Membrane concentration of antioxidants from Castanea sativa leaves aqueous extracts by di-
A filtration with two UF membranes was reported [27], where the ultrafiltration–diafiltration process with PES membranes increased the antioxidant properties of the concentrated streams.

Due to the low selectivity for isolating and purifying phenolics, multistage processing has to be considered. A number of processes like alcohol precipitation, isoelectric solubilization and ultrafiltration are used to remove macromolecules (i.e. proteins, pectin, etc.). Solvent and supercritical fluid extraction methodologies can separate smaller molecules (i.e. phenols or sugars) from the resultant substrates. Resin adsorption, chromatography and nanofiltration have a great potential for isolating and purifying target compounds [33].

**Coupling with other separation techniques**

1. **Coupling adsorption with nanofiltration**

Combining adsorption with membrane separation techniques (ultra-, nanofiltration and reverse osmosis) is successfully used in multistage processes for isolation of polyphenols from extracts of plant materials, and purification of waste liquids from the food industry (Table 2). Active carbons and macroporous resins (strong or weak cation or anion exchangers as XAD – 7, XAD – 16, EXA – 90 и EXA – 118, [34-40] ) are between the most used adsorbents [41]. Adsorption can essentially alter the ratio of flavonoids to total phenols. Examples are given in [42] where functional groups (ester, amino or amide group), introduced into the adsorbent matrix, produce the hydrogen-bonding interaction and enhance the adsorption selectivity towards flavone compounds, and were used for purification of total flavonoids from Ginkgo biloba L., Radix puerariae and Hypericum perforatum L.

In this study, adsorption and nanofiltration were performed with aqueous and ethanolic extracts from

<table>
<thead>
<tr>
<th>Plant extract</th>
<th>Solvent</th>
<th>Process</th>
<th>Adsorbent</th>
<th>Membrane</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Persimmon</td>
<td>C\textsubscript{3}H\textsubscript{12}OH</td>
<td>UF</td>
<td>Macroporous resin AB - 8</td>
<td>Polysulphon.UF (MWCO=10 kDa)</td>
<td>[31]</td>
</tr>
<tr>
<td>Green tea leaves</td>
<td>H\textsubscript{2}O - sol. of Fe\textsubscript{2}SO\textsubscript{4}</td>
<td>UF+AD</td>
<td>Resins: XDA, D113H, PA, D301, D001H, NKA-11, AB-8, D151H, 001X6</td>
<td>Ca-Ti (celluloseacetate-Ti)</td>
<td>[30]</td>
</tr>
<tr>
<td>Grape pomace</td>
<td>C\textsubscript{2}H\textsubscript{5}OH</td>
<td>NF+AD</td>
<td>Sepabeads SP700 resin</td>
<td>Nanomax 95-MWCO=250kDa; Nanomax 50-MWCO=350 kDa; Inside Ceram-MWCO=1000 kDa</td>
<td>[28]</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>H\textsubscript{2}O–EtOH – HCl sol.</td>
<td>UF-AD.</td>
<td>Styrene ion-exchange resin 717</td>
<td>Hollow-fiver UF (MWCO=5 kDa)</td>
<td>[29]</td>
</tr>
<tr>
<td>Pigmented orange pulp wash</td>
<td>H\textsubscript{2}O–EtOH</td>
<td>Two-step</td>
<td>neutral resin Relite EXA-118; anion exchange resin (Nekroolith RAM 1)</td>
<td>UF: fluoropolymer spiral ETNA10PP-2517/48DRY (MWCO 10 kDa) RO: spiral thin film FF-ROHR98PP</td>
<td>[24]</td>
</tr>
</tbody>
</table>
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Sideritis. Fig. 5 shows the change in the flavonoids/polyphenols ratio after adsorption on activated carbon from apricot stones and ion-exchange resin Amberjet. The subsequent fractionation or concentration is obtained with OSN membranes Duramem (Evonik-MET, UK) with molecular mass cut-off (MWCO) in the range of 200-500 Da (for concentration) and 500-900 Da (for fractionation). Fig. 6 presents the dependence of the measured rejections of the polyphenolic content on the MWCO of the membrane.

Processes involving adsorption for recovery and concentration of bioactive phenolics from industrial waste streams were reported in literature [41]. Adsorption in combination with membrane separation is applied either as preceding or succeeding the membrane module stage. In the first case adsorption is used for modification of the extract, while in the second it is aimed mainly for purification of the permeate solution. The review of published results is encouraging for further research in combining the adsorption with nanofiltration for fractionating the polyphenolic content of plant extracts.

2. Combining precipitation with nanofiltration

Nanofiltration of natural extracts often results in retentates concentrated near to saturation [7]. The concentration of molecules at the membrane surface increases and reaches its solubility limit. This results in precipitation of the feed solution components and formation of a deposit layer on the membrane surface. The phenolic compounds are considered as the major foulants in the UF and NF process. A relationship is observed between the type of fouling and polyphenols rejection. Some authors report maximum polyphenols rejection when the intermediate pore blocking is the governing fouling mechanism [15]. Coupling of UF or NF with low temperature precipitation in a pretreatment step can help fractionation of the polyphenolic content and solve problems with fouling to a great extend. After cooling, the separation of low-soluble substances gradually increases until no further precipitation takes place [43]. Other examples can be found in membrane concentration of antioxidants from Castanea sativa leaves [27], where the selectivity of phenolics was increased by ethanol precipitation of the soluble protein.

Fig. 6. Total phenols rejection vs MWCO for ethanolic extracts of Sideritis.

Sideritis. Fig. 5 shows the change in the flavonoids/polyphenols ratio after adsorption on activated carbon from apricot stones and ion-exchange resin Amberjet. The subsequent fractionation or concentration is obtained with OSN membranes Duramem (Evonik-MET, UK) with molecular mass cut-off (MWCO) in the range of 200-500 Da (for concentration) and 500-900 Da (for fractionation). Fig. 6 presents the dependence of the measured rejections of the polyphenolic content on the MWCO of the membrane.

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Fig. 7. Example with grape seeds: Pre-fractionation of HMM polyphenols by precipitation.
The result was an increase by about 15% purity and activity of the final product. The idea of coupling low temperature precipitation and nanofiltration for prefractionation of HMM polyphenols from grape seeds extracts is illustrated on Fig. 7.

3. Combining crystallization with nanofiltration

Membrane crystallization is a new challenging separation technique, allowing the control of supersaturation through evaporation of the volatile solvent across the membrane and the nucleation and growth of crystals. Results with hybrid NF-MC systems are reported in inorganic applications in the production of sodium chloride and epsomite [44], treatment of sulphate wastes [45], as well as for crystallization of organic materials [46] like bio-macromolecules. Microporous hydrophobic membranes, as heterogeneous nucleant surface for protein molecules, induce the form of crystal nucleation. Compared with the traditional crystallization methods, membrane crystallization is more rapid and can control the crystallization process better [47]. Recently, MC has been also used for the production of pharmaceutical cocrystals from water/ethanol solvent mixtures by choosing the opportune initial solution composition [46, 48]. This possibility extends the potential of MC technology to the isolation of biologically-active compounds like flavonoids in crystal form from natural extracts.

CONCLUSIONS

OSN is successfully applied for concentration of extracts and purification of residual solvent. The number of larger scale implementations is increasing, proving the efficiency of the proposed methods for fouling control. Multistage membrane processing is largely applied.

Nanofiltration can also be successful in applications, involving fractionation rather than purification. The latter is obtained either by diafiltration or by sequential filtration with membranes with different MWCO. Modification of the extracts can be also achieved by combining with adsorption as a preceding the membrane separation step.

Adsorption following the membrane separation is used for purification of the permeate solution.

Coupling of UF or NF with low temperature precipitation in a pretreatment step can help fractionation of the polyphenolic content and solve problems with fouling to a great extend.

Other challenging separation technique is reported like membrane crystallization. It is recently used for the production of pharmaceutical cocrystals from water/ethanol solvent mixtures.

The combination of membrane filtration with other separation techniques with higher selectivity extends the potential of membrane technology for isolation of biologically-active compounds like polyphenols and flavonoids from natural extracts.

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STUDY OF THE CHROMATOGRAPHIC BEHAVIOUR OF PROTODIOSCINE ON A C8 CORE-SHELL 2.6 µm SHORT (5 cm) COLUMN AND ITS DETERMINATION WITH UV/ELSD DETECTION

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ABSTRACT

The separation capabilities of a core-shell C₈ short (3x50mm) 2.6µm column's have been tested on protodioscin and a new method for its determination in plant extracts with UV detection is proposed. The higher efficiency of the core-shell column allows reduction of the separation time down to 10 - 15 min in isocratic mode (including column conditioning time), when SPE pre-cleaning of samples from stronger retained plant extract matrix components is applied. The sensitivity achieved was enhanced as well: LOD for protodioscin with UV detection reached to 2 ng injected amount, and 2 µg injected amount with ELSD detection. The application of gradient elution is more complicated because it requires very high purity solvents as mobile phase constituents. The column tested needs more than 20 min for conditioning and this hampers the significant reduction of the separation time in gradient elution.

The application of the column for analysis of plant extracts/preparations is effective when isocratic elution of protodioscin with 24 – 26 % acetonitrile/water mobile phase, modified with 1.3 - 1.6 % propanol for peak symmetry improvement, is exploited in combination with polymer-based RP SPE clean-up.

Keywords: protodioscin, Kinetex C8 2.6 µm column, HPLC/UV/ELSD.

INTRODUCTION

Protodioscin (PD), 3β,22α,25R)-26-(β-D-glucopyranosyloxy)-22-hydroxyfurost-5-en-3-ylO-6-deoxy-α-L-mannopyranosyl-(1→2)-O-[6-deoxy-α-L-mannopyranosyl-(1→4)]-β-D-glucopyranoside, CAS No 55056-80-9 belongs to the chemical class of furostanol saponins, with chemical structure shown on Fig. 1.

It is an active principal in some medicinal herbs: Dioscorea (dioscoreaceae) [1-3], Asparagus (asparagaceae) [4,5], Tribulus (zygophillaceae) [6-9]. Most of them have been used in traditional medicine and are used nowadays in modern phytopharmacy. PD, as their ingredient, is of particular interest not only for its therapeutic properties, but also because of its specific for Bulgaria higher content in the widespread plant Tribulus terrestris L. [6-10].

The curative properties of formulations prepared from the listed medicinal herbs in treatment and prophylaxis of cardiovascular diseases [3, 8, 10, 18] and reproductive system disturbances [8,16,18] are attributed to the steroidal saponins content [3, 8-11] and mostly to PD [21, 22]. Because of its leading contribution to the biological action of the extracts obtained from Tribulus terrestris, with its particular PD concentration, or furostanol saponins concentration in general represented as PD, is used for standardization of extracts and the raw materials used in their production [23]. That is why the interest in convenient, fast and sensitive methods for PD determination in plants and their extracts is growing. Such methods are also needed in the control of the technological processes for PD extraction and final preparations testing, as well as in biological media for pharmacokinetic studies [24, 25].

Spectrophotometric methods, used for group determination of saponins in plant extracts [26], are nonspecific and for this reason are being gradually abandoned [27].
A thermo luminescence method is described as a non-invasive technique for rapid plant diagnostics of the physiological status (energetics of photosystem II reaction) of Tribulus terrestris [27] that correlates with the optimal content of steroidal saponins in the plant.

The poor quantitative information which this method proposes, however, makes it practically unsuitable for process control and precise raw materials evaluation.

The selective determination of PD in plant extracts and preparations mostly demands methods with a chromatographic separation step [1, 3 - 11, 16, 23 - 27, 30].

Gas chromatography is inappropriate for PD analysis because of its large molecule (Fig. 1).

There are thin layer chromatographic methods [8, 29], that use [29] RP_{18} HPTLC plates as stationary phase, 0.1M KH_{2}PO_{4}/acetonitrile/methanol/triethylamine 5:4:1.0.1 as a mobile phase, treatment with 0.1M H_{2}SO_{4} for developing the plates, and densitometry at 366 nm. Such methods do not need expensive equipment and show high sensitivity (LOQ 0.03 µg). In some cases these methods permit group differentiation of furostanol and spirostanol saponins [8], but they have limited selectivity and accuracy and can not distinguish individual representatives of these classes and quantitatively analyze them.

The application of instrumental column liquid chromatographic methods is also accompanied by problems in separation, as well as in detection. The big, flexible, with very different in polarity sectors and conformational forms, molecule of PD (Fig 1) compromises the optimization of the chromatographic system parameters. The shifted towards the far ultraviolet, nonspecific range of light absorbance maximum of PD (202-203 nm [1]), restricts the use of the most popular UV detector [6, 26].

The relatively low concentration of PD in plant extracts is yet outside the detectable concentration range of refractive index detectors. Therefore most HPLC methods for PD analysis realize separation with gradient elution and UV-transparent mobile phases, most often water/acetonitrile, and evaporative light scattering detection (ELSD) [1,7,8,22,24,27] or mass spectral detection [5, 8 - 11, 23, 26]. In these cases conventional C_{18} analytical columns with gradient of 15-20% ACN to 35-100% CAN are used. Under these conditions, PD determination (along with other steroidal saponins and some flavonoids) takes up from 20 to 50 minutes (excluding column reconditioning time). A detection limit of about 10 - 100 ug/ml for PD is achieved [1, 6] using ELSD. LOD drops to 0.02 - 0.3 ug/ml [5,11,14,26] when a tandem mass spectral detection is employed.

A method for PD determination uses a core-shell (Kinetex) C_{18} column in gradient elution mode and electrochemical (puls amperometric) detection, by which the time for separation of four saponins is shortened to less than 30 minutes with LOQ 0.1-0.3 ng (20-60 ng/ml) [24]. The method is used for PD determination in biological media for pharmacokinetic studies, but still has the disadvantage of long separation time, and electrochemical detectors are usually outside the conventional inventory of a HPLC laboratory.

The use of a core-shall C_{8} chromatographic column for PD analysis is still not described.

As it is well known, the “core-shell” technology permits higher efficiency in comparison to porous silica-based HPLC columns used in the literature, and lower separation time as a result. That is why a reduction of separation time in PD analysis is expected as well.

The aim of our work is to study the behavior of a short core-shell C_{8} 2,6 µm (Kinetex) HPLC column with UV detection on the HPLC analysis of PD.

EXPERIMENTAL

Instruments

A ser. 200 quaternary HPLC pump (PE) with mod. 785A UV-detector, 12 µl flow cell (ABS), mod LC-135, 4 µl flow cell (PE), mod. 500 evaporative light scattering detector, ELSD (Alltech) and mod. 112A oven/injector (ABS), with Kinetex C_{8} 3 x 50 mm, 2.6 µm column (Phenomenex), were used in chromatographic experiments.

Fig. 1. Chemical structure of Protodioscin. Mol. formula: C_{51}H_{84}O_{22}; MM: 1049.2 Da.
Chemicals

Protodioscin (PD) “reference substance” > 98 % purity (ChromaDex), “gradient grade” acetonitrile, ACN (Sigma), “suprapur” n-propanol (Fluka) and MilliRO/MilliQ “HPLC-grade” water, “HPLC-grade” tetrahydrofurane (Fluka) and 0.45µm nylon membrane filters (Merck-Millipore) were used for samples/standards and mobile phase preparation. Tribestan® powdered substance was examined as a preparation from Tribulus terrestris plant.

RESULTS AND DISCUSSION

The retention of PD on the C₈ “core-shell” Kinetex 3 x 50 mm 2.6 µm HPLC column was studied by obtaining the chromatograms of PD solutions at 0.8 ml/min flow rate and a mobile phase consisting of different water/ acetonitrile concentrations.

A chromatogram obtained with 23 % ACN is shown on Fig. 2. Fig. 3 represents the relationship between PD retention time (RT) and the mobile phase composition.

The chromatogram on Fig. 2 shows fronting of PD peak when ACN/water only is used as mobile phase. Different modifiers of the mobile phase were tested and THF, n-propanol and i-propanol at concentrations of 1.3 – 2 % in the ACN/water mobile phase showed improvement of the PD peak symmetry. Propanol at concentration of 1.3 - 1.6 % is preferable on account of its lower UV cut-off. The chromatogram on Fig. 4 obtained at 0.8 ml/min with ACN/water/n-pentanol 24:74.4:1.6, and double detection (detectors connected in series), shows excellent symmetry of the PD peak, and the difference between sensitivity with UV (204 nm) and ELSD detection is excellent as well.

The limit of detection (LOD) for PD with ELSD, as shown on Fig. 4B, with 1.2 µg injected amount. The LOD for PD with UV (204 nm) detection was tested by building of a standard graph with series of chromatograms of standard solutions with decreasing PD concentrations, as shown on Fig. 5.

![Fig. 2. Chromatogram of 10 µg/ml protodioscin on the Kinetex C₈ 3 x 50 mm 2.6 µm at 0.8 ml/min 23 % ACN/H₂O.](image)

![Fig. 3. RT/ACN-concentration dependence for the Kinetex 3 x 50 mm 2.6 µm core-shell column at 0.8 ml/min mobile phase flow at ambient temperature.](image)

![Fig. 4. Chromatogram of 10 µl 125 µg/ml protodioscin solution, obtained with the Kinetex C₈ 3 x 50 mm 2.6 µm HPLC column at 0.8 ml/min ACN/water/n-pentanol 24:74.4:1.6, and double detection (detectors connected in series).](image)

![Fig. 5.](image)
The chromatogram of 5 µl 0.3 µg/ml PD, represented on Fig. 6, shows the LOD of 1.5 ng injected amount, reached with the LC-135 photodiod array (DAD) detector with 4 µl flow cell at 205 nm.

Fig. 7 presents the temperature dependence of PD retention on the C₈ Kinetex column. Contrary to literature data for C₁₈ Kinetex column [23], the RT on Kinetex C₈ decreases with temperature, together with the column back pressure. 35°C can be a convenient column temperature, keeping an acceptable back pressure of 32 MPa at 0.8 ml/min 24% ACN/water, and a lower risk of thermal decomposition for the sensitive sample components.

SPE was applied for sample clean-up from components stronger retained in the analytical column. Strata-X (a polymer based C₁₈ sorbent, Phenomenex Inc.) showed better results with a 94% recovery, after elution with 1 ml 50% ACN/water (Fig. 8). The cartridge was activated with 3 ml ACN and washed with 3 ml water before sample loading. Elution was carried out with 2 ml 18% ACN/water. Chromatograms obtained after washing, first elution with 1 ml 50% ACN/water and second elution to check the recovery, are presented on Fig. 8.

Separation of PD by gradient elution from a Kinetex C₈ column was tested as well. After column conditioning for 30-40 min with mobile phase ACN/water 15:85, a gradient of the ACN-concentration to 50:50 for 5 min was applied after injection of 5 µl 25 µg/ml PD in 25% ACN, and after injection of 5 µl 25% ACN only (Fig. 9). The PD peak symmetry and efficiency were improved with gradient elution without mobile phase modification, but a big peak of impurities from the mobile phase, trapped in the column at lower ACN concentration, was observed. Its area increases with the column conditioning time. The Kinetex column tested needs more than 30 min for conditioning after gradient and this leads to longer analysis time than for the isocratic analysis of PD after SPE clean-up.

CONCLUSIONS

The results obtained show a Kinetex (C₈ 3x50 mm 2.6 µm) column as a good possible alternative for PD determination in natural plant extracts. When an ACN/water mobile phase is used, a modifier as n-propanol, i-
propanol or tetrahydrofuran at concentration 1.3 – 2 % is required for peak symmetry improvement. A modified mobile phase with 23 – 26 % acetonitrile in water is optimal for isocratic separation. Acidification of the mobile phase, used in most of the published methods, does not affect PD retention with this column, but can be useful for improvement of its separation from sample matrix constituents. Use of UV detection is possible when high purity solvents with low UV cut-off, like gradient grade water and acetonitrile, are used. UV detection permits more than 50-fold lower LOD to be reached, in comparison to ELSD detection. On the other hand, because of the higher efficiency, a significantly higher increase of sensitivity can be accomplished with a core-shell C₈ column, in comparison with conventional analytical columns packed with fully porous silica-based stationary phases. Because of this higher efficiency and good selectivity towards polar compounds, as PD is, separation can be much faster, decreasing the analysis time more than 5 times. On account of the longer time for conditioning that this column demands, however, the gradient elution requires more time and very high purity solvents to be used. At gradient elution, starting from less than 20 % ACN, efficiency and sensitivity together could be increased for multicomponent analysis but at a price of longer reconditioning and thus longer analysis time. Sample clean-up with polymer-based RP-cartridges results in higher recovery in comparison

Fig. 8. Chromatograms of eluates from polymer-based RP-18 SPE cartridge after loading 1 ml water solution of 1 mg/ml Tribestan®.

Fig. 9. Chromatgram of 5 µl 25 µg/ml protodioscin (A) and chromatogram of a blanc (B) obtained with gradient elution from the Kinetex C₈ 50 x 3 mm 2.6 µm column from 15 % to 50 % ACN in water for 5 min.
with silica-based ones.

The isocratic analysis of PD with the core-shell C₈ short Kinetex column is effective, because it is faster (less than 20 min total analysis time) when SPE is applied to clean the sample from strongly retained components.

Acknowledgements

The authors are grateful to Phenomenex Inc. and Dr. Heiko Behr for the technical support for preparation of this work.

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EFFECTS OF THE SURFACE TREATMENT ON A PAPER AND PRINT MATERIALS

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ABSTRACT

The quality of the polygraphic production is ameliorated considerably through the process of improvement, when the choice of raw materials, equipment and technology is properly done. Different methods for improvement are used depending on the kind and destination of the production and they may be implemented separately or in combinations one with another. Different polygraphic products are submitted to improvement: label-packing production, covers for books and journals, art reproductions, cards, amendments for books and journals, post stamps, advertising materials, etc.

In the present investigation two of the different means for improvement are studied: varnishing and laminating.

The technology for improvement of the printed production through varnishing and laminating and their influence on the quality of the polygraphic production and the color reproduction is investigated.

For realization of the goals of the experiment in the present investigation out a set of experiments for establishing the changes occurring in the physical-mechanical properties of the printing production after lamination and UV-varnishing are carried, as well as the changes of the color reproduction of the test samples.

Keywords: color differences, cold laminating, UV-varnishing, physical-mechanical properties, border properties, color reproduction.

INTRODUCTION

The market requires more and more products with the best possible quality, advertising materials for the vast consumer masses, which have to posses the ability to be used everywhere at any time, products with high run lengths and printed materials for direct advertising [1].

A significant part of the illustrated production after printing the run requires additional treatment (improvement), which gives the ability to enhance the service features of the printed production, as well as to import finished appearance [2 - 4].

During the process of amelioration, assuming that the right prime materials, equipment and technological process are choosen, the quality of the polygraph production is significantly enhanced. Depending on the kind and destination of the production, different methods for amelioration are adopted, which may be applied individually or in a certain combination one with another [5 - 7].

Besides rendering an attractive outlook, the varnishing and the laminating prevents the image from erasing, humidity, sun rays impact, shortens the drying time of the imprint.

The aim of this research is to evaluate the influence of the UV-varnishing and laminating on the physical and mechanical properties and the color reproduction of printed materials in real production conditions.

EXPERIMENTAL

During the present research experiments have been carried out for amelioration of the physical and mechanical properties of printed production through lamination...
and UV- varnishing. An attempt was done for determining the color reproduction changes of examined samples after UV-varnishing and after cold laminating. The assessment was carried out on five identical color reproductions, on which the color characteristics were measured before and after cold lamination and UV-varnishing. On each reproduction six particular fields for measurements have been marked.

The following materials were used:
- Uncoated offset paper 80 g/m², produced in EC;
- Coated paper 150 g/m², produced in EC;
- Coated paper 200 g/m², produced in EC;

The offset printing machine, which has been used is four color sheet feed “KBA RAPIDA 105”.

The printing inks, which have been used, are manufactured by “Huber grupp”, Refecta Ecolutensive series.

For amelioration were used:
- UV- varnish for entirely varnishing senolith 360020/50 of Weiburger Germany, fulfilled on produced in Switzerland machine Kolibri 74 of “Seineman”.
- 15 μn laminating film, BOPP film produced by “Manuli” Italy. The reproductions were laminated on laminator for cold lamination “Lotus” 72 of “Seineman” – Switzerland. The following indices were determined on the trial samples before and after printing, as well as after UV-varnishing and cold lamination:
  - breaking length (m);
  - folding resistance (number);
  - water absorption according the method Cobb 60 (g/m²).

Examination of the color reproduction changes after UV-varnishing and laminating was carried out with spectrophotometer/densitometer of type SpectroEye of Gretag Macbeth and the values for Lab and ΔE were determined on the unprinted and saturated fields of CMYK inks. All measurements are in accordance with ISO 12647-1[8]: D50 illuminant, 2º observer, 0/45 or 0/45 geometry, black backing in accordance with.

### Table 1. Qualitative indices of paper samples before printing.

<table>
<thead>
<tr>
<th>Paper kind g/m²</th>
<th>Breaking length, m</th>
<th>Folding resistance, nb</th>
<th>Water absorption Cobb 60 (g/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MD</td>
<td>CD</td>
<td>MD</td>
</tr>
<tr>
<td>80</td>
<td>4381</td>
<td>2380</td>
<td>95</td>
</tr>
<tr>
<td>150</td>
<td>5150</td>
<td>3201</td>
<td>140</td>
</tr>
<tr>
<td>200</td>
<td>5843</td>
<td>3365</td>
<td>159</td>
</tr>
</tbody>
</table>

### Table 2. Qualitative indices of paper samples after printing.

<table>
<thead>
<tr>
<th>Paper kind g/m²</th>
<th>Breaking length, m</th>
<th>Folding resistance, nb</th>
<th>Water absorption Cobb 60 (g/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MD</td>
<td>CD</td>
<td>MD</td>
</tr>
<tr>
<td>80</td>
<td>4263</td>
<td>2350</td>
<td>93</td>
</tr>
<tr>
<td>150</td>
<td>5102</td>
<td>3262</td>
<td>132</td>
</tr>
<tr>
<td>200</td>
<td>5798</td>
<td>3320</td>
<td>148</td>
</tr>
</tbody>
</table>

### Table 3. Qualitative indices of paper samples after UV – varnishing.

<table>
<thead>
<tr>
<th>Paper kind g/m²</th>
<th>Breaking length, m</th>
<th>Folding resistance, nb</th>
<th>Water absorption Cobb 60 (g/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MD</td>
<td>CD</td>
<td>MD</td>
</tr>
<tr>
<td>80</td>
<td>4683</td>
<td>2715</td>
<td>90</td>
</tr>
<tr>
<td>150</td>
<td>5428</td>
<td>3495</td>
<td>133</td>
</tr>
<tr>
<td>200</td>
<td>6132</td>
<td>3568</td>
<td>142</td>
</tr>
</tbody>
</table>

### Table 4. Qualitative indices of paper samples after laminating.

<table>
<thead>
<tr>
<th>Paper kind g/m²</th>
<th>Breaking length, m</th>
<th>Folding resistance, nb</th>
<th>Water absorption Cobb 60 (g/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MD</td>
<td>CD</td>
<td>MD</td>
</tr>
<tr>
<td>80</td>
<td>5983</td>
<td>3452</td>
<td>169</td>
</tr>
<tr>
<td>150</td>
<td>7253</td>
<td>3718</td>
<td>172</td>
</tr>
<tr>
<td>200</td>
<td>8063</td>
<td>3918</td>
<td>198</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

The results received during the studies are depicted on Tables 1, 2, 3 and 4, as well as on Figs. 1, 2 and 3.

On Table 1 and Table 2, are shown according to the results received for tearing strength, folding resistance and water absorption. The carried out examinations depict that the physical and mechanical properties lightly decrease after printing, which probably is due to a complex of technological factors, which exercise influence on the printing substrate, as well as to the technical characteristics of the printing machine.

The received imprints are subjected to amelioration with UV- varnish and cold laminating. On Table 3 and Table 4 are shown the results from the examinations for determining the qualitative indices after the additional treatment of the imprinted samples. From the data in the Tables and Figs. 1, 2 and 3 can be seen that at both methods for amelioration of printed samples, the tearing strength raises regardless from the kind and mass of used paper samples, whereas the folding resistance increases significantly after lamination. A trend towards diminishing the folding resistance is observed after UV-varnishing. This fact probably is due to the changes of the elastic – plastic properties of the treated with UV-varnish samples. On Fig. 1, 2 and 3 are shown the changes of particulate paper qualitative indices after the relevant printing and amelioration and the values for transverse and longitudinal directions are mean.

Water absorption diminishes considerably for both amelioration methods.

Experiments for partial determining the influence of UV-varnishing and lamination on the color background were carried out.

The researches were executed with spectrophotometer and the four fields (C, M, Y, K) were measured off five scales, as well as on unprinted sections and the values L*, a*, b* were determined. On each sample three measurements were done and middle value results were drawn. The values for ∆E were defined and for all analysis they rest under one. The results obtained show that significant changes in color reproducibility were not established both for varnishing and laminating. Deviations were in the limits of permissible mistakes. Visually was perceived increase of opacity and amelioration of ocular perception. It is necessary additional studies to be carried out in future and color profiles for the outgoing devices to be drawn, including the stage of varnishing and laminating.
CONCLUSIONS

The following conclusions were drawn, based on the results from this investigation:

During the process of amelioration, assuming that the right prime materials, equipment and technological process are picked up, the quality indices and the physical and mechanical properties are significantly enhanced (tearing length, water absorption according to the method Cobb_60, folding resistance in number of double bendings) on the studied samples. Solely the physical and mechanical characteristic - number of double foldings diminish when amelioration is by varnish. For this reason it can be recommended the use of lamination or partially UV - varnishing in places where multiple foldings may take place.

Water absorption diminishes considerably for both amelioration methods. Consequently, the conclusion that not only the strength characteristics of imprints, but also their protection properties are influenced by cold lamination and UV - varnishing can be taken out.

Refinement of polygraph production leads to amelioration of exterior look, strength characteristic and defense properties of the imprint. The results pose practical interest and could be used for polygraphic formatting of book covers, postcards and packings.

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EXPERIMENTAL DETERMINATION OF THE VOLUMETRIC MASS TRANSFER COEFFICIENT

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ABSTRACT

The volumetric mass transfer coefficient \( k_L a \) is often used in order to compare the efficiency of bioreactors and as an important scale-up factor. In bioreactors, a number of methods are available for estimation the overall volumetric oxygen mass transfer coefficient: the dynamic method, the steady-state method based on a preliminary determination of the oxygen uptake rate, the gaseous oxygen balance, the carbon dioxide balance. Each method provides a different estimation of the value of \( k_L a \). We examined the sensitivity of the various methods and compare the \( k_L a \) values obtained in order to select the most suitable method as a function of the type of bioreactor used. In this work we applied dynamic gassing-out method for measuring the volumetric mass transfer coefficient \( k_L a \) in three type gas-liquid reactors (stirred tanks, bubble columns and airlift). The aim of this work is on the basis of our experimental data to obtain several correlations for evaluation of \( k_L a \).

Keywords: volumetric oxygen transfer coefficient, bubble columns, CSTR, airlift reactors.

INTRODUCTION

Aeration and agitation are important variables to provide effective oxygen transfer rate during aerobic bioprocesses. Hence, the knowledge of the volumetric mass transfer coefficient \( k_L a \) is required. The determination of \( k_L a \) in a bioreactor is essential in order to establish its aeration efficiency and to quantify the effects of operating variables on oxygen supply.

Oxygen transfer in aerobic bioprocesses is essential and any shortage of oxygen vastly affects the process performance. Therefore, oxygen mass transfer is one of the most important phenomena in the design and operation of mixing-sparging equipment for bioreactors [4]. It can be described and analyzed by means of the volumetric mass transfer coefficient, \( k_L a \). The values of \( k_L a \) are affected by many factors, such as geometrical and operating characteristics of the reactor (type of impeller, the geometry of the bioreactor, the agitation speed and the air flow rate), media composition and properties, concentration and microorganism’s morphology and biocatalyst’s properties [3].

In aerated systems the critical limiting factor in providing the optimal environment is the oxygen transfer rate (OTR). The mass balance for the dissolved oxygen in the well-mixed liquid phase can be written as:

\[
\frac{dC_L}{dt} = k_L a(C_*^L - C_L) - r_O = OTR - OUR
\]

(1)

When oxygen uptake rate, \( OUR = 0 \), the oxygen mass balance in the liquid phase can be simplified to:

\[
\frac{dC_L}{dt} = k_L a(C_*^L - C_L) = OTR
\]

(2)

or

the oxygen mass transfer rate can be described as proportional to the concentration gradient. For aerobic fermentation the maximum value of the concentration gradient is limited due to the low solubility of oxygen. Therefore, the maximum mass transfer rate from the gas to the liquid in the bioreactor can be estimated by \( k_L a.C_*^L \).
as \( C_L^* \) is the saturation concentration in the liquid phase.

Integrating:

\[
\int_{C_{L,t}}^{C_{L,1}} \frac{1}{C_{L} - C_{L}} dC = k_a a \int_0^t dt
\]

Hence a plot of

\[
\ln \left( \frac{C_L^* - C_{L,1}}{C_L^* - C_{L,2}} \right)
\]

vs. \( t \) should result in a straight line of slope \( k_a a \).

**METHODS**

The methods for measuring the \( k_a \) can be classified depending on whether the determination is made in the

<table>
<thead>
<tr>
<th>Measurement method</th>
<th>( k_{l,a} \times 10^2 ) [( \text{s}^{-1} )]</th>
<th>Assay time</th>
<th>Scale applied</th>
<th>Assumptions/Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfite oxidation</td>
<td>0 - 0,3</td>
<td>Hours</td>
<td>Laboratory scale</td>
<td>The rate of reaction is assumed to be zero order in sulfite. Alteration of driving force, diffusion coefficient, and coalescence properties; complex kinetics boundary layer reduction. This method is fairly labor intensive.</td>
</tr>
<tr>
<td>Absorption of CO(_2)</td>
<td>0 - 0,1</td>
<td>Minutes</td>
<td>Laboratory scale</td>
<td>Assumptions about kinetic reaction must be made. Possible alteration of the driving force. Change of the coalescence behavior.</td>
</tr>
<tr>
<td>Dynamic measure of pH</td>
<td>0 - 0,03</td>
<td>Half an hour</td>
<td>Any scale</td>
<td>Assumptions about kinetic reaction must be made. Salt addition does not alter the mass transfer rate of CO(_2).</td>
</tr>
<tr>
<td>Hydrazine oxidation</td>
<td>0-0,5</td>
<td>Minutes</td>
<td>Pilot plant</td>
<td>Hydrazine does not accumulate. No chemical enhancement.</td>
</tr>
<tr>
<td>Bio-oxidation of catechol</td>
<td>&lt; 0,8</td>
<td>Minutes</td>
<td>&lt; 100ml</td>
<td>Available of oxidative enzyme; limited to small scales.</td>
</tr>
<tr>
<td><strong>Physical</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dynamic</td>
<td>0 - 0,1</td>
<td>Minutes</td>
<td>&gt;100 ml</td>
<td>A nonrespiring system can be employed to simulate the fermentation broth. The response time of the electrode, ( \tau_r ), is a critical parameter. Gassing time can be significant at larger scales.</td>
</tr>
<tr>
<td>Biological Dynamic gassing out</td>
<td>0 - 0,1</td>
<td>Minutes</td>
<td>Any scale</td>
<td>High DO concentration is necessary. Nongassing period must be short and OUR independent of DO concentration. Invasive probes are necessary and response time must be considered. Hydrodynamic changes may disturb the microbial metabolism.</td>
</tr>
<tr>
<td>Biological dynamic method with high OUR</td>
<td>0 - 0,1</td>
<td>Minutes</td>
<td>Any scale</td>
<td>OUR is independent from DO concentration. Invasive probes are necessary and response time must be considered.</td>
</tr>
<tr>
<td>Gas phase analysis</td>
<td>0 - 0,3</td>
<td>Hours</td>
<td>&gt;100 ml</td>
<td>For large scales, the assumptions of well-mixed gas and liquid phase may not be valid. This method may not be the best choice in case of small bioreactors, where the difference between ( F_{in} ) and ( F_{out} ) may be very small because of the short contact time. The accuracy depends on the precision of oxygen analyzer.</td>
</tr>
</tbody>
</table>
absence of microorganisms (chemical and physical methods) or in the presence of biomass (biological methods). In Table 1 are summarized methods for the volumetric mass transfer coefficient determination. Chemical and biological methods require a reaction in the liquid phase to reduce the dissolved oxygen (DO) concentration to a level below saturation. The most often used chemical method is chemical oxidation, and from biological methods - cellular respiration. The physical methods are based on the measurement of the oxygen concentration in the liquid or in the exhaust gas flow during absorption/desorption process. The methods differ in the procedure of gas interchange, in the gas used, and in the model for the gas-phase description [2].

### EXPERIMENTAL

The $k_{L}a$ was determined by physical dynamic method as described by Benyahia and Jones [14]. The activated sludge liquid was deoxygenated by stripping with nitrogen. Then, nitrogen was replaced by air, and the dissolved oxygen concentration in the liquid was measured until equilibrium was reached. The air flow was uninterrupted during the switch from nitrogen to air so that the consistent fluid dynamic conditions were maintained in the reactor throughout the experiment. When $k_{L}a$ is considered to be independent of time, integration of equation with $C_{L}=0$ at $t=0$ gives:

$$C_{L}(t) = C_{L}^{0} \left( 1 - \exp \left( -k_{L}a \frac{t}{L} \right) \right)$$
The values of $k_{L_a}$ were determined from the slope of the straight line obtained from a plot of $\ln(C_L^* - C_L)$ against the time. This method for evaluation of $k_{L_a}$ is applicable when assuming a well-mixed liquid phase, a constant air concentration along the column height and a fast response of oxygen electrode to a change in the dissolved oxygen concentration.

Stirred tank, bubble column and airlift reactor were used to conduct experiments for $k_{L_a}$ determination using of a dynamic gassing-out method.

Stirred tank reactor: measurements were performed in six pitched turbine stirred fermentors with total volume 50 l (35 l working volume, d/D ratio = 0.375) and 1300 l (1000 l work volume, d/D ratio = 0.6).

Bubble columns reactors: the experiments were made with 3 different bubble columns. The first one – with total volume 50 l and 35 l work volume, the second – with 85 l total volume and 58 l working volume, and the third – 1300 l and 1000 l total and work volume, respectively. Airlift reactor: measurements have been carried out in the pilot-plant size airlift reactor, riser with $H_r = 2.8$ m and diameter $d_r = 0.2$ m and downcomer with $H_d = 0.86$ m and diameter $d_d = 0.06$ m, working volume $V = 0.062$ m$^3$; $A_d/A_r = 0.09$, where $A_d$ and $A_r$ are downcomer and riser areas, respectively.

Table 3. Experimental results.

<table>
<thead>
<tr>
<th>Reactor type</th>
<th>Total volume [l]</th>
<th>Work volume [l]</th>
<th>$H_r$ [m]</th>
<th>$d_r$ [m]</th>
<th>$A_r$ [m$^2$]</th>
<th>$d_r/H_r$</th>
<th>Impeller</th>
<th>$d_r/d$</th>
<th>Derived correlation/Estimated values for $k_{L_a}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stirred tank</td>
<td>50</td>
<td>35</td>
<td>0.5</td>
<td>0.36</td>
<td>0.102</td>
<td>0.72</td>
<td>Six pinched turbine</td>
<td>0.375</td>
<td>$k_{i,a} = 0.0638 , rps^{0.165}$</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>1000</td>
<td>1.68</td>
<td>1</td>
<td>0.785</td>
<td>0.6</td>
<td>Six pinched turbine</td>
<td>0.3</td>
<td>$k_{i,a} = 0.0147 , rps^{0.8858}$</td>
</tr>
<tr>
<td>Bubble column</td>
<td>50</td>
<td>35</td>
<td>0.5</td>
<td>0.36</td>
<td>0.102</td>
<td>0.72</td>
<td>-</td>
<td>-</td>
<td>$k_{i,a} = 0.4637 , L_G^{0.8414}$</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>58</td>
<td>3</td>
<td>0.19</td>
<td>0.028</td>
<td>0.06</td>
<td>-</td>
<td>-</td>
<td>$k_{i,a} = 0.2096 , L_G^{0.7661}$</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>1000</td>
<td>1.68</td>
<td>1</td>
<td>0.785</td>
<td>0.6</td>
<td>-</td>
<td>-</td>
<td>$k_{i,a} = 0.4496 , L_G^{0.8802}$</td>
</tr>
<tr>
<td>Airlift with external loop</td>
<td>92</td>
<td>62</td>
<td>3</td>
<td>0.2</td>
<td>0.031</td>
<td>0.06</td>
<td>$d_d$ [m]</td>
<td>$A_d/A_r$</td>
<td>$k_{i,a} = 1.1458 , L_G^{1.1706}$</td>
</tr>
</tbody>
</table>
and riser cross-sectional area, respectively. More details are given in Table 3.

In all experiments as a gas phase was used air and desalted water and tylozin as a liquid phase. The oxygen concentration is followed with a P2 – type dissolved oxygen probe and a 703P polarographic oxygen meter from Uniprobe. The probe was located at 300 mm from the bottom of the column at an angle of 45°.

RESULTS AND DISCUSSION

The experiments were carried out in STR at 300 rpm stirring speed and gas phase flow rate 0.25 l/s. The value of \( k_{l,a} = 0.076 \text{ s}^{-1} \) was obtained by comparison of the numerical results from model solution and the experimental data for dissolved oxygen concentration [15]. It is obvious that the values of \( k_{l,a} \) are not so sensible to the variation of the input air flow rate in comparison with variation of the agitation speed, especially in large reactors. Experimentally obtained values of \( k_{l,a} \) in bubble column with work volume 1000 l and 35 l are 0,069 s\(^{-1}\) and 0,066 s\(^{-1}\), respectively [16].

In Table 3 are presented experimentally obtained correlations for evaluation of \( k_{l,a} \).

CONCLUSIONS

The most suitable method selection for \( k_{l,a} \) measurement requires to take into account the range of the variables as power input, volume and type of the reactor, characteristics of gas and liquid phase. The dynamic oxygen method is the most widely used, with a small degree of approximations for gas–liquid mixing in the reactor. This method is suitable for large scale bioreactors with errors less than 10 %, over the entire range of the operating conditions encountered in the industrial fermentor operations.

The steady state sulfite method is not recommended as it gives inaccurate values in comparison with the other methods applied in industrial scale. The use of pure oxygen for accurate estimation of the volumetric mass transfer coefficient is highly uneconomical when other methods are available with a sufficient degree of accuracy.

The response methods are also found to be satisfactory when applied to stirred vessels. Their applicability for media with high viscosity and non-coalescing fermentation media have to be tested.

On the base of our experimental data empirical correlations were developed for calculation of \( k_{l,a} \) values. It was found that the predicted \( k_{l,a} \) values were sufficiently well comparable with the observed, especially in small scale stirred tank reactors.

**Nomenclature**

- \( A_d \) downcomer cross-sectional area [m\(^2\)]
- \( A_r \) riser cross-sectional area [m\(^2\)]
- \( C \) oxygen concentration [kg.m\(^{-3}\)] or [-]
- \( d \) diameter [m]
- \( k_{l,a} \) volumetric mass transfer coefficient [s\(^{-1}\)]
- \( H \) length of the reactor [m]
- \( U \) velocity [m.s\(^{-1}\)]
- \( V \) volume [l]

**Subscripts**

- \( d \) downcomer
- \( G \) gas
- \( L \) liquid
- \( r \) riser

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KINETIC STUDY OF THE DISCOLORATION OF RHODAMINE B WITH PERSULFATE, IRON ACTIVATION

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ABSTRACT

The discoloration of the fluorescent dye, Rhodamine B (Rhd B) by persulphate (KSP), was investigated by spectrophotometric methods. The discoloration reaction of Rhd B by KSP is slow. It's first order with respect to Rhd B and KSP. It's effective at any pH and was found to increase linearly for pH< 4, temperature, and after addition of Fe(II) and Ag(I). The rate of discoloration remained the same after addition of Co(II), Ni(II), Cu(II) and carbonate salts, but decreased after addition of ethanol and chloride salts. The TLC experiment showed the formation of colored intermediates. The activation parameters ($E_a$, $\Delta G^\#$, $\Delta H^\#$, and $\Delta S^\#$) of the discoloration reaction of Rhd B by KSP in absence and in presence of Fe(II) were calculated.

Keywords: Rhodamine B, persulfate, metal activation, matrix effect, kinetic.

INTRODUCTION

Textile industry produces a large amount of dyed wastewater. The non-biodegradable nature of the spent dye baths constitutes serious environmental problems [1]. Rhodamine B (Rhd B), is one of the important xanthene cationic dyes, is largely applied in industry as a dye for paper, silk, wool, jute leather, cotton (Fig. 1). The xanthene dyes (Rose Bengal, Eosin Y and Rhodamine 6G,…) are used also as fluorescent markers in structural microscopic studies, photosensitizers, and laser dyes. They have long been known to be toxic to insects (insecticide). They are harmful if swallowed by human and animals, and cause irritation to the skin, eyes and lung [2-3].

The main technologies available for the treatment of dyes involve the transfer of the pollutant from a liquid phase to another phase, concentrating the dye on an adsorbent (for example) so that it can later be discarded in a landfill or incinerated [4-5]. This phase exchange is not an ideal remedy. Destructive oxidation treatments provide more permanent solutions such as electrodegradation [6, 7], photodegradation using TiO$_2$ [8-13] are applied for removal of dyes (especially cationic dyes) from textile effluents.

Chemical oxidation of contaminants by oxidants has been studied to develop novel remediation technologies: KBrO$_3$ [14, 15], KClO$_3$ [16], O$_3$ [17], UV/O$_3$ [18], activated O$_2$ [19], Fenton’s reagent [20 -21], photo Fenton [22], H$_2$O$_2$ [23] have been widely tested in laboratory for the degradation of basic dyes.

The use of persulfate (KSP) has recently been the focus of attention for an alternative oxidant in the chemical oxidation of contaminants [24-37]. It’s one of the strongest oxidants known in aqueous solution (Table 1) [27, 38]. It has great capability for degrading numerous organic contaminants through free radicals (SO$_4^\cdot$ and OH$^-$) generated in the persulfate system [30, 31]. It offers some advantages over other oxidants: Ease of storage and transport, high stability, high aqueous solubility
and relatively low cost.

Base activation [36, 37], UV-irradiation [25, 26, 35], thermal activation [34, 39-41], metal activation [42-46], and soil mineral activation [30] have been used to generate a sulfate radical (E°: 2.5-3.1 V), a stronger oxidant than persulfate (2.01 V) [41, 45]:

$$S_2O_8^{2-} + \text{heat/UV} \rightarrow 2SO_4^{2-}$$

$$S_2O_8^{2-} + 2M^{n+} \rightarrow 2SO_4^{2-} + 2M^{(n+)+}$$

$$SO_4^{2-} + H_2O \rightarrow HO^+ + H^+ + SO_4^{2-}$$

The present work is focused on the kinetic study of the discoloration of Rhd B (model molecule of xanthenes dye) with persulfate by UV-Visible spectrophotometry. The effect of various parameters such as initial pH, initial concentration of persulfate and Rhd B, transition metals concentration, and salts concentration was studied. A comparison between the degradation of Rhd B and Fluorescein (which has similar structure) with persulfate is undertaken to interpret better the results.

**EXPERIMENTAL**

Rhodamine B is used as purchased from Sigma (C_{28}H_{31}N_2O_3Cl, CAS: 81-88-9, MW: 479.02 g). The other chemical reagents used are from BDH (Analar or GPR). 20 mg L⁻¹ (4.18x10⁻³ M) of Rhd B solution is prepared in distilled water in order to study its discoloration by KSP. The concentration of the dye in the reactional mixture is selected in such a way the absorbance of the dye at 560 nm followed Beer’s law. The concentration of KSP in the reactional mixture (0.01 M) is selected in such a way the rate of the reaction is not very slow. The kinetic study of the discoloration of Rhd B by persulfate was carried on a double beam spectrophotometer, Specord 200 (Analytical Jena). 1 M of salt solutions (carbonate, chloride, and sulfate), and 0.1 M of transition metals solutions (Co(NO_3)_2, Ni(NO_3)_2, and CuSO_4), were also prepared to study the matrix effect on the discoloration rate. 5x10⁻² M of AgNO_3, Fe^Ⅱ(NH_4)_2(SO_4)_2, 6 H_2O, and 10⁻² M of the surfactant (SDS) were also prepared for the same reason. H_2SO_4 and NaOH solutions were used to study the effect of pH on the discoloration rate of Rhd B with KSP.

**Kinetic Study**

The order with respect to Rhd B was carried out in the presence of a large excess of persulfate. The reactional mixture was prepared as follows: x mL (2 < x < 4) of 20 mg L⁻¹ (0.93x10⁻³ M) of Rhd B, (7-x) mL of H_2O and 2 mL of 5x10⁻² M KSP ([KSP]_f: 0.11 M). Quickly after the addition of the dye, the absorbance of the solution was recorded every 1 min. during 60 minutes at 560 nm (λ_max of Rhd B). The rate expression for the discoloration reaction is:

$$\text{Rate} = k[S_2O_8^{2-}]^m[Rhd\ B ]^n = k_{app}[Rhd\ B ]^n$$

where k is the rate constant of the reaction, m and n are the pseudo order of the reaction with respect to Rhd B and K_2S_2O_8 respectively.

**Effect of initial pH**

The effect of pH on the degradation rate was studied in presence of several concentrations of NaOH or H_2SO_4. The following mixtures were prepared for this purpose: 2 mL of 20 mg L⁻¹ Rhd B ([RhdB]_f: 0.93x10⁻² M), 2 mL of 5x10⁻² M of KSP ([KSP]_f: 0.11 M), 5 mL of the acid
Concerning the effect of metal salts, several experiments were done at fixed concentration of KSP and Rhd B in the mixture as follows: 3 mL of 20 mg L\(^{-1}\) Rhd B \([\text{Rhd B}]_0: 1.25x10^{-5} \text{M}\), 2 mL of a predetermined concentration of KSP ranging from 5x10\(^{-2}\) M to 10\(^{-3}\) M, \(x\) mL of Fe(II) \((\text{Fe}^{II}(\text{NH}_4)_2(\text{SO}_4)_2) \cdot 6 \text{H}_2\text{O}\), or Ag(I) solution of the same initial concentration of KSP and (5-x) mL of water.

Matrix effect

The effect of salt such as KCl, Na\(_2\)SO\(_4\), and Na\(_2\)CO\(_3\) (1 M), on the rate constant was carried out at several concentrations of the mentioned salts by replacing some volume of water by the salt solution \((x\ \text{mL}, \ 0 \leq x \leq 5\) ), while keeping the concentration of the others reactants constant. The effect of the surfactant (SDS) and ethanol, on the discoloration rate were also studied in the same manner.

RESULTS AND DISCUSSION

UV-Visible spectroscopy and TLC Analysis

The visible spectrum of Rhd B decreases slowly with time especially the absorbance at 560 nm \((\lambda_{\text{max}}\) of Rhd B). The general shape of Rhd B spectrum does not vary during its reaction with KSP. The reaction between Rhd B and KSP leads to total discoloration of Rhd B (Fig. 2a). The discoloration is very slow compared to that with crystal violet and malachite green [27]. The slow decrease in the intense peaks of Rhd B at 560 and 260 nm is accompanied for the first time by an increase in the absorbance at 630, 470 and 370 nm (Fig. 2a, 2b). Then the decrease continues in the whole spectrum.

The TLC study (Silica gel – pure ethanol) shows the appearance of two spots other than that of Rhd B: the lower one, orange less intense than the upper one (violet) (Fig. 3). The two color intermediate products disappear with time, in favors of two others intermediates with higher \(R_f\). The Rhd B spot persists even after long time (one day) but its color faded, and then it disappears completely. The same behavior is observed with the other spots. Finally the Rhd B / KSP mixture become colorless. The discoloration of low concentration of Rhd B by KSP leads to the formation of colored intermediates undetectable clearly by UV-visible spectroscopy. The decrease in the whole UV - visible spectrum is probably a consequence of total mineralization of Rhd B. No blue shift (progressive decrease from 560 to 498 nm) is observed during the discoloration as observed during the degradation of Rhd B under visible light ir-
radiation by Zn\textsubscript{1-x}Cd\textsubscript{x}S/TiO\textsubscript{2} [47], and ZnCd/TiO\textsubscript{2} [48]. The degradation products of Rhd B are function of the oxidant used [49, 50]. There are several pathways for the Rhd B degradation:

- N-deethylation (formation of Rhd B110), followed by deamination [49, 52].
- Break in the chemical bond of xanthone molecule between the C\textsubscript{1} and C\textsubscript{15} atoms (elimination of the phenyl ring containing COOH) leading to the formation of Pyronin G [50].
- A break in the -O- bridge giving an intermediate having a similar structure to malachite green (increase in A\textsubscript{630}).
- Further degradation of these intermediate is possible [27, 51, 52].

**Order with respect to Rhd B**

Rhodamine B shows a strong absorption band at 560 nm and follows Beer’s law for low concentrations (2–8 mg L\textsuperscript{-1}). The relation found between the absorbance A\textsubscript{560} and Rhd B concentration in mg L\textsuperscript{-1} is \( A = 0.196 \times [\text{Rhd B}] \) (mg L\textsuperscript{-1}) \( R^2: 0.993 \). The order with respect to Rhd B is not zero according to the plot of A\textsubscript{560} vs. time (Fig. 4a). The functions ln A and 1/A vary linearly with time. The constant k\textsubscript{obs} is the slope of the plot

\[
\ln A_{560} \text{ or } \frac{1}{A_{560}} \text{ vs time (} k_{obs} \propto k_{app}.\)
\]

For all the experiments concerning the determination with respect to Rhd B, the correlation coefficient (R\textsuperscript{2}) for order one is closer to one than that for 2nd order. Order one is confirmed by applying the differential method (\( \ln V_0 = 1.27 \times \ln[Rhd B] \), \(-10.27\), R\textsuperscript{2}: 1). The constant k\textsubscript{obs} remains the same with the increase in the dye concentration (\( k_{obs} = 2.9 \times 10^{-4} \)). Order one is also observed by discoloration of Rhd B by UV/KSP [29], by photo-Fenton reagent [22], and by photo-degradation in presence of TiO\textsubscript{2} [9].

**Order with respect to KSP**

The increase in KSP concentration increases the discoloration rate of Rhd B. For 10\textsuperscript{-3} M of KSP (in the mixture), the absorbance of Rhd B remained the same during 1 h, but with 10\textsuperscript{-2} M of KSP, the absorbance decreases significantly. The rate constant (k\textsubscript{obs}) increases linearly with the increase in KSP concentration (\( k_{obs} \times 10^4 = 200 \times [\text{KSP}] \), R\textsuperscript{2}: 0.983). So the order with respect to KSP is one. Order one is also observed for the degradation of crystal violet by KSP [27].

**Effect of initial pH**

Initial pH of solution had great effect on Rhd B degradation rate during UV/S\textsubscript{2}O\textsubscript{5}\textsuperscript{-} system. Rhd B is stable in acidic and in basic medium, it does not loose its color with time in these mediums. Its maximum
wavelength remained the same whatever the pH. The results showed that the discoloration rate constant does not vary in neutral and in basic medium, but increases linearly with the decrease in pH for pH ≤ 4 (Fig. 4b). The radical $\cdot SO_4^-$ is rather stable and more numerous at low pH, while increasing system pH results in the transformation of $\cdot SO_4^-$ to hydroxyl radical OH $^*$ ($\cdot SO_4^- + H_2O \rightarrow OH^+ + SO_4^2^- + H^+$) [29]. The acidic medium has positive effect on the Rhd B discoloration due to shift to right in the equilibrium of the reaction mentioned. The obtained result is in accordance with that obtained by action of UV/ KSP on Rhd B [29] and by action of KSP on Orange G [45].

Matrix effect

Metal Activation

The chemical oxidation of organic pollutants by persulfate can be accelerated by metal ion activation, through enhancing sulfate radical generation. In the present case Ni(II), Co(II) and Cu(II) did not increase the discoloration rate constant, whereas the ions Ag (I) and Fe(II) accelerate it considerably (Fig. 5 and 6). For the same concentration of metal ion, Fe(II) decolorizes the mixture (Rhd B + KSP) faster than Ag (I). The discoloration behavior of Rhd B in presence of Fe(II) is somehow special:

The control mixture (presence of Fe(II) without KSP) shows no discoloration of Rhd B. For 5x10⁻² M (or 5x10⁻³ M) as initial concentration of KSP and Fe(II): The decrease in Fe(II) concentration in the medium increases the discoloration rate (result not shown). For the experiment done with 5x10⁻² M of KSP and Fe(II), the mixtures with) Fe(II)/[KSP] ≥ 2, the discoloration is completely stopped, but for other mixtures with low ratio (≤ 0.5), the color disappears completely in less than 1 minute.

The repetition of the experiment mentioned above with 5x10⁻³ M of KSP and 10⁻³ M of Fe(II) (instead of 5x10⁻³ M) as initial concentration showed different attitude: the discoloration rate increases with the increase in Fe(II) volume (0.3 ml < x < 4 ml or 3x10⁻³ M – 4x10⁻³ M) (Fig.5a). Linear relation is observed between $k_{obs}$ and Fe(II) ($R^2$: 0.97). This behavior is the opposite of that observed with higher concentrations of KSP and Fe(II).

Basing on this, we think about the existence of an optimum ratio of Fe(II)/[KSP]. This ratio corresponds to 1 when using 10⁻³ M as initial concentration of KSP and Fe(II) (2 ml of 10⁻³ M KSP + x ml of 10⁻³ M Fe(II)).

Table 1. The standards potentials of some oxidants used in advanced chemical oxidation [27, 38].

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>BrO₃⁻/Br₂</th>
<th>ClO₃⁻/Br₂</th>
<th>H₂O₂/H₂O</th>
<th>O₃/O₂</th>
<th>OH*</th>
<th>S²O₈⁵⁻/SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>E⁰ (V)</td>
<td>1.51</td>
<td>1.46</td>
<td>1.76</td>
<td>2.07</td>
<td>2.38</td>
<td>2.01</td>
</tr>
</tbody>
</table>
The optimum ratio of Fe(II)/[KSP] is also confirmed by varying the volume of 10^{-3} M KSP with respect to that of 10^{-3} M Fe(II) (Fig. 5b). There is scavenger effect [27, 45].

Concerning the effect of Ag(I), the control mixture (presence of Ag(I) without KSP) shows no discoloration of Rhd B. For an initial concentration of KSP (5x10^{-2} M), the addition of x ml of 5x10^{-2} M Ag(I) (0 ≤ x ≤ 5), the discoloration of Rhd B became very fast, and increased linearly with the increase of Ag(I) concentration. The repetition of the experiment with an initial concentration of KSP and Ag(I) equal to 0.01 M gave the same results but the discoloration is slower ($k_{obs} = 0.226\times[Ag^+] + 2\times10^{-5}$, with $R^2$: 0.982) (Fig. 6). No Scavenger effect is observed with Ag(I) as was the case with Fe(II). Similar result is observed during the discoloration of crystal violet by KSP [27]. For another initial concentration of KSP and Ag(I) (2.5x10^{-3} M), the increase in Ag(I) concentration in the reactional mixture increases slightly the rate constant, whereas in the same conditions, the rate constant is higher with Fe(II). The order with respect to Rhd B in presence of Ag(I) becomes zero order, whereas it is rather 2 in presence of Fe(II), so the action of Ag(I) on the discoloration of Rhd B by KSP is different from that of Fe(II).

**Effect of wastewater constituents**

The high redox potential of sulfate free radical makes it very reactive in destroying organic contaminants. However, parallel reactions with other species, could result in scavenging of sulfate radical and could possibly limit its oxidation efficiency. Competition for sulfate radical could be from wastewater constituents such as chloride ions, carbonate and phosphate [45]. The equations below show the chemical reaction mechanism of persulfate with chlorides in aqueous solutions [31]:

$$SO_4^{2-} + Cl^- \leftrightarrow SO_3^{2-} + Cl^−$$

$$Cl^− + Cl^− \leftrightarrow Cl_2^−$$

$$Cl_2^− + Cl_2^− \leftrightarrow Cl^− + Cl_2^+$$

When chloride concentrations were less than 0.05 M, presence of chloride ions had insignificant impacts on Rhd B degradation. However, beyond these concentration levels, Rhd B degradation rates reduced significantly with an increase in chloride concentrations (Fig. 7a). The presence of sulfate or carbonate even in high concentration (0.5 M) did not reduce the discoloration...
rate significantly. Chloride was the ion that had the most negative effect. The reaction between sulfate and sulfate radical will generates sulfate radical. Similar results are observed with Lee et al. [31] and Soares et al. [12].

**Effect ethanol and surfactant**

Ethanol decreases the discoloration rate of Rhodamine B. Linear relation is observed between $k_{obs}$ and the volume of pure ethanol added ($k_{obs} = -0.373 \times V(\text{ethanol}) + 1.87$ with $R^2:0.985$). The presence of SDS in low concentration ($1 \times 10^{-4}$ M - $4 \times 10^{-4}$ M) did not affect the discoloration rate of Rhodamine B by KSP. The increase in SDS concentration did not allow the measurement of the absorbance accurately due to the micelle formation.

**Effect of Temperature**

The increase in temperature ($15^\circ C$ – $33^\circ C$) increases the discoloration rate of Rhodamine B (Fig.7b). The activation parameters associated with the discoloration are calculated according to Arrhenius and Eyring equations [27] (Table 2). The activation energy in presence of Fe(II) is lower than in its absence. The decrease in the activation energy in presence of Fe(II) confirms the catalyst effect of Fe(II) (metal activation).

**CONCLUSIONS**

The discoloration of Rhodamine B is pseudo first order with respect to Rhodamine B and to persulfate. The discoloration increases with temperature, in acidic medium, after addition of Fe(II) and Ag(I), but decreases with the addition of NaCl and ethanol. There was no effect on the rate constant upon addition of Cu(II), Ni(II), or Co(II) and carbonate. Colored intermediate products are observed by TLC during the discoloration. The reaction of Rhodamine B with KSP leads probably to total mineralization of the dye.

**REFERENCES**


<table>
<thead>
<tr>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^#$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^#$ (kJ mol$^{-1}$ K$^{-1}$)</th>
<th>$\Delta G^#_{298}$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>36.5 (27.3)</td>
<td>34 (24.8)</td>
<td>- 0.198 (-0.201)</td>
<td>93.0 (86.8)</td>
</tr>
</tbody>
</table>

Table 2. Activation thermodynamic parameters of the degradation of Rhodamine B by persulfate. ($12$ mg L$^{-1}$ Rhod B ($2.5 \times 10^{-3}$ M) + $0.01$ M K$_2$S$_2$O$_8$) The values between () correspond to those in presence of $5 \times 10^{-3}$ M Fe(II).


32. C.S. Liu, K. Shih, C.X. Sun, F. Wang, Oxidative degradation of propachlor by ferrous and copper ion...


THE INFLUENCE OF FERTILIZATION UPON THE CONTENT OF MOLYBDENUM IN TOMATOES

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ABSTRACT

The molybdenum content in the stems, leaves and fruit of tomatoes was determined by a new extraction method with Triphenyltetrazolium chloride. The method is rapid and simple with good reproducibility. It was established that fertilization has an effect upon the molybdenum content in the plant samples of tomatoes. Results show that the accumulation of molybdenum in tomatoes strongly depends on the chemical composition of the fertilizer, the content of molybdenum in it and the amount of fertilizer necessary for fertilization of the soil.

Keywords: molybdenum determination, triphenyltetrazolium chloride, plants, fertilization.

INTRODUCTION

The content of heavy metals in fruits and vegetables is one significant problems in terms of protection of health of people and environment. These elements have influence on the physiological processes in the plant itself, its development and yield. Moreover, heavy metals in products may have negative influence on the health of people.

Elements like Fe, Cu, Ni, Co, Mn, Mo, Zn, V, Cr belong to the group of biogenic microelements which contains mainly heavy metals. These elements are indispensable in too small amounts for growing, development and normal fruitfulness in plants [1]. A lot of research has been done [2-6] for clarification of the role of the biogenic elements in activation of different physiological and biochemical processes in plant, animal and human organism. From all publications it can be seen that biogenic microelements can catalyse many biological reactions, they differ with high and versatile biological activity. They take part in the regulation of oxidation-reduction processes, as they have direct or indirect influence on photosynthesis, breathing and biosynthesis of carbohydrates, proteins, vitamins, pigments.

The biogenic element molybdenum takes part in the processes of fixation of the atmospheric nitrogen [7]. In publications [8, 9] it is proved that in deficiency of molybdenum in the nutrient medium, in the tissues of plants huge amounts of nitrates are accumulated, some physiological diseases are provoked and nitrogen exchange is upset.

Molybdenum affects the biochemical processes and chemical composition of plants. It is a transition element which is essential for most organisms and occurs in more than 60 enzymes, catalyzing diverse oxidation-reduction reactions [10, 11]. Many researchers [2, 8, 12, 13] have studied thoroughly the role of molybdenum as a constituent of the enzyme nitratereductase, with the help of which the nitrates in plants can be reduced. For this reason the molybdenum content in the crop production should be controlled [14 - 18].

It is established that some physiological diseases in plants are caused by molybdenum deficiency. Most sensitive to the deficiency of molybdenum are some vegetable crops, like tomatoes that are the subject of the present research. Tomatoes belong to plants which are
indicators of molybdenum deficiency and some visual symptoms appear on them [1, 19].

In [20] it is determined that the high concentrations of molybdenum have positive influence upon the content of antioxidants in the fruit of tomatoes. There is similar research about the biogenic microelement manganese in the vegetable crop tomatoes. In [21], the content of manganese in tomatoes was investigated from the point of view of its changes with fertilization and yield. It was established that the presence of manganese in soil leads to its accumulation in tomatoes, and in fertilization its extraction from soil, as well as its assimilation by plant and amassment in fruit are easier [22]. In this publication it was determined that the content of antioxidants in tomatoes like vitamin C, lycopene and β carotene is not influenced by the content of Mn.

In [31 - 33] the influence of different fertilization upon growth, yield and nutrition status of tomatoes is studied.

The aim of the present research was to trace out how the content of molybdenum in the fertilizer and soil influenced the accumulation of this microelement in tomatoes. With this aim, two fertilizers were used - potassium sulphate and potassium nitrate with different content of molybdenum, and soil with low content of this metal. In view of obtaining more specific information, two methods concerning the analysis for the content of molybdenum in plants were used.

**EXPERIMENTAL**

The experiment was carried out in eight variants at two levels of potassium fertilization, as two sources have been tested - potassium sulfate and potassium nitrate. The plants were cultivated in seedlings in a steal-glass hot-house.

Before setting the trial for determining the type and rate of fertilizers to be applied in the main fertilization and in monthly feeding-up of the plants, an agrochemical analysis of the soil in a water extraction had been performed. The mineral nitrogen (\(\text{NH}_4\text{N} + \text{NO}_3\text{N}\)) - 2.1 mg/100g soil, the mobile forms of \(\text{P}_2\text{O}_5\) and \(\text{K}_2\text{O}\) - 20.5 mg and 17.7 mg/100 g soil, respectively, the humus content - 2.1 % and soil reaction \(\text{pH}_{(\text{H}_2\text{O})}\) - 6.9 - 7.0 have been determined.

The basic fertilization was carried out on the basis of the agrochemical analysis of the soil and it comprised of 30 kg/dka of triple superphosphate and potassium fertilizer. Nitrogen was applied three times: before planting, first earthing up, and 20 days later in the form of \(\text{NH}_4\text{NO}_3\). Potassium was applied twice: before planting and emergence of the first raceme, as large as a peanut. The fertilization of soil was done with 16 kg/dka, 32 kg/dka and 48 kg/dka, respectively, with \(\text{K}_2\text{SO}_4\) and \(\text{KNO}_3\).

**Preparation of soil for analysis of molybdenum**

The experimental work was carried out on a strongly leached meadow-maroon soil. A sample of 1 g of air-dry soil (previously ground and sieved) was extracted with a nitric acid mixture (32 mL of nitric acid 15.8 mol/L, r » 1.42 g/ml), diluted with water to 1 litre) and left for 16 h at a room temperature, followed by boiling under reflux for 2 h [23]. Then the extract was clarified and made up to the volume of 50 ml with nitric acid. Molybdenum was determined in this very solution using flame atomic absorption spectrometry.

**Determining molybdenum in fertilizers**

Two fertilizers have been tested - potassium sulphate (consisting of \(\text{K}_2\text{O} - 50 \%\); \(\text{Cl} - 1.5 \%\); \(\text{MgSO}_4\) and \(\text{CaSO}_4\) - 5.2 %) and potassium nitrate (consisting of nitrogen - 13.5 %; \(\text{K}_2\text{O}\) - 46 %). 1 g \(\text{K}_2\text{SO}_4\) and 8 g \(\text{KNO}_3\) were dissolved in distilled water and then added to the volume of 50 ml. Mo in these solutions was determined by flame atomic absorption spectrometry.

**Determining molybdenum in plant material**

A wet burning of the plant samples was carried out and a mixture of sulfuric and nitric acids were used for the oxidation of the organic substance. A portion of 2 g of air-dry plant material was placed into a Kjeldahl flask and moistened with 4 ml distilled water. 5 ml conc. sulfuric acid and 10 ml conc. nitric acid were added. The flask was slightly heated to avoid splashing of the solution, decomposition and fuming away of nitric acid. When all the organic material was oxidized, the solution was heated at a higher temperature for 10 min [24]. After cooling, it was diluted with water and filtered. Then the solution was transferred into a volumetric flask of 50 ml and diluted up to the mark with distilled water. Aliquot parts of this solution were taken for analysis.

In plant material molybdenum is determined by a new extraction spectrophotometric method with triphosphate.
nyltetrazolium chloride developed by us [25] and a TV method [26].

Different methods for analysis for the content of elements in plants can be used [29, 30].

Method with triphenyltetrazolium chloride

An analysis for molybdenum content in variants of plant samples was carried out using a new extraction method with Triphenyltetrazolium chloride (TTC). Molybdenum(VI) forms an ion-pair with the tetrazolium cation of triphenyltetrazolium chloride which is extracted in 1,2-dichloroethane. The method is presented in detail in [25].

Apparatus - Spectrophotometer UV-VIS, Carl Zeiss Jena (Germany) with 1-cm light path quartz cells; Atomic Absorbtion Spectrophotometer Perkin Elmer (Germany).

RESULTS AND DISCUSSION

The form in which molybdenum is translocated is unknown, but its chemical properties indicate that it is most likely transported as MoO\textsubscript{4}\textsuperscript{2-}, rather than in a complexed form. The proportion of various molybdenum constituents in plants naturally depends on the quantity of molybdenum absorbed and accumulated in the tissue. Plants preferentially absorb MoO\textsubscript{4}\textsuperscript{2-} and therefore the molybdenum nutrition of plants can be manipulated by altering soil acidity. The speciation and availability of molybdenum in the soil solution is a function of pH. At water pH >5.0 molybdenum exists primarily as MoO\textsubscript{4}\textsuperscript{2-}, but at lower pH levels the HMoO\textsubscript{4} forms dominate.

Plants differ in their ability to absorb molybdenum from the root medium, and the sufficiency range for molybdenum in plants varies widely. The source of nitrogen supplied to plants influences their requirement for molybdenum. Nitratefed plants generally have a high requirement for molybdenum. The strong depressive effect of SO\textsubscript{4}\textsuperscript{2-} on MoO\textsubscript{4}\textsuperscript{2-} uptake can lower the molybdenum concentration in plants to levels that are nontoxic.

The content of molybdenum in soil and fertilizers used in the experiment is presented on Table 1. As can be seen, the content of Mo in soil is low - 1 mg/kg. The amount of naturally occurring molybdenum in soils depends on the molybdenum concentrations in the parent materials. The total molybdenum content of soils differs by soil type and sometimes - by geographical region.

Table 1. Content of molybdenum in soil and fertilizer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mo, mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>1</td>
</tr>
<tr>
<td>Potassium sulphate</td>
<td>18.93</td>
</tr>
<tr>
<td>Potassium nitrate</td>
<td>8.74</td>
</tr>
</tbody>
</table>

Table 2. Content of Mo in tomatoes in different fertilization.

<table>
<thead>
<tr>
<th>Fertilization</th>
<th>Yield kg/dka</th>
<th>Content of Mo mg/kg dry matter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>FRUIT</td>
</tr>
<tr>
<td>basic fertilization</td>
<td>3245</td>
<td>11.0</td>
</tr>
<tr>
<td>fertilization with</td>
<td></td>
<td></td>
</tr>
<tr>
<td>48 kg/dka K\textsubscript{2}SO\textsubscript{4}</td>
<td>4737</td>
<td>10.0</td>
</tr>
<tr>
<td>fertilization with</td>
<td></td>
<td></td>
</tr>
<tr>
<td>48 kg/dka KNO\textsubscript{3}</td>
<td>4917</td>
<td>30.53</td>
</tr>
<tr>
<td>fertilization with</td>
<td></td>
<td></td>
</tr>
<tr>
<td>32 kg/dka K\textsubscript{2}SO\textsubscript{4}</td>
<td>4298</td>
<td>11.07</td>
</tr>
<tr>
<td>fertilization with</td>
<td></td>
<td></td>
</tr>
<tr>
<td>32 kg/dka KNO\textsubscript{3}</td>
<td>4361</td>
<td>10.16</td>
</tr>
<tr>
<td>fertilization with</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16 kg/dka K\textsubscript{2}SO\textsubscript{4}</td>
<td>3767</td>
<td>32.65</td>
</tr>
<tr>
<td>fertilization with</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16 kg/dka KNO\textsubscript{3}</td>
<td>4315</td>
<td>10.12</td>
</tr>
</tbody>
</table>

*Relative Standard Deviation for TTC method (n = 4)
Soils normally contain between 0.013 and 17.0 mg kg\(^{-1}\) total molybdenum [27].

In the fertilizers the content of molybdenum is significantly higher. For the fertilizer potassium sulphate its content is more that two times higher than its content in fertilizer potassium nitrate. Besides the molybdenum in soil determined by analyses, the following elements can be found as well, in mg/kg: Ca - 3171, Mg - 3834, Fe - 149.6, Zn - 110.6 and Cu - 40.6.

The content of molybdenum in tomatoes related to fertilization is presented in Table 2. In plant material molybdenum is determined by means of the new extraction spectrophotometrical method with triphenyltetrazolium chloride developed by us [25] and the TV method [26], for comparison. The experimental data from both methods show that the proposed extraction spectro-photometrical method with Triphenyltetrazolium chloride can be successfully used for determination of microquantities of molybdenum in plant material.

As can be seen, despite the low content of molybdenum in soil of 1 mg/kg in the basic fertilization, in the fruit about 11 mg/kg Mo can be found. This content changes significantly different for fertilization with the different fertilizers. Fertilization with potassium sulphate which is with higher content of molybdenum, leads to an abrupt increase in the content of molybdenum in the fruit of tomatoes but with the increase of the fertilization norm, this content decreases. In fertilization with 48 kg/dka the content of molybdenum in the fruit of tomatoes is lower than that in the basic fertilization. In fertilization with potassium nitrate the effect of the increase of the content of molybdenum in the fruit of tomatoes can be seen in the higher degree of fertilization.

Plants can absorb nutritious substances from the environment not only with their rhizome, but with the rest of their overground organs - stems and leaves. The absorption of substances is a surface process which indicates that from all of the overground organs leaves are with much significance, because of their larger surface. The content of molybdenum changes in an analogous way in the leaves of tomatoes (Table 2). It is necessary to mention that the content of molybdenum in leaves in basic fertilization is about three times higher than that in the fruit of tomatoes. The basic fertilization was carried out on the basis of the agrochemical analysis of the soil with 30 kg/dka of triple superphosphate and potassium fertilizer. Differences in change of the content of molybdenum in the leaves and fruit of tomatoes can be seen in the fertilization with potassium nitrate. Initially, fertilization leads to decrease in the content of molybdenum in leaves, but after that it increases proportionally in the tomatoes (fruit).

In fertilization with potassium sulphate in stems (Table 2), the content of molybdenum changes in a different way than that in fruit and leaves. The experiment shows that in fertilization with potassium nitrate, the content of molybdenum in fruit, leaves and stems changes in a similar manner. In all instances, in stems the initial high content of molybdenum from the basic fertilization decreases, but with the increase of the fertilization norm begins to increase. Still the initial values that correspond to the basic fertilization cannot be reached.

These results show that the accumulation of molybdenum in tomatoes strongly depends on the chemical composition of the fertilizer, the content of molybdenum in it and the amount of fertilizer necessary for fertilization of the soil.

As yield and quality not always change in parallel, a higher significance attains the effect of fertilization on the nutritious value of the production, which is very important for human health. Fertilization itself together with other agronomical projects, provides an opportunity for obtaining high yields. In this aspect, the subordination between yield and the content of molybdenum was investigated.

The general conclusion that can be drawn from the above discussed results is that when using as fertilizer potassium sulphate, fertilization between 32 and 48 kg/dka should be preferred, whereas when using the fertilizer potassium nitrate, fertilization should be limited up to 32 kg/dka.

---

Table 3. Ratio of nitrogen, phosphorus, potassium in different fertilization.

<table>
<thead>
<tr>
<th>N</th>
<th>Variants</th>
<th>N : P : K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>basic fertilization</td>
<td>1.5:1.3:0</td>
</tr>
<tr>
<td>2</td>
<td>K(_6) (K(_2)SO(_4))</td>
<td>1.5:1.3:1.0</td>
</tr>
<tr>
<td>3</td>
<td>K(_{16}) (K(_2)SO(_4))</td>
<td>1.5:1.3:1.3</td>
</tr>
<tr>
<td>4</td>
<td>K(_{24}) (K(_2)SO(_4))</td>
<td>1.2:1.0:1.5</td>
</tr>
<tr>
<td>5</td>
<td>K(_6) (KNO(_3))</td>
<td>1.5:1.3:1.0</td>
</tr>
<tr>
<td>6</td>
<td>K(_{16}) (KNO(_3))</td>
<td>1.5:1.3:1.3</td>
</tr>
<tr>
<td>7</td>
<td>K(_{24}) (KNO(_3))</td>
<td>1.2:1.0:1.5</td>
</tr>
</tbody>
</table>
It should be noted that the content of molybdenum in the leaves of tomatoes is higher than that in stems and fruit. Maybe this is due to the fact that the most important processes of change in substances take place in the green leaves. It is proved that higher amounts of molybdenum can be found in leaves. Microelements that enter there can do good for the growing and development of the plants.

The effect of fertilization on increasing plant yield is often related to an increased ability of the plant to utilize nitrogen. The activities of nitrogenase and nitrate reductase are affected by the molybdenum status of plants, and their activities are often suppressed in plants suffering from molybdenum deficiency.

The molybdenum nutrition of plants can be affected by the interaction of molybdenum with other nutrients in the soil, such as phosphorus and sulfur. The experiment shows that with the increase of the content of sulphur introduced in the soil as the fertilizer K$_2$SO$_4$, the amount of the absorbed Mo by plants decreases. This can be seen from the analysis of stems, leaves and fruits of tomatoes for Mo content. It is well established that the plant uptake of molybdenum is enhanced by the presence of soluble phosphorus and decreased by the presence of available sulfur. The effect of sulfur on molybdenum absorption by plants appears to be related to the direct competition between SO$_4^{2-}$ and MoO$_4^{2-}$ during root absorption. This subordination is confirmed by research of other authors [28]. They showed that the addition of SO$_4^{2-}$ to the culture medium reduced absorption of radioactive molybdenum by tomatoes, and decreased molybdenum absorption by tomatoes (Lycopersicon esculentum Mill.) in soil. Sulfate and MoO$_4^{2-}$ are strongly competitive during root absorption, and sulfur fertilization has been shown to decrease the uptake of molybdenum by plants.

Plants differ in their ability to absorb molybdenum from the root medium, and the sufficiency range for molybdenum in plants varies widely. The source of nitrogen supplied to plants influences their requirement for molybdenum. Nitratefed plants generally have a high requirement for molybdenum. The ratios of N: P: K in different kinds of fertilization are given on Table 3. The experiment shows that in fertilization with 16 kg/dka K$_2$SO$_4$ in ratio N:P:K = 1.5:1.3:1.3, the content of Mo is in fruit 32.65 mg/kg, in stems - 22.22 mg/kg, in the leaves - 44.14 mg/kg of tomatoes.

The assimilation of Mo by plants is an intricate physiological process which depends on biological peculiarities of the plant organism, as well as on soil and climatic conditions. The entrance, transport and metabolism of the microelement Mo in plant organisms are in close relationship with the other physiological processes, with the general physiological state of the plant tomatoes and with the character of exchange of rhizome cells.

CONCLUSIONS

Fertilization with potassium sulphate that is with higher content of molybdenum, leads to an abrupt increase in the content of molybdenum in the fruit of tomatoes but with the increase of the fertilization norm, this content decreases.

In fertilization with potassium nitrate the effect of the increase of the content of molybdenum can be seen in a higher degree of fertilization. Differences in the change of the content of molybdenum in the leaves and fruits of tomatoes can be seen in fertilization with potassium nitrate.

These results show that the accumulation of molybdenum in tomatoes strongly depends on the chemical composition of the fertilizer, the content of molybdenum in it and the amount of fertilizer necessary for fertilization of the soil.

A new extraction-spectrophotometric method for the determination of molybdenum with triphenyltetrazolium chloride was used. The method is rapid, simple and with a good reproducibility.

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TEXTURAL CHARACTERISTICS OF SnO\textsubscript{2} - DOPED TITANIA/NANOSILICA AND TRANSITION OF PHASE OF BOUND WATER

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ABSTRACT

The present paper deals with analysis of the textural characteristics of titania/silica composites containing tin (IV) oxide as a dopant in various concentrations. The oxide systems are synthesized by hydrolytic deposition of TiO\textsubscript{2} and SnO\textsubscript{2} onto highly dispersed silica (S\textsubscript{BET} = 294 m\textsuperscript{2}/g). Half of each obtained sample was calcined at 600 °C. Values of the main structural parameters were calculated from adsorption-desorption nitrogen isotherms. \(D_{\text{HH}}\) values combined with atomic force microscopy (AFM) images indicate formation of different aggregates at small, medium and high concentrations of the dopant. Subzero freezing points of bound water \(T_\text{f} < 0\) °C obtained using differential scanning calorimetry (DSC), show the confined space effects depending on structural features of the formed aggregates.

Keywords: SnO\textsubscript{2} doping agent, water phase identification, nano-, meso- and macropores studied.

INTRODUCTION

Titania and related mixed oxides are well-known catalysts [1 - 9]. Their catalytic activity has been shown to be related to both chemical (phase) structure and textural characteristics [7 - 17] depending on the synthesis techniques (e.g., sol-gel [5, 8, 10 - 12, 14 - 18], CVD [19 - 21], co-precipitation [22 - 24], impregnation [25 - 30], etc.) and reaction conditions (temperature, nature of precursors, stoichiometry, sequence of components introducing, etc.). For instance, it is stated in [17], that increasing TiO\textsubscript{2} content in the aerogels provokes dropping down specific surface area and pore volume. Hence, the average reaction rate of epoxide conversion described in the mentioned study decreased monotonously. Moreover, it was shown [17] that the reaction selectivity has varied in a strong manner with the conversion. Thus, the higher the titania content, the less the selectivity of silica/titania catalysts. Miller et al. [8] reported of different textural and catalytic properties of prehydrolyzed (two-step hydrolysis technique), PH, and non-prehydrolyzed (one-step hydrolysis technique), NPH, silica/titania composites: the PH-samples possessed higher specific surface area, larger pore sizes and total pore volumes, demonstrating more effective activity in olefins isomerization, when compared to the respective characteristics of the NPH-silica/titania. The effect of drying and heating on S\textsubscript{BET}, pore size distribution, and total pore volume of the silica/titania aerogels was discussed by Brodsky and Ko [18]. They carried out drying procedure at 343 K and 473 K for the mixed oxides. Dropping down S\textsubscript{BET} in the course of calcination of the samples dried at 343 K, goes to almost the same values of specific surface area as for aerogels, dried at 473 K. But the latter have
larger $V_p$ despite its smaller decrease gradient, due to subsequent heating. After calcination both mixed oxide systems lose their ability to catalyze isomerization of 1-butene to cis/trans 2-butene.

The behavior of water, i.e. water phase transition, confined in various materials was studied using differential scanning calorimetry (DSC) to discover different states of water in free or bound forms [31 - 35]. According to the rules, bound water is unfrozen at subzero temperatures and its content depends on various conditions, such as the number of freezing-thawing cycles; amount, sizes and shapes of pores; cooling-warming rate, etc. In fact, the thermodynamics of water confined in pores may be described by the Gibbs-Thomson relation for the freezing point depression [34, 36, 37] derived from the Kelvin equation for adsorbates interacting with the pore walls [36, 38]:

$$\Delta T = T_{\text{bulk}} - T_{\text{pore}} = 2T_{\text{bulk}}(\sigma_{\text{wall-ice}} - \sigma_{\text{wall-water}})V_{\text{water}} / R \cdot \Delta H$$

where $T_{\text{bulk}}$ and $T_{\text{pore}}$ correspond to the bulk and pore transition (freezing or melting) temperatures, $\sigma_{\text{wall-ice}}$ and $\sigma_{\text{wall-water}}$ represent wall-solid and wall-liquid interfacial tensions, $V_{\text{water}}$ molar volume of water, $R$ - pore radius, $\Delta H$ - molar enthalpy of phase transition. Thin layers of water being close to the pore walls are formed and their phase transition temperature ($T_m$) differs from the value for bulk water (273.15 K). The reduction of the phase transition point $\Delta T$ is inversely proportional to the pore radius $R$. As a rule, this phenomenon is characterized by formation of bound water and belongs to first-order phase transition.

Our work undertakes to survey textural characteristics of the triple system silica/titania, doped by tin (IV) oxide, depending on SnO$_2$ concentration and calcination effect, and thermal properties of water inside the voids between synthesized oxide particles.

**EXPERIMENTAL**

The mixed oxides were synthesized by low-temperature hydrolysis of SnCl$_4$ and TiCl$_4$ to deposit SnO$_2$ as a doping agent and TiO$_2$ - as a functional phase onto the silica surface. The synthesis was carried in a glass reactor, equipped with a mechanical Teflon stirrer, an air blow-through emitter device and a heating system. Nanosilica A-300 (50 g, $S_{\text{BET}} = 294$ m$^2$/g produced at a pilot plant at Chuiko Institute of Surface Chemistry, Kalush, Ukraine) was added into the reactor after pre-heating (6 h at 450°C in a muffle), and then a portion of water, enough for hydrolysis, was added within stirring at room temperature. In 1 h saturated solution of SnCl$_4$ was introduced to form SnO$_2$ from 0.14 up to 30 mass % against titania. Then in 30 min TiCl$_4$ was injected into the mixture to generate TiO$_2$ in 15 mass % against nanosilica. After all the precursors had been added, the system was heated up to 100°C and thermally treated during 1.5 h at stirring. To remove HCl the reactor has been blown through by the air stream for 1 h. Finally the mixture was cooled down to room temperature.

All obtained samples were heated to 100°C in a drying box and kept for 3 h in order to remove residual water and hydrochloric acid. Each triple composite signed as SiO$_2$/SnO$_2$/TiO$_2$ was halved and one part was calcined at 600°C for 6 h, until anatase as a crystalline phase of TiO$_2$, was formed, and the part of the samples was left untreated.

To analyze the textural properties of the nanocomposites, low-temperature nitrogen adsorption-desorption isotherms were recorded using a Micromeritics ASAP 2405N adsorption analyzer. The specific surface area ($S_{\text{BET}}$) was calculated according to the standard BET method [38 - 40]. The total pore volume $V_p$ was evaluated using the nitrogen adsorption data at relative pressure $p/p_0 \approx 0.98 – 0.99$. To calculate the pore size distributions, the data from the desorption branch were used. The proposed computational way is based on usage of a regularization procedure under non-negativity condition for the pore size distribution function ($f(R_p) > 0$ at any pore radius $R_p$), at fixed regularization parameter $\alpha = 0.01$. The pores as the voids between spherical particles packed in random aggregates were examined. This approach based on the Nguyen-Do method [41, 42] was modified to be applied for various nanomaterials. The $f_s(R_p)$ and $f_s(R_p)$ functions were used to estimate contributions of different types of pores (classified according to their sizes) to total pore volume $V_p$ and specific surface area $S_{\text{BET}}$: nanopores ($V_{\text{nano}}, S_{\text{nano}}$ at $R_p < 1$ nm), mesopores ($V_{\text{meso}}, S_{\text{meso}}$ at $1 \leq R_p < 25$ nm) and macropores ($V_{\text{macro}}, S_{\text{macro}}$ at $R_p > 25$ nm) [43]. To verify the model, the criterion $\Delta w$ is used [44]:

$$\Delta w = \frac{S_{\text{BET}}}{\int_{R_{\text{min}}}^{R_{\text{max}}} f_s(R_p)dR_p} - 1$$

It reflects the condition of the appropriate use of the proposed pore model.
The calculation of nanooxide fractality (roughness) was performed on the basis of the FHH- method [40], described in detail by Avnir and Jaroniec [45]. These can be used in the range of multilayer adsorption. For this purpose, the adsorption branch within $p/p_0 = 0.01 \div 0.8$ values has been used, where attraction between adsorbent and adsorbate is caused chiefly by van der Waals forces [45, 46]. Fractal Dimension ($D_f$) is calculated from the plot corresponding to the eq. 2:

$$\ln(V/V_0) = (D_f - 3) \cdot \ln(\ln(p_0/p)) + \text{const},$$

where $V$, $V_0$ are the adsorbed and saturation volumes of nitrogen, respectively; $p$ and $p_0$ are the equilibrium and saturation pressure of the adsorbed nitrogen, respectively.

The morphology was studied using AFM (NanoScope V, Veeco, USA) with 5120×5120 pixel density and resolution power of 0.1 nm.

Phase transitions of water were studied with the DSC method (DSC PYRIS Diamond Perkin Elmer, USA) with scanning rate of 5°C/min, and thermal parameters such as water freezing enthalpy $\Delta H_{\text{water}}$ and temperature $T_{\text{water}}$ were estimated from the calorimetric diagrams.

RESULTS AND DISCUSSION

All curves of the nitrogen adsorption isotherms for composites (Fig. 1) are of type II (corresponding to the textural porosity of powders with nonporous nanoparticles) [40] and characterized by presence of narrow hysteresis loops. For non-calcined samples, the loop onset is observed at higher pressure ($p/p_0 \approx 0.8$) than that for calcined samples (0.7). This is owing to stronger aggregation of the nanoparticles in aggregates, after calcination. Additionally, for samples at $C(\text{SnO}_2) = 1 - 5$ mass %, the $S_{\text{BET}}$ value decreases after calcination (Tables 1 and 2). Changes in the $S_{\text{BET}}$ values are of a nonlinear character with the increase of dopant content in both systems. The highest value is for thermally untreated composite at 4 mass % of SnO$_2$ (Table 1, Fig. 2).

Actually, the largest magnitudes of the specific surface area are observed at middle concentrations (1 - 6 mass %), as compared to minimal and maximal amounts of dopant. The calcination brings to other, more complex behavior of $S_{\text{BET}}$ on plot of Fig. 2: there is a maximum at $C(\text{SnO}_2) = 6$ mass %, viewed among other composites and this value is higher than that for the sample without treatment. The specific surface area

<table>
<thead>
<tr>
<th>$\text{SiO}_2/\text{SnO}_2/\text{TiO}_2$</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>$S_{\text{nano}}$ (m$^2$/g)</th>
<th>$S_{\text{meso}}$ (m$^2$/g)</th>
<th>$S_{\text{macro}}$ (m$^2$/g)</th>
<th>$V_p$ (cm$^3$/g)</th>
<th>$V_{\text{nano}}$ (cm$^3$/g)</th>
<th>$V_{\text{meso}}$ (cm$^3$/g)</th>
<th>$V_{\text{macro}}$ (cm$^3$/g)</th>
<th>$R_p$ (nm)</th>
<th>$\Delta w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>non-calcined C(\text{SnO}_2)$_2$ mass %</td>
<td>0.14</td>
<td>244.6</td>
<td>12.3</td>
<td>222.7</td>
<td>9.5</td>
<td>0.468</td>
<td>0.005</td>
<td>0.325</td>
<td>0.138</td>
<td>11.6</td>
</tr>
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<td>1</td>
<td>272.0</td>
<td>22.6</td>
<td>243.1</td>
<td>6.3</td>
<td>0.449</td>
<td>0.009</td>
<td>0.342</td>
<td>0.098</td>
<td>10.1</td>
<td>-0.195</td>
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<th>$S_{\text{nano}}$ (m$^2$/g)</th>
<th>$S_{\text{meso}}$ (m$^2$/g)</th>
<th>$S_{\text{macro}}$ (m$^2$/g)</th>
<th>$V_p$ (cm$^3$/g)</th>
<th>$V_{\text{nano}}$ (cm$^3$/g)</th>
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is smaller in the non-calcined samples with dopant’s low concentration, and at 10 and 30 mass % it comes to increase in comparison to the calcined analogues. This phenomenon can illustrate the dependence of particles morphology on the SnO\(_2\) content. The doping oxide provokes more intensive consolidation of the particles by heating at low concentrations than at the high ones.

The verification parameter \(\Delta w\) takes the absolute values from \(|0.020|\) to \(|0.256|\) (Table 1), and shows a good agreement of the proposed pore model with the real one.

The data (Tables 1 and 2) demonstrate that the main contribution to pore size corresponds to mesopores - more than 80 % for all studied SiO\(_2\)/SnO\(_2\)/TiO\(_2\) systems.

At low concentrations of the dopant, the contribution of nanopores \(S_{nano}\) decreases slightly after calcination and \(S_{meso}\) share is growing up, as clearly visible. As a matter of fact, nanovoids at \(R < 1 \text{ nm}\) could cause the difference between the \(S_{BET}\) values at low concentrations of SnO\(_2\) for both systems (Fig. 4). Macropores do not exert a significant impact on \(S_{BET}\) change profile. Thus, the SBET changes may be a function of nano- and mesopores contributions.

Despite the negligible effect on SBET, macropores contribute to the total pore volume. The increment of \(V_p\) with \(R_p\) growth (Fig. 4) and the incremental pore
size distributions (IPSDV) for all types of pores (Fig. 5) reaffirm the predominant role of mesopores. However, the calcination results in growth of the macropores contribution, especially at \( C(SnO_2) = 0.14, 1, 4, 5 \) and 10 mass %. This is clearly seen by the peak shift on the IPSDV, plotted against large pore sizes (Fig. 5, b). By way of illustration, in the case of \( C(SnO_2) = 4 \) mass % the macropore share is augmented almost 2 times after calcinations, as compared to the initial analogue showing a multimodal character of the PSD. It should be pointed out that the composite at \( C(SnO_2) = 6 \) mass % demonstrates stability in the PSD before and after calcination.

As the PSD diagrams and data (Tables 1 and 2) show, if the composite contains \( SnO_2 \) at concentration of 30 mass %, high temperature brings the opposite effect, since the macropores are of appreciable prepotency before calcination and their share is 1.3 times higher than that without calcination.

Thereby, we keep observing lack of correlation between \( S_{BET} \) and \( V_p \) within the dopant concentration change, since it is precisely this fact that is explained by availability of textural porosity and non-uniformity of the pore shapes. The value of specific surface area is defined by the composite particle sizes and the total pore volume of voids between nanoparticles. Atomic force microscopy (AFM) images of composites at \( C(SnO_2) = 0.14, 5 \) and 30 mass % (Fig. 6, a-f) show certain changes in the aggregate morphology. The more compacted aggregates of non-calcined SiO\(_2\)/SnO\(_2\)/TiO\(_2\) at \( C(SnO_2) = 0.14 \) mass % (Fig. 6, a) cause \( S_{BET} \) diminution since the specific surface area of calcined SiO\(_2\)/SnO\(_2\)/TiO\(_2\) is larger (Tables 1 and 2, Fig. 6, d). The oxide systems at the middle of the doping oxide concentration at \( C(SnO_2) = 5 \) mass % exhibit marked consolidation of the aggregates, arranged into an ordered structure due to calcination. The situation at \( C(SnO_2) = 30 \) mass % for both systems is the outcome of the complex relation between \( V_p \) and \( S_{BET} \).

As it has been noted, the number of macropores drops down after calcinations, but \( S_{BET} \) gets a little larger since its losses relative to nanosilica \( S_{BET} \) are 28.2 and 23.7 % for non-calcined and calcined samples, respectively. The heated system becomes more compact, including smaller oxide particles (Fig. 6-e,f) by comparison to the uncalcined sample. The latter contains agglomerates built of aggregates with large voids (Fig. 6-b,c).

Fig. 7 shows surface roughness dependence by fractal dimension (\( D_f \)) values. It was established that the values obtained are from 2.40 to 2.65. In our case, the formation of pore structural stuff [46] has been built from aggregates, i.e. the pattern of the objects is far from the isotropic form. Fig. 7 shows that, there are two
slants seen on the plot $D_s - C(\text{SnO}_2)$ for both systems, which is in close dependence on the SnO$_2$ content. The trends have obverse characters, which may be caused by the heating effect. At concentrations of SnO$_2 = 0.14 - 4$ mass %, the $D_s$ values of the calcined samples are a little smaller than those in noncalcined composites.

Calorimetric investigations clear up the realization of the processes of pore structure changes. The peaks situated in Fig. 8 and Fig. 9 indicate appearance of bound water, which is characterized by depression of the freezing point ($t_{fr} < 0 \, ^\circ\text{C}$), relative to the freezing point of free bulk water ($t_{fr} = 0 \, ^\circ\text{C}$).

The peaks areas under the appointed base line, correspond to the specific enthalpies of water freezing $\Delta H$ ($J/g$) and their absolute values illustrate the quantity of frozen water confined in the oxide composites (Table 3).

Except for sample at $C(\text{SnO}_2) = 0.14$ mass %, all other samples exhibit decrease in $\Delta T$, showing that the number of narrow pores drops down. This is a natural corollary of the heating effect.

The systems, most concentrated by dopant (Fig. 8, 9-c), have bimodal profiles even after calcination. The higher-temperature peak stays at the same phase transition position ($t \approx -4 \, ^\circ\text{C}$). This may be explained by a stable domain shaping inside the large pores (macropores), because their amount steepens after calcination. However, the values of the enthalpies of freezing for all calcined samples are higher, and their changes are non-linear in the course of the rise in dopant content.
The calcination effect causes elimination not only of bulk water after synthesis, but also of the molecules bound chemically and physically inside the composites structure, i.e. the surface of the calcined composites becomes more active than the non-calcined ones. Thus, water is adsorbed in a large quantity in contact zones of adjacent nanoparticles in aggregates of the annealed silica/titania composite.

**CONCLUSIONS**

Textural features of SnO$_2$-doped silica/titania composites synthesized via hydrolysis at low-temperature were studied. It has been found that pore size distribution (PSD) profiles of calcined and non-calcined materials are bi- or trimodal, and illustrate: (1) - the mesopore domination giving more than 80 % in both composites, (2) - macropores contribution rise after calcination in systems doped with 0.14; 1; 4; 5 and 10 mass % of SnO$_2$ and (3) - stability of the PSD profile of the system at 6 mass % of SnO$_2$.

It was established that, there is a nonlinear change in the total pore volume and the specific surface area, which increase with SnO$_2$ concentration, that is usual for mixed oxides.

The calculations based on the Frenkel-Halsey-Hill method with values for fractal dimension $D_s$ from 2.40 to 2.65 are usual for nanooxide materials, i.e. the doped silica/titania are formed of aggregates of nanoparticles.

As our analysis shows, congruous changes in the total pore volume vs. the average pore radius indicate that there is no particles consolidation and the voids shapes are kept uniform enough. This is observed for both systems.
Calorimetric data, obtained by the DSC method, corroborate the supposition of higher surface activity of calcined samples on account of bigger water domains formation, which is in line with the higher values of specific freezing enthalpies $\Delta H_{fr}$, observed in the calcined samples. As the results indicate, there is no a linear dependence of $\Delta H_{fr}$ vs. dopant concentration in the both samples sets. The calcination effect causes to shrinkage of the temperature range of endothermal peaks, i.e. the water domains formation becomes more uniform in comparison with the thermally untreated samples.

All samples are shown to be apt to confine water in their voids, i.e. there is only a form of “sub-zero” water, present inside the pores and “in-bulk” water is absent. This confirms agsin the porous character of the synthesized stuff.

Acknowledgements

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REFERENCES


Fig. 9. Thermograms for the SiO$_2$/SnO$_2$/TiO$_2$ composites calcined at 600 °C. C(SnO$_2$): 0.14 (a), 1 (b), 4 (c), 5 (d), 6 (e), 10 (f), and 30 (g) mass %.


30. S. Yoshida, S. Takenaka, T. Tanaka, H. Hirano, H. Hayashi, Highly dispersed titanium oxide on silica:
EFFECT OF pH ON THE CORROSION BEHAVIOUR OF HIGH NITROGEN STAINLESS STEEL IN CHLORIDE MEDIUM

B. Tzaneva

ABSTRACT

The general and pitting corrosion of austenitic Cr23N1.2 steel in 3.5% NaCl solutions have been investigated. The open circuit potential, the cyclic potentiodynamic and the galvanostatic methods have been employed in order to investigate the effect of pH (1-12) on the passivity and the tendency to pitting corrosion. Optical microscopy has been used to detect the surface sites for pit formation and the growth of pit nuclei. The results obtained for chromium–nitrogen steel have been compared with these for austenitic 304 stainless steel. The results from the galvanostatic method confirm these, received by potentiodynamic method that in the region of pH 2-10, the character of the environment has not an important influence on the protective properties of the passive layers formed in 3.5% NaCl solutions. In spite the similar electrochemical results, a considerable difference in the pit shape and the pit initiation sides is established.

Keywords: corrosion resistance; pitting; high nitrogen stainless steel; pH; sodium chloride; galvanostatic; cyclic potentiodynamic polarisation

INTRODUCTION

Corrosion resistance of the stainless steels generally depends on the stability of the passive layers, formed on their surface. Regarding this, one of the most important parameters is the hydrogen index of the environment (pH). It is well known, that pH affects directly the cathodic processes of hydrogen and oxygen depolarisation. pH has strong influence also on the kinetics of the anodic processes through solubility of the corrosion products and theirs protective properties. In general, in both neutral and alkaline environments, the stainless steel passive layers are stable, because of the incorporation of hydroxide groups in their composition. Lowering the pH value favours the dissolution of the passive film and hence makes worse its protective properties [1]. According to Rozenfeld [2], the dependence of the corrosion potential on pH for the steel Cr18Ni10Ti in 0.1M NaCl is expressed as follows:

\[ E = a + b \log \text{pH}, \]

where \( a = 0.40 \) and \( b = 0.03 \) are experimentally obtained constants. Other authors have found that a critical value of pH exists, under which the corrosion rate sharply increases. Thus, for the steel Cr18Ni9, the critical pH value is 1.5 [3]; for chromium and chromium-nitrogen steels it is about pH 3 [4].

The stability of the passive state of the stainless steel depends also on the presence of aggressive ions in the environment, such as chloride ions. In this case under anodic polarisation above a critical potential value, defined as pitting potential (\( E_{\text{pit}} \)), a local breakdown of the protective layers occurs and pitting corrosion takes place. The free corrosion potential of the metal can be shifted in positive anodic direction not only by external polarisation, but also by oxidizing agents in the environment like oxygen, whose potential depends on pH. The pitting potential is not neither thermodynamically, nor kinetically defined value. It depends on both, the...
electrochemical heterogeneity of the surface and the processes of formation and repassivation of pits nuclei. Therefore, the determination of the pitting corrosion resistance of steels can be done only on the base of the experimental results. According to some authors, pH of the environment in the region 3–9 does not have considerable influence on the potentials of pitting and repassivation of stainless steels [5–8].

The presented paper describes a part of the study, related to assessment of the stability of nickel-free high nitrogen stainless steel Cr23N1.2 against general and pitting corrosion in chloride environments with pH 1–12. The results are compared to these for conventional austenitic chromium-nickel stainless steel Cr18Ni9 (AISI 304 SS).

EXPERIMENTAL

Two types of austenitic stainless steels have been investigated in this work: high nitrogen chromium steel Cr23N1.2 (22.35 % Cr, 1.23 % N, 1.10 % Mn, 0.04 % C, 0.36 % Si, balance Fe) and conventional steel Cr18Ni9 (17.49 % Cr, 9.37 % Ni, 1.29 % Mn, 0.05 % C, 0.52 % Si, balance Fe). The experimental specimens were disk shaped with a working area of 0.5 cm\(^2\). The preliminary treatment of the specimens included subsequently polishing by abrasive paper 220, 400 to a 600 grit finishing, rinsing with water and drying. Just before the start of the experiment the specimens were polished to an 800 grit finish, followed by rinsing with distilled water and degreasing with an alcohol-ether mixture.

The solutions used were 3.5 wt. % NaCl (corresponding to 0.6 M chloride ions) with adding of HCl or NaOH for pH adjusting in the region 1 – 12. Concentrated solution of NaCl was added in order to achieve total concentration of the chloride ions 0.6 M. The test solutions were prepared using analytical grade reagents and distilled water. The electrochemical tests were performed under open air conditions at room temperature (20 ± 2 °C).

Three electrochemical techniques were used in the corrosion measurements. Open circuit potential (OCP)-time dependence was recorded in the test solutions for an hour at room temperature. Just after OCP record the specimen surface was anodically galvanostatic charged under current density 60 μA cm\(^{-2}\) and the potential change with time was recorded. Cyclic potentiodynamic polarisation measurements were performed with potential scan rate 1mV s\(^{-1}\), starting from the potential -0.7 V vs. SCE, at which the specimen was kept for 5 min, followed by anodic polarisation (in positive potential direction). After passing through the passive state and the current density exceed 10\(^{-4}\) A cm\(^{-2}\), polarisation in the reverse (negative potential direction) was carried out down to the point where the curve intersected the anodic one.

The electrochemical measurements were carried out in a conventional three-electrode cell with a platinum counter electrode and a saturated calomel electrode (SCE) as a reference electrode. The measurements were performed using PAR 263 potentiostat-galvanostat and Power Suite corrosion measurement and analysis software. After the polarisation tests the specimens were rinsed with distilled water, dried in air and the surfaces were investigated with an optical microscope.

RESULTS AND DISCUSSION

Open circuit potential

Fig. 1 presents OCP variation with time for the steels Cr23N1.2 and Cr18Ni9 in 3.5% NaCl solutions (pH 1 – 12). The initial part of the curves manifests the considerable differences in the behaviour of the two steels.

The dependences OCP-time for chrome-nitrogen steel (Fig.1) begin with sharp shift of the potential in positive direction. Starting from about -0.2 ± -0.4 V vs. SCE the OCP in some seconds reach to about 0.1±0.3
V vs. SCE. This shows extremely high rate of formation of passive film with low conductivity. After a short time the potential shifted towards less noble direction. On the curves OCP-time fluctuations exist, which fade in 30 min and the potential reaches a stationary value of about – 0.25 V vs. SCE. The described results for chrome-nitrogen steel clearly show that in contact with 3.5% NaCl solutions with pH 1 to 10 the steel surface is charged positively and reaches a critical potential value, where local processes of dissolution starts. The OCP fluctuations probably result from a strongly exhibited and variable in time electrochemical inhomogeneity of the surface.

In solution with pH 12 for the steel Cr23N1.2 only a smooth and stable increase of the potential is seen. Such kind of dependence is characteristic of the chromium-nickel steel in solutions with all studied pH values, which shows a good stability of the protective layers. Despite the start course of the curve OCP-time, the stationary value of the OCP for both steels in the most test solutions is close.

Cyclic potentiodynamic polarization method

The results presented in Fig. 2 are typical cyclic polarization curves for Cr23N1.2 and Cr18Ni9 steels obtained in 3.5% NaCl at room temperature and pH in the range 1-12. Corrosion parameters determined from the potentiodynamic curves as corrosion potential \( E_{\text{corr}} \), corrosion current density, as well as pitting potential \( E_{\text{pit}} \) and repassivation potential \( E_{\text{rp}} \) are shown on Figs. 3 and 4.

According to the summarized results three different
behaviour types of the steels can be separated: (i) Active state in strongly acidic solutions; (ii) State of spontaneous passivity and its breakdown at anodic polarisation by the pitting corrosion and (iii) Stable passive state and its transformation to transpassivity under anodic polarisation.

(i) In solutions with pH 1-2 for Cr23N1.2 and pH 1 for Cr18Ni9, the steels are in active state, characterized with high corrosion current density and active-passive transition under anodic polarisation. For the chromium-nitrogen steel the corrosion potential is about -0.6 V vs. SCE and the critical current density is reaching $3.6 \times 10^{-3}$ A cm$^{-2}$ (Fig. 4). The more negative values of $E_{corr}$ and $E_{piti}$ as well as higher corrosion current for Cr23N1.2 steel indicate its lower corrosion resistance compared with the chromium-nickel steel in acidic chloride solution. Similar results, showing sharply decreasing in corrosion stability of the chromium-nitrogen steel at pH lower than 3 are received from H.-Y. Ha et al. [4].

(ii) The analysis of obtained results shows, that at pH value above 2 for the chromium-nitrogen steel and above 1 for the chromium-nickel steel, the pH of the chloride solution has not a considerable influence on the corrosion behaviour of the steels. In this pH region, the austenitic steels are in passive state, the width of the passive region is about 0.6-0.7 V. In the region of pH 4-8 the steel Cr23N1.2 has better corrosion stability to general and pitting corrosion as compared to the chromium-nickel steel.

The anodic polarisation above the pitting potential leads to a sharp current increase as a result of development of pits. Fig. 3 shows that $E_{piti}$ of the chromium-nitrogen steel is increased only with 0.08 V when increasing the pH from 2 to 10. The relatively feeble influence of pH on this characteristic potential shows a stability of the passive film, probably due to the high content of chrome and especially of nitrogen in this steel. The pitting potential for the chromium-nickel steel is considerably more sensitive to the increase of pH and it grows with 0.25 V in the pH region 2-10. The $E_{piti}$ values for Cr18Ni9 become more positive as compared to these for the chromium-nitrogen steel in alkaline media with pH 8-10. This behaviour is due to the presence of nickel in the steel composition, which has good corrosion stability in neutral and alkaline media [9].

Widespread opinion exists in the literature, that the increase of the chromium content in the stainless steels composition favours the passivation process [2, 9]. Similar positive influence has also been established for nitrogen and some mechanisms have been proposed for this phenomenon [10]. The results, obtained in this paper, however, does not support the expectations for a better repassivation ability of the chromium-nitrogen steel compared with the chromium-nickel steel. On the contrary, despite the high chromium and nitrogen content in the studied steel Cr23N1.2, its potentials of repassivation are more negative with about 0.2 V at low values of pH and with about 0.35 V in alkaline media compared with the same potential for the Cr18Ni9. It is also unusual that the $E_{piti}$ decreases with the rising of solution pH for the chromium-nitrogen steel.

These results show that the positive effect of the nitrogen and chromium on the processes of restoring of the passive state is not sufficiently strong. More probably, the rupture in the passive films, formed on the chromium-nitrogen steel, occurs on the places, where their repassivation is very difficult. Such places are, for example, the grain boundaries (if the accumulation of the non-metallic inclusions exists).

(iii) In solutions with pH 12, under anodic polarisation the samples of austenitic stainless steels acquired a passive state, with breakdown at the transpassivity potential – about 0.63 V vs. SCE.

**Galvanostatic method**

This method gives the possibility for determination of the minimal positive potential, at which the surface activation begins (pitting potential, $E_{piti}$). According to this method, the sample is anodically charged at constant current and the change of the potential with time is recorded. If the steel is susceptible to pitting corrosion, characteristic fluctuations of the potential appear on the curve, related to the repair/breakdown events. Through the magnitude and the width of the peaks, a conclusion about the transient surface state can be made [11-13].

For example, as wider are the peaks in the lower part (at more negative potentials), as stable is the pit growth. After certain time the potential fluctuations fade and it is possible totally to disappear; the potential decreases and reaches a stationary value $E_{stat}$ which shows stable pits growth [11, 13]. As the values of the $E_{piti}$ are usually close to these of the repassivation potential, determined potentiodynamically, some authors define this stationary value as potential of repassivation [14].
Fig. 5 shows typical chrono-potentiometric curves received for steels Cr23N1.2 and Cr18Ni9 in 3.5% NaCl solutions (pH 1-12) at applied current density of 60 μA cm$^{-2}$. This current density was determined as the most proper according to the literature [11, 14] and the experimental data, following the method of Rosenfeld and Danilov [11]. According to the results from the potentiodynamic method, the passive current density for both steels is in the range 2-20 μA cm$^{-2}$ in all studied model solutions. Hence, the chosen current density for anodic polarisation 60 μA cm$^{-2}$ on one hand, is sufficiently high, in order to promote the pit formation in the studied pH region of 3.5% NaCl solutions and on the other hand it is low and has not an important influence on the values of the characteristic potentials, determined from the curves [14].

The fluctuations of the potential, observed on the galvanostatic dependencies, indicate a rupture of the passive layer, and their very small magnitude and width of the peaks are indications for the development and fast repassivation of metastable pits. After about 20-30 min the fluctuations are calming down, which is an indication for the stable pit growth. The values of the $E_a$ does not depend on the solution pH. For the steel Cr23N1.2 in solutions with pH 2-10, the potential does not achieve stationary value after an hour anodic polarisation. Only for the steel Cr23N1.2 in the solution with pH 12 the dependence potential-time has not a maximum and after about two minutes achieves the highest stationary value of about 0.68 V vs. SCE. This behaviour is characteristic for the state of stable passivity, the potential deviation from the start linear growing is due to the establishing of transpassive potential [15]. This form of the curve for the chromium-nitrogen steel shows that at pH 12, the formation of pits does not take place on the passive surface. At the same pH the potential of Cr18Ni9 shifts to the values of the transpassive state, but after reaching it, sharply decreases with about 0.7 V vs. SCE to the values of $E_{st}$, characteristic for lower pH.

In contrast with the curves of chromium-nitrogen steel, these for the chromium-nickel steel show fluctuations in the region of the maximum, which can be related to difficulties in the passive film rupture in the beginning and trend toward its restoring. The fluctuations in the curve during the lowering of the potential are few but are wider and with bigger intensity which show formation of small number but larger pits compared with these, formed on the chromium-nitrogen steel.

The effect of pH on the values of $E_{pit}$ and $E_{st}$ determined chronopotentiometrically, is presented in the Fig. 6. The values of $E_{pit}$ for both steels are close and stay in the region 0.34 ÷ 0.42 V vs. SCE. At pH 1, $E_{pit}$ decreases with about 0.36 V compared with the value at pH 2, which shows sharp decrease in the protective properties of the passive film on the surfaces of both steels. The values of $E_{pit}$, determined galvanostatically, for both steels are close to these, determined through cyclic potentiodynamic method. Thus, the results from the galvanostatic method confirm these, received by potentiodynamic method that in the region of pH 2-10, the character of the environment has not an important influence on the protective properties of the passive
layers, formed in 3.5% NaCl solutions.

Microscopic observations

With an aim of determination of the character and dimensions of the corrosion damages, after each polarisation test the surface of the samples was investigated in detail at magnifications 50х, 200х and 500х. The samples, subjected to anodic polarisation in 3.5% NaCl solutions with pH 1-10, are affected by pitting corrosion. The main differences in the corrosion attack of the steels Cr23N1.2 and Cr18Ni9, for all solution conditions, are the shape and location of the surface defects. The pits, formed on the chromium-nitrogen steel, are predominately with irregular shape, situated along the grain boundaries (Figs. 7a and 7b). The pits on this steel are open and uniformly distributed by size. In a solution with pH 1, chromium-nitrogen surface is affected also by corrosion dissolution, leading to manifestation of the structure (Fig. 7a). Increasing the pH of the solution from 1 up to 10, results in lowering of the number but increases the size of the larger pits respectively from about 0.03 to 0.06 mm. In all model solutions the pits on the chromium-nitrogen steel are an open type.

In the 3.5% NaCl solution with the lowest pH, the surface of the steel Cr18Ni9 is not affected from general corrosion, but the number and dimensions of the pits is several times greater than those on the chromium-nitrogen steel. At pH 1 on the surface of Cr18Ni9, the average number is 20-30 macropits/cm², which are subsurface, with irregular shape and depth about and over 0.15 mm. The micropits number is also considerable. With pH raising from 2 to 8 an important change in the shape and in the number of pit nucleus is not observed. In contrast to the pits on the steel Cr23N1.2 in the same pH range, the pits on the chromium-nickel steel are separated by shape and type. Enormous number of shallow open micropits (about and over 50-60 micropits/cm²) with pit hole less than 0.010 mm and few macropits (up to 8-10 macropits/cm²), hidden under lacy cover (Fig. 8) are registered. Despite the small pit mouth, the macropits reach considerable dimensions and penetrate into the steel to the depth of over 0.12 mm. At pH 10 the pits number on the chromium-nickel steel decreases to 3-4 macropits/cm², but some of them have a diameter about 0.25 mm (Fig. 8b).

In solutions with pH 12 some discrepancies between the results from the two polarisation methods are registered. According to the potentiodynamic dependencies, the pitting corrosion at this pH value does not appear, while the results from the galvanostatic method shows definitely a local break in the passive layer for the steel
Cr18Ni9. The microscopic observations of the chromium-nickel steel surface after the galvanostatic test at pH 12 show well-defined single pits with dimension about 0.06 mm, which are not observed after the potentiodynamic tests. Most probably the cited differences are due to the difference between the two electrochemical methods. In the cyclic potentiodynamic method the anodic polarisation is growing up gradually until the pitting potential, the passive layer on the steel has already thickness and structure, different from those, formed at the open circuit potential. During the galvanostatic method, the fast polarisation with relatively high anodic current is applied and maintained on the natural passive layer for longer time. The high positive potential, reached in this case, gives an opportunity to the created local ruptures to grow in short time and turn into big and stable pits. Despite the high pH value, in the galvanostatic conditions the repassivation process is straitened because of the large size and closed type of the pits, which facilitates the growth of acidity in the pit solution.

CONCLUSIONS

The susceptibility to general and pitting corrosion of the chromium-nitrogen steel Cr23Ni1.2 in 3.5% NaCl solution with pH 1 and 2 is lower as compared to this one of the chromium-nickel steel Cr18Ni9. At pH value above 2, the pH of the chloride solution has not a considerable influence on corrosion behaviour of the steels. In 3.5% NaCl solutions with pH 1÷10, the anodic polarisation leads to development of pits, which are different not only in shape, but also in depth of penetration. The pits on the chromium-nitrogen steel Cr23Ni1.2 are of open type, with irregular shape and they are formed mainly on the grain boundaries. In contrast, the pits on the steel Cr18Ni9 are of closed type and penetrate in bigger depth as compared to those of the steel Cr23Ni1.2. The possibility for formation of lacy cover depends in great extent on the steel composition and the sensibility of the repassivation potential on the pH changes.

Acknowledgements

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EFFECT OF PHOSPHATE ADDITIVES ON PHYSICAL-CHEMICAL PROPERTIES OF AMMONIUM NITRATE

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ABSTRACT

The composition of nitrogen phosphorus fertilizers is offered obtained by mixing of two components: the melt of ammonium nitrate and Central Kyzyl Kum’s phosphorite taken in such a proportion guaranteeing the end product production containing $P_2O_5$ in a range: 1.05-5.04 %. The effect of phosphate additive on the physical-chemical properties and trademarks of ammonium nitrate are studied. It has been shown that the introduction of phosphate additives in ammonium nitrate’s melt leads to a significant improvement of ammonium nitrate’s quality indicators.

Keywords: ammonium nitrate, phosphate raw material, nitrogen phosphorus fertilizer.

INTRODUCTION

Ammonium nitrate (AN) is the most widespread fertilizer in the world and the most efficient nitrogen fertilizer containing at least 34.4% of nitrogen [1]. It can be applied at all types of soils and for all plants being a basic and feeding fertilizer for them.

Currently the world production of ammonium nitrate exceeds 43 million tons a year. In the Uzbekistan, three Open Joint Stock Companies (OJSK): “Maxam-Chirchik”, “Navoiazot” and “Ferganaazot” did produce more than 1.7 million tons of ammonium nitrate by 2012. However ammonium nitrate is used not only as a fertilizer but as an explosive component [2]. Series of terrorist attacks worldwide including Uzbekistan state were carried out with ammonium nitrate oxidizer leading to necessity of tight security measures at its handling [3]. Thus, in particular, China, Brazil, Colombia, Algeria, and the Philippines began to consider ammonium nitrate as an explosive and banned its use as a fertilizer. The Uzbekistan’s State Joint Stock Company “Uzkimyosanoat” annually spends USD 25000 for special guard measures at transportation of each batch from its productive factory to a farmer’s field.

Therefore, nowadays for the producers of ammonium nitrate it is very important to apply agriculture nitrate-based fertilizers with a less explosive property retaining however high agrochemical efficiency. So we decided to obtain such a stabilized ammonium nitrate by the introduction of phosphorite raw material (PRM) (Central Kyzyl Kum, Uzbekistan) into usual ammonium nitrate’s melt.

EXPERIMENTAL

For the experiments the ammonium nitrate produced at Open Joint Stock Company “Maxam-Chirchik” (34.6 % N) and the PRM (characterized with the following composition, mass %: $P_2O_5$(total) – 17.20; CaO – 46.22; Al$_2$O$_3$ – 1.24; Fe$_2$O$_3$ – 1.05; MgO – 1.75; F – 2.00; CO$_2$ – 16.00; $P_2O_5$ (acceptable) : $P_2O_5$ (total) = 18.49 %) have been used. Ammonium nitrate was melted in a metal cup...
on a hot plate. Into the melt the PRM was injected pre-
liminary taken in an amount providing the end product’s
$P_2O_5$ content in a range of 1-5 %. At $180^\circ C$ for 30 min-
utes it was thoroughly mixed. The cooled product was
powdered and chemically analyzed. Acceptable form
of $P_2O_5$ and CaO components were determined at test
procedure based on application of 2 % citric acid. The
chemical composition of nitrogen phosphorus fertilizers
(NPF) so obtained is shown at Table 1.

For PRM granulation the ammonium nitrate was
melted at 180ºC, then the calculated amounts of phos-
phates salts were introduced into a number of pool,
carefully stirred for 30 minutes, poured smoothly into
granulator represented with a metal cup with a perforated
bottom (diameter of holes 1 mm). Pumped to the top
of the cup the melt was sprayed from a height of 30 m
down to a plastic film lying on the ground. After that the
strength of granules of 2-3 mm in diameter obtained was
determined using the special device MIP-10-1 according
to Standard [4] based on measuring the strength (kg)
needed for granules destruction. The static strength of
granules (kg/granule) was calculated using the formula:

$$ X = \frac{P_1 + P_2 + P_3 + \ldots + P_{20}}{20} $$

where $P_1, P_2, P_3, \ldots, P_{20}$ - efforts crushing
granule (kg).

Static strength of granules Y (kgf/cm$^2$) was calculated using the formula:

$$ Y = \frac{\sum_{i=1}^{20} P_i \cdot S}{20 \cdot S} = \frac{\sum_{i=1}^{20} P_i \pi d_{av}^2}{20 \pi d_{av}^2} = 0.063 \left( \frac{\sum_{i=1}^{20} P_i}{d_{av}} \right) $$

where $P_i$ - the force required to break a single granule (kg);

$S$ - cross-sectional area of granules, cm$^2$;

d$_{av}$ - the average diameter of granules, cm.

To present the results of tests in MPa units the value
calculated (2) was divided by 10.2. For comparison the
strength of pure AN pellets with a diameter of 2-3 mm
was measured as well.

Porosity of pellets was determined by the volumetric
method [5]. The essence of the porosity of pellets accord-
ing to this method was as follows. Into a 25 ml burette
equipped with a crane a certain amount of cryoscopic
benzene was put ($V_1$). Then 10 g of AN or NPF were
put there and after 1-2 min the changes of the burette’s
volume ($V_2$) were fixed. Then the crane was opened, the
benzene located between the fertilizer’s granules was
pulled down into the second burette (volume also 25
ml) and its volume was measured ($V_3$). Porosity $P_{por}$ (in
percentages) was calculated according to formula (3):

$$ P_{por} = \frac{V_1 - V_2}{V_2 - V_3} \times 100 $$

The porous AN used as a component of explosive
mixtures possesses this rate acceding 20 %.

The caking of AN and NPF was determined ac-
cording to a rapid method [4] based on the following
principle. The preform of nitrogen phosphorus fertilizer
equal to 100 g was placed into a split cylindrical mold
with an inside diameter 50 mm. The die was closed and
left under the installed load of 3.1 kg, then it was put
into an incubator at 60ºC for 8 hours. After a specified
time the compression loads were removed, the cassette
was released and held for 2 hours at room temperature.
After its cooling the top panel from the cassette was
removed and the resulting pellet carefully was removed
from the mold. Briquettes were tested to destruction at
device MIP-10-1.

<table>
<thead>
<tr>
<th>The ratio of the AN:PRM</th>
<th>Humidity, %</th>
<th>N, %</th>
<th>$P_2O_5$acceptable, %</th>
<th>$P_2O_5$acceptable, %</th>
<th>CaO acceptable, %</th>
<th>CaO acceptable, %</th>
<th>$P_2O_5$water-solubility, %</th>
<th>$P_2O_5$acceptable, %</th>
<th>CaO acceptable, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN</td>
<td>0.28</td>
<td>34.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100 : 7</td>
<td>0.35</td>
<td>32.25</td>
<td>1.05</td>
<td>1.03</td>
<td>2.70</td>
<td>2.44</td>
<td>0.94</td>
<td>98.09</td>
<td>90.37</td>
</tr>
<tr>
<td>100 : 13</td>
<td>0.36</td>
<td>30.75</td>
<td>2.01</td>
<td>1.95</td>
<td>5.69</td>
<td>4.79</td>
<td>1.45</td>
<td>97.01</td>
<td>84.18</td>
</tr>
<tr>
<td>100 : 20</td>
<td>0.42</td>
<td>29.15</td>
<td>3.00</td>
<td>2.87</td>
<td>8.35</td>
<td>6.60</td>
<td>1.52</td>
<td>95.66</td>
<td>79.04</td>
</tr>
<tr>
<td>100 : 30</td>
<td>0.56</td>
<td>27.10</td>
<td>4.10</td>
<td>3.83</td>
<td>11.01</td>
<td>8.05</td>
<td>1.57</td>
<td>93.41</td>
<td>73.11</td>
</tr>
<tr>
<td>100 : 40</td>
<td>0.68</td>
<td>25.24</td>
<td>5.04</td>
<td>4.45</td>
<td>13.12</td>
<td>9.02</td>
<td>1.61</td>
<td>88.29</td>
<td>68.75</td>
</tr>
</tbody>
</table>
The caking of samples X (in MPa) was calculated using the formula (4):

\[ X = \frac{P}{S} \]  

(4)

where P - breaking effort (N), kg;  
S - cross-sectional area of the sample, cm\(^2\).

Bulk density of the fertilizer granules (Ø 2-3 mm) was determined according to State Standard at temperature 25°C [6]. Determination of the dissolution rate of nitrogen phosphorus fertilizer’s granules was conducted according to State Standard; the method consisted of visual observation and dissolution time recording for fertilizer pellets (Ø 2-3 mm) lowered into distilled water at 25°C, bathed into a chemical glass of 100 ml volume.

The hygroscopic point of the fertilizer granules (Ø 2-3 mm) has been determined by exsiccator method [7] at 25°C. The determination of increase or decrease of humidity of substance at constant temperature and certain relative humidity of air was carried out for 3 hours. The required relative humidity of air was created in the exsiccator at the certain concentration of sulphuric acid.

RESULTS AND DISCUSSION

The chemical analysis of the products showed that the melt activates nitrate phosphate raw material, in other words it transforms the indigestible \( P_2O_5 \) into the digestible for the plants state (Table 1). If in the source of phosphate raw material the ratio of masses of digestible form to the total \( P_2O_5 \) form was only 18.49 %, the products of its interaction with the melt of ammonium nitrate obtained the value of such ratio in the range of 88.29 - 98.09 %. The products contained 25.24 - 32.25 % N, 1.05 - 5.05 % \( P_2O_5 \) and 2.44 - 9.02 % CaO.

At Fig. 1 the values of strength of nitrogen phosphorus fertilizer’s granules obtained by mentioned above method are offered. The data at Fig. 1 show that the addition into a melt AN of ordinary phosphoric flour in an amount of 7 - 40 g per 100 g of AN increases the strength of granules - from 4.26 to 7.8 MPa, in other words it let to increase the strength of granules NPF over 2.6 - 5.0 times in compare with the strength of granules of pure AN. Increasing the mass of additives in phosphate raw material’s melt AN leads to an increase of their strength’s values.

Various impurities presented in the phosphate raw material (CaO, \( P_2O_5 \), Al\(_2\)O\(_3\), Fe\(_2\)O\(_3\), SiO\(_2\), etc.) do effect on the structural properties of the NPF granules. Introduced into the melt of AN special phosphate additives form the fine inclusions in the structure of crystalline blocks of a fertilizer. Reducing the size of the individual
crystals of salt and increasing of their packing density significantly promote the increasing of the fertilizer granules’ strength. It leads naturally to an increasing of the bulk density’s values - from 0.925 to 1.033 g/cm$^3$ versus the value of the bulk density of pure ammonium nitrate: 0.855 g/cm$^3$ (Fig. 2). Increasing of the bulk density of fertilizer supports a decrease of porosity of the studied samples, and this in turn indicates an increase in the strength of NPF granules.

The addition of phosphate raw material into the melt of ammonium nitrate also reduces the porosity and specific surface area of the internal NPF granule (Fig. 3). The experimental data indicate that the addition into the ammonium nitrate’s melt of phosphate raw material taken in above mentioned amount reduces the porosity of the obtained NPF granules ($\phi$ 2-3 mm) from 9.15 to 7.08 %.

The data of NPF caking showed the fertilizers’ caking values decreasing from 2.77 to 1.7 kg/cm$^2$, that is 1.6 times according to the increase of phosphate additives mass from 7 to 40 grams. At the optimum mass ratio of the entered phosphate additive and the melt (AN: PRM = 100:40) the NPF caking reduced by 2.7 times compared to the caking of pure ammonium nitrate: 4.67 kg/cm$^2$.

We also determined the rate of dissolution of AN and NPF granules (Table 2). The data indicate that the introduction of a phosphate additive into the melt of ammonium nitrate fertilizer’s granules their dissolution rate is reduced in compare with the pure ammonium nitrate. At the increasing of mass portion of phosphate raw material from 7 to 40 % the obtained NPF granules’ samples demonstrate the increasing of dissolution period for them from 66.4 to 100.8 seconds in compare with granules made of pure nitrate: 46.8 seconds, thus it increases by 2.2 times. Reducing of the NPF granules dissolution rate, from our pint of view, occurs as a result of granules strength’s increasing: the more is strength of granules, the slowly is the dissolution of fertilizer’s granules.

The delayed solubility of NPF granules to a certain degree has a positive effect on the absorption of the fertilizer’s nutrients by plants through their root system, in the other words the granules containing phosphates will gradually give nutrients, resulting in significantly increase of their efficiency.

The hygroscopic points’ values of fertilizer samples were the following: for AN – 62.0 %, AN:PRM = 100:7 – 54.5 %, AN:PRM = 100:20 – 54.0 % and for AN:PRM = 100:30 and AN:PRM = 100:40 – 53.5 %.

The relative air’s humidity at the Uzbekistan is the following: monthly mean minimum – 46%, monthly mean maximum – 74 %, mean yearly – 60 %. According to Pestov’s scale [7] all Uzbekistan’s nitrogen-phosphorous fertilizers are hygroscopic. They are more hygroscopic than the parent ammonium nitrate. Despite of that the presence of water indissoluble components of phosphate additive and formation of crystallohydrates prevent from melting of end-product and accordingly reduces the negative influence of hygroscopy on agglutination in storage of ammonium nitrate.

Table 2. The rate of NPF beads dissolution in water.

<table>
<thead>
<tr>
<th>Mass ratio AN:PRM</th>
<th>N, %</th>
<th>P$_2$O$_5$, %</th>
<th>Time of granules dissolving, see</th>
<th>Average value</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0,0</td>
<td>34,6</td>
<td>---</td>
<td>51</td>
<td>46,8</td>
</tr>
<tr>
<td>100:7,0</td>
<td>32,25</td>
<td>1,05</td>
<td>68</td>
<td>66,4</td>
</tr>
<tr>
<td>100:13,0</td>
<td>30,75</td>
<td>2,01</td>
<td>80</td>
<td>75,4</td>
</tr>
<tr>
<td>100:20,0</td>
<td>29,15</td>
<td>3,00</td>
<td>82</td>
<td>83,0</td>
</tr>
<tr>
<td>100:30,0</td>
<td>27,10</td>
<td>4,10</td>
<td>96</td>
<td>91,2</td>
</tr>
<tr>
<td>100:40,0</td>
<td>25,24</td>
<td>5,04</td>
<td>104</td>
<td>100,8</td>
</tr>
</tbody>
</table>

Fig. 4. Effect of phosphate additives on the caking of the ammonium nitrate.
CONCLUSIONS

The possibility of obtaining of nitrogen phosphorus fertilizers by phosphate raw materials (Central Kyzyl Kum) introducing into a melt of ammonium nitrate was studied. The chemical composition of fertilizers showed that the phosphate raw material in the molten nitrate is activated, in other words the indigestible $P_2O_5$ in the raw material transforms into digestible state suitable for plants. This allows turning phosphate raw materials into an effective phosphorus fertilizer without using the scarce acid reagent.

The introduction of phosphate raw materials of Central Kyzyl Kum into a melt of ammonium nitrate leads to significant quality improvements (strength, bulk density, porosity, caking, hygroscopicity and the dissolution rate of granules) of the ammonium nitrate.

This method is basic for new fertilizers producing at OJSC “Navoiazot”. The granulated nitrogen phosphorus fertilizer possesses an excellent physical, chemical and production characteristics. It does not deteriorate and corresponds to TSh 6.1-0023849-111:2007 State Standard. From the beginning of 2009 more than 200000 tons of nitrogen phosphorus fertilizers have been produced casting USD 37.5 millions and sent to consumers.

REFERENCES

PRODUCTION OF POROUS GLASS-CRYSTALLINE MATERIALS USING DIFFERENT TYPES OF NATURAL AND RECYCLED RESOURCES

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ABSTRACT

In this article the results of experimental studies aimed at obtaining glass-crystalline porous materials based on various types of natural and recycled materials are presented. The possibility of using cheap water-containing natural and recycled materials as bloating agents was established. The influence of the content of such additives on the structure and properties of porous glass-crystalline materials at different firing temperatures was evaluated. Prospects of using the developed materials as insulation products in the construction industry are shown.

Keywords: pores, heat insulation, foam glass, glass-crystalline material, bloating agent, breakage glass, slag.

INTRODUCTION

Currently, the question of insulation of residential buildings in order to keep them warm and reduce energy costs on their heating is very acute. In today’s building materials market, there are many insulating materials of organic and inorganic origin. Due to the relatively low cost, the most common ones are mineral wool and plastic foam. However, these materials have significant exploitation drawbacks.

Plastic foam is characterized by low rates against high temperatures. Most of them are smoldering or burning well, emitting toxic products of combustion. Under prolonged influence of high temperature, oxygen, light, etc., certain physical and chemical processes (thermal, mechanical, photochemical degradation) occur in polymers, leading to a significant loss of properties of the foam due to a decrease in the molecular mass of the polymer, the formation of free radicals and reduced length of chain macromolecules [1].

On the contrary mineral wool is frost-resistant, does not burn, and has a temperature range up to 873K. However, its use as an independent heat insulator in most cases is impractical because it shows self-packing and shrinkage, leading to reduction in durability. In addition, mineral wool is a collaterally-hydrophilic material with water absorption up to 600 %. Directly moisture does not cause the destruction of wool, but it can be a habitat for the development of house fungis, which form organic acids (oxalic, citric acid), that ruin it [2].

In our opinion, among the existing insulation materials the best exploitation characteristics has foam glass. It belongs to the cellular inorganic heat insulators with closed or open pores having size of 0.1 - 5 mm. Foam glass is obtained with heat treatment of a mixture of thin ground glass powder with a bloating agent. The material properties depend on the way of production, the composition of the glass and the type of bloating agent. Foam glass has a unique set of properties: small water absorption, resistance to decay, microorganisms, insects and rodents; fire resistance, chemical resistance to most environments; it can be cut, drilled, ground [3]. Foam glass is the insulation material that is suitable for long-term use in building structures.

However, in the manufacture of foam glasses the use of special welded glass, relatively expensive bloating agent and high firing temperatures cause its high cost. Thus, there is a need to study the possibility of involvement in the synthesis of porous material of new raw materials, mostly recycled.

Among the various industrial wastes, concentrated in Ukraine, and non-deficient natural raw materials,
of particular interest for the synthesis of porous glass-crystalline materials as bloating agent is the slag of blast-furnace and open-hearth furnace production, asbestos cement products breakage (building slate) and loam. This is possible, because all of these materials include certain components (carbonates, hydrates, calcium and magnesium silicate hydrates, etc.) that can form enough of the gas phase at temperature intervals close to the softening temperature of glass breakage. However, we believe that a significant effect on the bloating of the mass of glass, except carbonate may have water including compounds.

Bezborodiy M. [4] found that a “fluxing” nature of OH-ions is shown by the fact that the continuous silicate network is broken into individual silicate islands that are as much smaller in size and as much bigger in number, as there are more OH-ions in the melt. It was found that the decrease in glass viscosity with increasing of water content was most evident in the low-temperature region. The authors explain this fact by breaking of connections due to penetration of OH groups into the structure of the glass. In this regard, we believe that the use of natural and recycled water including materials as bloating agent, is of particular interest. Moreover, the role of bound water contained in natural rocks, wastes from industry and other bloating agents in the preparation of porous materials is not fully studied.

In studies of the influence of the gas phase composition on the kinetics of foam forming in foam glass, conducted by E. Schultz [5], it was found that the first condition for foaming is the presence of water vapor in the glass. Its presence reduces viscosity and surface tension of the glass, which greatly facilitates the development of pyroplastic foams. It can be concluded that for lowering of the temperature for obtaining porous materials, it is preferable to have bound water, which can enter the bloating agent mixture with the help of adding in it substances, containing hydration water.

The method of producing foam glass without using of traditional bloating agent has been developed by the authors [6]. By milled (to specific surface 5000 g/cm²) bottle or widowpane glass breakage by semi-dry pressing, shaped samples are produced with their next thermal and humidity treatment. This treatment is carried out in order to watering and the formation of silanes - water (hydroxyl groups, connected directly with silicon [7]). Obtained silanes - water acted as a bloating agent under the foaming temperature of 1073K.

However, this method is time consuming. Firstly, you need to grind the glass breakage to a large specific surface area (5000 g/cm²), and secondly - to carry out energy-intensive thermal and humidity treatment in complex, non-standard units.

The aim of this study was to obtain and study porous glass-crystalline materials with high exploitation characteristics, based on rationally selected composite mixtures of different types of non-deficient natural and recycled materials, containing hydration water.

**EXPERIMENTAL**

For porous glass-crystalline materials we used flat glass breakage with the additions of metallurgical slag (blast furnace, produced by the EVRAZ DMZ Petrovskogo and open-hearth of Interpipe NTRP), breakage of asbestos cement products (BACP), and loam of the Sursko-Pokrovskiy field in the Dnepropetrovsk region.

Charges were prepared by separate dry grinding of the raw materials in a ball mill to a particle size, which is characterized by a specific surface of 3000 g/cm². From the obtained raw mixtures with the use of the method of semi-dry pressing (w = 10 %) were formed cylindrically shaped samples with a diameter of 24 mm and a height of 9 - 10 mm. After drying at indoor temperature for 24 hours, the samples were fired in a laboratory furnace in the temperature range of 973 - 1173K with keeping at the maximum temperature for 0.5 - 1 hour, and that was followed by slow cooling. Formation of the samples was carried out in order to simplify the subsequent measurements. From the proposed mass composition porous materials can be obtained with the use of conventional powder technology of foam glass production [5, 8].

The sample volume of irregular geometrical shape was determined using a sand volumeter [9]. The specific gravity was determined in accordance with the state standard of Ukraine (SSU) № B V.2.7-42-97, the compressive strength was measured using a universal durability testing machine FP-10, according to the all-Union State Standard (AUSS) №8462-85. Heat conductivity of the obtained porous materials was measured on the instrument according to AUSS 7076-99.

X-ray phase analysis of the raw materials and the samples was carried out according to the method of powder on a DRON-3.0 diffractometer and Cu-Kα r-
The identification of the crystalline phases was carried out [10].

Differential thermal and thermogravimetric analyzes of the raw materials were performed on a derivatograph of the Paulic-Paulic-Erdey system. The raw materials have been analyzed in air at the speed of heating of 10°C/min.

Scanning electron microscopic analysis was performed on the microscope REM-106Y. Images were obtained when working in secondary electrons. The maximum residual pressure in the microscope column (in the gun) was not more than 6.7 x 10^{-4} Pa (5 x 10^{-6} mm Hg. Cent.) and gun current - 111 mA.

RESULTS AND DISCUSSION

We conducted a preliminary analysis of the possibility for using experimental recycled and natural raw materials, as bloating agents. It was determined that the experimental blast furnace slag was mainly represented by four oxides - SiO_{2}, Al_{2}O_{3}, CaO and MgO, with their total content of about 97 mass % (Table 1). This slag belongs to basic slags, because it has a base module greater than 1. The phase composition of the blast furnace slag is represented mainly by a glass phase (95-97 %), in which crystalline formations are distributed; their identification has complications due to their small number (Fig. 1) [11].

According to the results of the differential thermal analysis (Fig. 2), an endothermic effect at 933K corresponds to the softening of the furnace slag glass phase, and intensive ekzo-effects at temperatures 1133 and 1253K, for its in-step crystallization. An exothermic effect at 1253K, which is accompanied by a mass gain (curves TG and DTG), may be partly connected with oxidation of the sulfide sulfur, which is part of the slag glass.

In addition, the thermogravimetric curve recorded sample mass loss of about 3.3 % in the temperature range 753 - 1053K, which is caused by the occurrence of processes of dehydration and decarbonization of compounds that are probably formed in the process of interaction of residual free lime with water during the wet granulation of the slag melt, and also with the ambient air, during the stay of already solid slag waste in the dumps.

We also studied an open-hearth slag that was preliminarily magnetically enriched. It should be noted that the studied slag is heterogeneous at its corn composition: it contains solid, hard milling inclusions of different nature, and their content reaches 35.52 mass %. Mainly, such inclusions are in large fractions of open-hearth slag (larger than 1 mm), which is suggesting their metallic nature. For further research the well milling non-magnetic part of the research open-hearth slag was chosen.

According to the X-ray phase analysis (Fig. 3) it was found that the main crystalline phase of the slag is β-quartz, which corresponds to the data of the chemical

![Fig. 1. XRD analysis of sample of blast furnace slag.](image1)

![Fig. 2. Differential thermal analysis of sample of blast furnace slag.](image2)

### Table 1. Chemical analysis of experimental samples of raw materials, mass %.

<table>
<thead>
<tr>
<th>Name of the material</th>
<th>SiO_{2}</th>
<th>TiO_{2}</th>
<th>Al_{2}O_{3}</th>
<th>Cr_{2}O_{3}</th>
<th>Fe_{2}O_{3}</th>
<th>FeO</th>
<th>CaO</th>
<th>MgO</th>
<th>MnO</th>
<th>K_{2}O</th>
<th>Na_{2}O</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Breakage glass [12]</td>
<td>72.60</td>
<td>-</td>
<td>1.60</td>
<td>-</td>
<td>0.10</td>
<td>-</td>
<td>8.10</td>
<td>3.60</td>
<td>-</td>
<td>0.50</td>
<td>13.50</td>
<td>-</td>
</tr>
<tr>
<td>Blast furnace slag</td>
<td>38.79</td>
<td>0.20</td>
<td>7.00</td>
<td>-</td>
<td>0.01</td>
<td>0.20</td>
<td>45.70</td>
<td>5.50</td>
<td>-</td>
<td>0.30</td>
<td>0.30</td>
<td>2.00</td>
</tr>
<tr>
<td>Open-hearth slag</td>
<td>28.00</td>
<td>-</td>
<td>6.50</td>
<td>2.00</td>
<td>20.36</td>
<td>6.10</td>
<td>15.00</td>
<td>3.00</td>
<td>0.24</td>
<td>tr.</td>
<td>0.30</td>
<td>0.24</td>
</tr>
<tr>
<td>Loam</td>
<td>70.02</td>
<td>0.11</td>
<td>8.50</td>
<td>-</td>
<td>2.29</td>
<td>6.67</td>
<td>1.57</td>
<td>2.02</td>
<td>0.73</td>
<td>8.09</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
In addition, in the open-hearth slag there is a fairly high number of calcium carbonate in the form of calcite (CaCO$_3$), with his characteristic diffraction peaks and calcium hydrosilicate, which is likely to be the result of the interaction of free lime from the ambient air and the quartz component.

The content of hydrosilicate and calcium carbonate in the phase composition of studied open-hearth slag is also confirmed by differential thermal analysis (Fig. 4), namely, the presence of significant mass loss in the analyzed samples. The highest loss (7.5 %) is observed in the temperature range 573 - 1073K. In the curve of the differential-thermal analysis there is an endo-effect with a minimum in the temperature range 693 - 703K, related to the dehydration of the calcium hydrosilicate, called afvillit (3CaO•2SiO$_2$•3H$_2$O), contained in the slag (Fig. 3), which, moreover, can be partially attributed to the decomposition of Mg(OH)$_2$. The entothermic effect at 1053-1073K and the corresponding mass loss are associated with calcium decarbonization [13].

In this work, research of clay materials of different deposits of Dnipropetrovsk and Zaporizhzhya regions was carried out [14]. It was found out that the most suitable for use as a bloating agent is loam.

Loam, used in this work, is a polymineral kind of clay material of hydromicakaolinite composition with inclusions of montmorillonite. Approximate quantitative

<table>
<thead>
<tr>
<th>Component</th>
<th>The content of the phases in the clay, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>10 - 20</td>
</tr>
<tr>
<td>Hydromicas</td>
<td>2 - 3</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>3 - 5</td>
</tr>
<tr>
<td>Quartz</td>
<td>50 - 55</td>
</tr>
<tr>
<td>Carbonates (calcite, dolomite)</td>
<td>17 - 20</td>
</tr>
<tr>
<td>Feldspars</td>
<td>2 - 3</td>
</tr>
<tr>
<td>Glaucnate</td>
<td>1 - 2</td>
</tr>
<tr>
<td>Accessory minerals</td>
<td>4 - 6</td>
</tr>
<tr>
<td>Carbonaceous shales</td>
<td>to 1</td>
</tr>
</tbody>
</table>
relationships among the mineral phases in its structure are shown in Table 2.

In order to study the processes occurring during the loam heat treatment, its thermogravimetric analysis was carried out (Fig. 5). In the thermogram in the temperature region 380 - 500K, an interlayer and free water removal was fixed. In the temperature range 800 - 873K a series of endo-effect was visible, which indicated modification transition of quartz and removal of chemically bound water. The double endo-effect in the temperature range 993 - 1223K is associated with the processes of magnesite and calcite decarbonization. Taking into account the above mentioned, we can predict that the use of loam in a composition mixture with breakage glass will ensure sufficient gas phase discharge during the softening of the glass mass and will contribute to the formation of pores.

Asbestos-cement products (slate) breakage, produced using 15 mass % Chrysotile asbestos and 85 mass % Portland cement were also used in our work. According to data from [15], chrysotile asbestos (Mg₆[Si₄O₁₀](OH)₈), which is magnesium hydro silicate, is dehydrated when heated to temperatures close to the temperature of liquid phase formation of the breakage glass, which may contribute to the formation of porous structure. Besides, calcium hydro silicates that are the main structure-building elements of the cement stone, dehydrate at temperatures 393 - 973K (depending on the type of calcium hydrosilicate) [16], which coincides with the temperatures of glass breakage softening.

We have investigated the raw mixtures, that contained breakage glass and various concentrations of the above mentioned additives, that can act as a bloating agent. Breakage glass served as the main component, which due to the high content of alkali oxides (15 %) helped to reduce the temperature of the material foaming.

Samples containing from 10 to 45 mass % of blast furnace slag were initially fired at a temperature of 1173K. The analysis of their properties allowed to define a clear tendency for lowering of the specific gravity of the material with reduction of the mass of blast furnace slag in the experimental charge from 45 to 20 mass %. Further reduction of the slag from 20 to 10 mass % led to a gradual increase of the specific gravity. The appearance of samples and pore distribution are shown in Fig. 6.

In order to obtain a glass-crystalline material with a lower specific gravity and a more uniform porous

Fig. 6. Appearance of test specimens (a) and the distribution of pores (b), fired at 1173K.

Fig. 7. Dependence of the specific gravity of the experimental mass in the content of blast furnace slag.
structure, we expanded the blast furnace slag concentration range in the experimental masses between 2.5 and 30 mass % with step of 2.5 mass %. These samples were fired at temperatures, lowered to the 1123 - 1073K range. This experiment revealed that at all experimental firing temperatures - 1123, 1098 and 1073K, there was a tendency of gradual decrease in the specific gravity of the samples with the increase of the content of the blast furnace slag in them from 2.5 to 17.5 mass % (Fig. 7). Further growth of this waste within the experimental charge led to a rise in their specific gravity due to increasing of the viscosity of the glass phase in them, because of growth of the content of silica, calcium and aluminum oxides. It should be noted, that the lowest values of the specific gravity had samples that were fired at a temperature of 1123K, though at the other two temperatures: 1098 and 1073K, samples swelling was significant. Masses, containing blast furnace slag from 7.5 to 12.5 mass % (Fig. 8), had a more uniform distribution of pores.

The analysis of the phase composition of the samples, containing glass breakage and blast furnace slag, fired at a temperature of 1123K, showed the formation and presence of such crystalline compounds as volastanit, rankinite and doublecalcium sodium disilicate in the studied material (Fig. 9).

The obtained glass-crystalline samples were characterized by a fine porous (d = 1 - 2 mm) structure, similar to the foam glass. When the content of blast furnace slag is from 15 to 22.5 % we may obtain glass-crystalline porous materials with pores (d = 2 - 5 mm), similar to the keramzit, which is produced according to a well-known ceramic technology with firing at 1423 - 1523K [17].

The products from the glass-crystalline synthesized materials are characterized by a compressive strength of 12.4 MPa and specific gravity of 300 - 600 kg/m³, and can be used as insulation materials and fillers in lightweight concrete.

It was found experimentally, that the optimal firing temperature of samples containing loam was 1023K. The
The analysis of the properties of the fired samples allowed us to determine a clear tendency for decreasing of the specific gravity with increasing of the loam content in the experimental charge from 5 to 17.5 mass %. Further increase of its content leads to a gradual increase in the specific gravity (Fig. 10).

As follows from Fig. 10, the lowest specific gravity can be reached with loam content of 17.5 mass %. However, such a sample has a somewhat heterogeneous structure with individual pores having diameter of 4 mm. The most homogeneous fine porous structure in the experimental samples is achieved when the content is 10 and 12.5 mass % (Fig. 11b).

Analysis of the phase composition of the sample containing 15 mass % of loam indicates the presence of a crystalline phase, which by its characteristic diffraction peaks can be attributed to devitrification (Fig. 12b). The pattern formed by the breakage glass without loam additives, fired at the same temperature and time is X-ray amorphous (Fig. 12a). Thus, loam contributes to the formation of the crystalline phase, which is usually present in devitrification of sheet glass.

We found out that for samples, containing BACP, the optimal firing temperature is 1023 K. These samples showed a tendency for reduction of their specific gravity with increasing of the number of BACP in the charge from 4.5 to 9.0 mass %. Further increase of its content leads to a gradual increase in the specific gravity (Fig. 13).

The samples, containing BACP, had an uniform porosity, specific gravity of 260 - 440 kg/m³, compressive strength 1.8 - 3.0 MPa and thermal conductivity of not more than 0.06 W/m K.

As shown in Fig. 14, as a result of the use as a bloating agent of 4.5 to 6.0 mass % BACP, the charge forms an almost invisible microporous structure. However, the specific gravity of such samples does not exceed 460 kg/m³, which is less than the specific gravity of the lightest samples of the previously developed porous materials, using fly ash (490 kg/m³) [18]. This fact indirectly indicates that the samples, containing BACP, have lower thermal conductivity than the material, obtained from using a carbon bloating agent. This assumption is confirmed for all materials in which the bloating agent’s...
role is played by hydrates.

For example, samples containing loam have a lower thermal conductivity (0.05 W/m K) than industrial foam glass, produced by the JSC «Plant of building insulation materials» (Zaporozhye), for manufacturing of which carbon bloating agent is used. According to the technical conditions of Ukraine № 26.133011391-001:2006 «Insulation blocks from foam glass», the thermal conductivity of industrial foam glass is regulated to be no more than 0.066 W/m K, while the thermal conductivity of our research samples, with loam as a bloating agent is 0.05 W/m K. In addition, the temperature for obtaining of such porous material is 75K lower than the industrial one.

The same pattern is visible on the samples, obtained with open-hearth slag, as a bloating agent (Fig. 15), the previous studies of which indicated a high content of calcium hydrosilicate of afvillit in it (3CaO•2SiO$_2$•3H$_2$O).

Fig. 16 shows that the use of less than 5 mass % of open-hearth slag as the bloating agent does not give a porous material, and the addition of more than 15 mass % is not reasonable, as it results in compaction of the porous structure.

The obtained samples were characterized by homogeneous fine porous structure, specific gravity of 220 - 420 kg/m$^3$ and compressive strength of 1,5 - 6 MPa.

X-ray analysis proved the glass-crystalline structure of the obtained porous materials (Fig. 9, 12-b). Crystallization of foam glass in most papers is considered as a negative phenomenon. According to the authors of [19], in the synthesis of new compositions of foam glass, special attention should be paid to the search of compositions with a minimum tendency to crystallize at the foaming temperature, as crystallization deteriorates the foaming process or even prevents the obtaining of foam glass. To prevent crystallization in foam glass we needed to choose such foaming temperature conditions so that we could avoid the crystallization process at the time of foaming or before the start of foaming the formation of crystalline phase was found in the initial state. When considering foam glass crystallization processes, it should be noted that in the literature we can find little data on directional crystallization of pore partitions of vitreous material. With a prevailing idea that the crystal-
In the classic foam glass, the content of non-melted particles or stable crystalline phases from raw materials is generally regulated at no more than 5%. This restriction is explained by the presence of large crystals in the glass that can cause the destruction between pore partitions and the growth of rate of water absorption and, as a result – reduce frost resistance and durability of the foam glass products.

On the other hand, the metastable state, which is characteristic for vitreous material under appropriate thermodynamic conditions, can cause uncontrolled crystallization, accompanied by destruction of the glass and its devitrification that leads to the loss of original properties of the foam glass products.

In connection with the above mentioned, in our opinion it is very important to search opportunities for obtaining of a porous material with a partially crystallized structure of pore partitions. The interest on this subject is due, firstly, to the fact that the crystallization to some extent deteriorates the foaming processes, resulting in the compacting and hardening of the foam glass structure, and secondly – the completeness of the crystallization processes in the porous material at the stage of technology is much better, than when the crystallization processes occur in exploitation.

To prove the assumption that fine porous crystallization between pore partitions increases the strength of the synthesized material, we carried out scanning electron microscopy of samples containing blast furnace slag (Fig. 17) with the highest compressive strength (4 - 12 MPa).

Fig. 17-a illustrates the partially crystallized structure of the synthesized porous material. In Fig. 17 many needle-shaped crystals of average length of 9 microns can be clearly seen. In our opinion they perform a reinforcing function, increasing the strength of the material.

**CONCLUSIONS**

The theoretical and experimental studies, confirmed by X-ray phase and differential thermal analyses, established the fundamental possibility for obtaining of glass-crystalline porous materials with non-deficient recycled and natural materials, containing hydration water in the structure. It was shown that the hydration water in the charge can significantly reduce the temperature of firing.
of such materials.

The rational concentration of bloating agents (natural and man-made) was established from the point of view of obtaining materials with desired properties.

Electronic microscopic analysis confirms the partial microcrystallization of the pore partitions of the developed porous material, which increases its strength.

The advantage of developed porous glass-crystalline materials is that they do not contain harmful to humans and the environment components. Their production can significantly reduce energy and material costs in comparison to the manufacturing of foam glass according to traditional technology [3, 20]. In addition, the use of waste of metallurgical and construction industries as a bloating agent will contribute to their partial utilization and improvement of the environment.

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IMPROVEMENT OF THE TEMPERATURE CONDITIONS IN INDUSTRIAL FURNACES THROUGH SELECTION OF THE BASIC PARAMETERS OF THE COMBUSTION PROCESS

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ABSTRACT

In practical applications it happens that some of the basic parameters characterizing the combustion process have been changed. This can be enforced by the necessity for substitution of a given energy source with another one and also by the intentional or spontaneous alteration in the construction or the exploitation mode of the respective furnace. In order to ensure a predictability of the variation of the combustion temperature, it is necessary to have information about the qualitative and quantitative influence of the basic indicators conditioning the combustion on the temperature field in the furnace.

In the present work the results from an investigation of the tendencies in the change of the theoretical combustion temperature for three widely used gaseous energy sources with considerably different chemical compositions are submitted and discussed. They have low, middle and high lower specific heating value, respectively, and are studied in view of changing values of the preheating degree of the air fed to the corresponding equipment and of its excess above the theoretical necessary amount. The obtained conclusions of this energy and ecological investigation can be useful for the comprehensive improvement of the efficiency of the heating units.

Keywords: combustion temperature, fuels, energy, ecology, efficiency.

INTRODUCTION

The sustainment of the project regimes in the present-day heating units is among the most important preconditions for their effective and faultless functioning. In most cases a maximal high temperature in the working area is aimed at, but it has to conform with a variety of factors and restrictions. The latter could have energy, constructive, ecological and economical, etc. nature. Thus for example, the maximum temperature should be less than about 2200 – 2300 K [1], above which burning with formation of a considerable amount of harmful for the environment nitrogen oxides starts.

In the literature exhaustive experiments with particular fuels are described [2 – 12]. They usually finish with a detailed analysis of fuel behavior in combustion. In our opinion, however, with some exceptions [13], there is still a need for research summarizing on the experience from the using of different energy sources.

It often happens in the practice, that some of the basic parameters characterizing the burning process should be changed. The substitution of one fuel with another one is a typical situation, which by the market dynamics or in the drive for achievement of more compatible environmental and technological indicators can be enforced.

A considerable disturbance in the ordinary conditions in the furnace can occur, by an intentional or spontaneous change of its construction or exploitation mode. In the course of time, the leak tightness of the operating chamber decreases even at a good maintenance. The thickness of the brickwork worsens, especially around the apertures of the unit. This leads to an increase of the air ratio, above the statutory values in the project. Furthermore, it is possible temporarily or constantly to have to open the windows for loading, emptying and control of the enforcement of the technological process, which produces the same result.

The listed most typical situations, as well as many other circumstances in the daily exploitation, lead inevitably to a violation of the temperature regime of a given furnace or other heat-technical unit, where a combus-
tion process is implemented. These disturbances reflect on the quality of the thermally processed product and spread over the whole technological flux in the considered object. As a result of that, serious damages for the enterprise, which can affect the equipment, as well as the made production and the environment might arise.

The expressed arguments ground the actual and original purpose of the present work, and the results from the fulfilled investigation of the dependence of the combustion temperature in the furnace on the basic parameters characterizing the burning – the lower heating value of the gaseous fuel, the temperature of the preheated air for supporting of this process and the air ratio, to be submitted.

Combustion temperatures and factors influencing them

For describing of the temperature fields in a given unit three concepts are mainly used [14]. Each of them has some conditional character. Nevertheless, by them the actual situation in the furnace and mostly the tendencies in its change can be judged.

A. Real combustion temperature

This indicator has a highest degree of representativeness. It is determined by the expression, which is valid at absence of heat loss due to accumulation in the brickwork, i. e. at stationary conditions (or ones close to them):

\[ T_r = T_0 + \frac{Q_l + Q_a + Q_f - Q_{ch} - Q_d - Q_m - Q_e}{c_g V_g} \]

where \( c_g \) is the average volumetric specific heat capacity of the flue gas, J/(m\(^3\).K), \( T_0 \) = 273 K – the temperature at normal conditions, \( T_r \) – the real combustion temperature, K, \( Q_a \) – the physical heat of the preheated air, J/m\(^3\), \( Q_{ch} \) – the heat loss due to incomplete combustion through chemical reasons, J/m\(^3\), \( Q_d \) – the heat loss due to dissociation, J/m\(^3\), \( Q_e \) – the heat loss to the environment, J/m\(^3\), \( Q_f \) – the physical heat of the preheated fuel, J/m\(^3\), \( Q_l \) – the lower specific heating value of the gaseous fuel, J/m\(^3\), \( Q_m \) – the heat loss due to incomplete combustion through mechanical reasons, J/m\(^3\), \( Q_m \) – the physical heat of the fuel lost due to incomplete combustion through mechanical reasons, J/m\(^3\) and \( V_g \) – the volume of the moist flue gas, obtained in the complete real combustion of 1 m\(^3\) gaseous fuel, m\(^3\)/m\(^3\).

The analytical or experimental assessment of the real combustion temperature is a complicated problem [14], which limits the practical application of this parameter.

B. Theoretical combustion temperature

It is defined on the basis of formula (1), as additional preconditions for absence of heat losses due to incomplete combustion through chemical and mechanical reasons and also to the environment, are introduced.

At these restrictions, the theoretical combustion temperature is obtained by the expression:

\[ T_{th} = T_0 + \frac{Q_l + Q_a + Q_f - Q_d}{c_g V_g} \]

in which with \( T_{th} \) is the theoretical combustion temperature, K.

This indicator reflects the situation with a perfectly working furnace, in which all other heat loses are eliminated, except the one due to dissociation of the products of a complete burning to such ones of an incomplete process, the occurring of which can not be prevented.

C. Calorimetric combustion temperature

A most idealized picture of the situation in a given heat-technical unit is obtained by the calorimetric combustion temperature because, except for the enumerated in point 2.2 preconditions, in its definition it is also assumed that the heat loss due to dissociation equals zero. In conformity with that, this indicator is calculated by the formula:

\[ T_c = T_0 + \frac{Q_l + Q_a + Q_f}{c_g V_g} \]

where \( T_c \) is the calorimetric combustion temperature, K. Obviously the inequality is in force:

\[ T_c > T_{th} > T_r \]

D. Factors, influencing the combustion temperatures

The analysis of equations (1) – (3) shows that on each of the three combustion temperatures the following factors impact:

1) The temperature of the preheated air. It takes part in the calculation of \( Q_a \).

2) The temperature of the preheated fuel. This pa-
rameter defines $Q_f$.

3) The kind of the fuel. In expressions (1) – (3), the lower specific heating value of the energy source is directly used.

4) The air ratio. The raising of the first three factors leads to increase of each of the combustion temperatures and vice versa, while the last one has a different effect, depending on the value of the indicator $\alpha$, which might be lower or higher than 1. After a more detailed analysis of formulas (1) – (3) it can be established that at insufficiency of air, the growth of its ratio with the fuel amount causes an enhancement of the combustion temperatures, whereas at excess of air exists an opposite trend.

EXPERIMENTAL

The presented ascertainments in the previous section, which are known or could be foreseen without particular difficulties, have only a qualitative character. In order to ascertain accurate quantitative dependences between the considered temperatures and the factors influencing them, by which the high-temperature units can be managed and measures for increase of their energy, ecological and economical efficiency can be realized, an implementation of purpose-oriented researches is necessary. The use of direct physical tests in different industrial objects is unthinkable because of their big price due to the high cost of material recourses, time and labor. As a logical alternative remains the application of appropriate software, with the help of which computer experiments to be performed and the existing relations to be determined.

In this investigation the computational tool used, is developed at in the Department of Physical Metallurgy and Thermal Equipment of the University of Chemical Technology and Metallurgy in Sofia, Bulgaria. It gives the possibility for implementation of calculations of the basic parameters, characterizing the combustion process at different conditions and is grounded on the conventional procedures [14 – 17].

For the achievement of a higher applicability of the obtained results, it is necessary to reduce their dependence on specific indicators for a concrete furnace unit. On account of that, in the fulfillment of this study the following preconditions are accepted:

The comparisons are conducted according to the theoretical combustion temperature, calculated by formula (2).

The heat loss owing to dissociation amounts to 3% of the lower specific heating value of the energy source.

Only the air is preheated in an utilizing unit (regenerator or recuperator), while the gaseous fuel is fed to the furnace at temperature, coinciding with the one at normal conditions ($T_0 = 273 K$), and because of that its physical heat equals zero. This assumption corresponds in a maximal degree to the usual practice [18 – 21].

Under investigation are three gases – blast furnace, coke and natural gases, which are representatives of the different categories of energy sources according to their lower specific heating value, typical of low-, middle- and high-caloric fuels. Their compositions and

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Measure</th>
<th>Blast furnace gas</th>
<th>Coke gas</th>
<th>Natural gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide content*</td>
<td>$CO_2$</td>
<td>% vol</td>
<td>10.50</td>
<td>3.00</td>
<td>0.50</td>
</tr>
<tr>
<td>Carbon monoxide content*</td>
<td>$CO$</td>
<td>% vol</td>
<td>28.00</td>
<td>7.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Hydrogen content*</td>
<td>$H_2$</td>
<td>% vol</td>
<td>2.70</td>
<td>58.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Oxygen content*</td>
<td>$O_2$</td>
<td>% vol</td>
<td>0.00</td>
<td>1.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Nitrogen content*</td>
<td>$N_2$</td>
<td>% vol</td>
<td>58.50</td>
<td>6.00</td>
<td>4.40</td>
</tr>
<tr>
<td>Methane content*</td>
<td>$CH_4$</td>
<td>% vol</td>
<td>0.30</td>
<td>25.00</td>
<td>93.20</td>
</tr>
<tr>
<td>Ethane content*</td>
<td>$C_2H_6$</td>
<td>% vol</td>
<td>0.00</td>
<td>0.00</td>
<td>0.70</td>
</tr>
<tr>
<td>Propane content*</td>
<td>$C_3H_8$</td>
<td>% vol</td>
<td>0.00</td>
<td>0.00</td>
<td>0.60</td>
</tr>
<tr>
<td>Butane content*</td>
<td>$C_4H_{10}$</td>
<td>% vol</td>
<td>0.00</td>
<td>0.00</td>
<td>0.60</td>
</tr>
<tr>
<td>Water steam mass content of the fuel</td>
<td>$\rho g/m^3$</td>
<td>15.00</td>
<td>15.00</td>
<td>15.00</td>
<td></td>
</tr>
<tr>
<td>Water steam mass content of the air</td>
<td>$\rho g/m^3$</td>
<td>12.00</td>
<td>12.00</td>
<td>12.00</td>
<td></td>
</tr>
<tr>
<td>Lower specific heating value of the fuel</td>
<td>$Q_f$</td>
<td>kJ/m$^3$</td>
<td>3865</td>
<td>15780</td>
<td>34476</td>
</tr>
</tbody>
</table>
characteristics are taken from [22].

The temperature of the air fed for supporting of the combustion process, $T_a$, K, is changed in intervals of 100 K from 273 K to 973 K.

The air ratio varies between 1.00 (this value fits a theoretical combustion) and 1.30 (this one corresponds to a rather high excess of the oxidizing medium for gaseous energy sources, regardless of the burner type [23]) with a step of 0.05.

The calculations are conducted by enhancement of the values of each of the last two factors in the set boundaries and fixing of the other one firstly on its minimum, and then on its maximum level.

In Table 1 are presented the most important indicators of the used at the study fuels and atmospheric air.

Fig. 1. Dependence of the theoretical combustion temperature on the air temperature at air ratio 1.00

Fig. 2. Dependence of the theoretical combustion temperature on the air temperature at air ratio 1.30

Fig. 3. Dependence of the theoretical combustion temperature on the air ratio at air temperature 273 K.

Fig. 4. Dependence of the theoretical combustion temperature on the air ratio at air temperature 973 K.
RESULTS AND DISCUSSION

In Figs. 1 – 4 the results from the calculations with the used software are displayed.

From Figs. 1 – 4 the following should be noted.

With the increase of the preheating degree of the air fed to the furnace, a clear tendency for raising of the theoretical combustion temperature in it can be noticed (Fig. 1 and 2).

At equal other conditions, the coke gas ensures the highest value of the indicator $T_{th}$ in comparison with the other investigated fuels. For the blast furnace gas this seems quite logical on account of its small lower specific heating value, while the comparison with the natural gas requires a certain deliberation. The explanation obviously is in the balance between the separate factors participating in formula (2). The indicator $Q_i$ of the coke gas has more than 2 times lower value than that of the natural one, but the proportions between the theoretical and the real volumes of the fed air and the prepared products of burning ensure the noticed higher value of the theoretical combustion temperature of the coke gas (Fig. 1 - 4).

With the increase of the parameter $T_\alpha$, the theoretical combustion temperature grows most rapidly for the natural gas, as it requires a highest amount of air for its complete oxidizing. The most slowly enhancement of $T_{th}$ is law-governed by its minimum air needs and the respective modest effect on the observed indicator (Figs. 1 and 2).

The described tendencies in Fig. 1 and 2 occur in theoretical combustion ($\alpha = 1.00$), and in the one with a considerable excess of air ($\alpha = 1.30$).

The increase of the air ratio leads to reduction of the theoretical combustion temperature with an approximately constant rate, when working with cold air (Fig. 3), and also when it is preheated to 973 K (Fig. 4).

The relations revealed in Fig. 1 – 4 should be taken into consideration by the experts in designing and exploitation of high-temperature equipment when undertaking changes in the organization of the combustion process and the flue gas heat utilization, as well as in unexpected circumstances and operation in emergency conditions.

In order to obtain of a clearer quantitative idea of the relative decrease of the theoretical combustion temperature when the air ratio increases from 1.00 to 1.30, $\Delta$, %, is calculated by the following formula:

$$\Delta^* = \frac{T_{th}^{\alpha=1.00} - T_{th}^{\alpha=1.30}}{T_{th}^{\alpha=1.00}} \times 100$$

and Fig. 5 is drawn. It presents the dependence of this indicator on the air temperature.

The relative differences between the theoretical combustion temperatures with a stoichiometric air amount and with excess of 30 % for the three fuels, presented in Fig. 5, show that the natural gas is most sensitive to an increase of the air ratio. At higher air preheating temperature in the utilizing unit, the values diminish from 15.51 % to 11.68 %. For the coke gas the same relationship is noticed, by lowering of the introduced indicator $\Delta^*$ from 14.69 % to 11.07 %. Considerably more weakly expressed in a quantitative aspect is this tendency for the blast furnace gas, where the reduction is from 8.33 % to 5.15 %. The modest and comparatively unessential change of these values is due to the lowest air
requirement of the last fuel, which reflects on the most weak sensitivity towards the factors $a$ and $T_a$.

With the purpose to achieve a more complete clarifying of the influence of the air ratio on the relative decrease of the theoretical combustion temperature when reducing the air temperature from 973 K at 273 K, $\Delta^{**}$, %, is determined by the expression:

$\Delta^{**} = \frac{T_{th}^{973K} - T_{th}^{273K}}{T_{th}^{973K}} \times 100$  \hspace{1cm} (6)

by which the graphical comparison, shown in Fig. 6 is made.

From Fig. 6 it can be seen that the relative difference between the theoretical combustion temperatures when preheating the air to 973 K and when feeding it in a cold state (with 273 K) increases with the increase of the air excess for all studied fuels. Again highest values and the most significant deviations between them (from 18.87 % to 23.22 %) are established for the natural gas, followed by the coke and the blast furnace. For the last fuel, the indicator $\Delta^{**}$ has more modest and slowly altering values – from 14.62 at $\alpha = 1.00$ to 18.21 % at $\alpha = 1.30$.

**CONCLUSIONS**

The tendencies in the changes of the theoretical combustion temperature for three widely used gaseous energy sources with a low, middle and high lower specific heating value at a variation of the preheating degree of the air fed to the corresponding furnace unit and of its excess above the stoichiometric necessary amount are determined and qualitative analyzed.

Two relative indicators allowing quantitative assessment of the change of the theoretical combustion temperature when the air ratio is changed from 1.00 at 1.30, as a function of its temperature, and also when reducing air temperature from 973 K at 273 K, depending on its excess, are introduced.

The presented investigation gives useful information about the trends in the changes of the theoretical combustion temperature, as well as for the real combustion temperature, and the temperatures of the flue gas and of the brickwork in separate points of the operating area.

The results obtained for the chosen three types of gaseous fuels according to their lower specific heating value can be used also for quantitative prediction of the expected disturbance in the temperature field of the furnace at changes of the exploitation conditions, which is a necessary stage in the energy investigation and the comprehensive improvement of the efficiency of each heat-technical unit.

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THERMODYNAMIC CALCULATIONS AND EXPERIMENTAL INVESTIGATION OF THE Ag-Zn SYSTEM


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ABSTRACT

Thermodynamic calculations and experimental investigation of binary alloys in the Ag-Zn system are presented in this paper. The results of the thermodynamic calculation of the Ag-Zn phase diagram are obtained using the CALPHAD method and the PANDAT thermodynamic software, while in the frame of the experimental investigation, thermal and structural analysis, as well as mechanical and electrical characteristics of the chosen samples are given.

Keywords: Ag-Zn alloys, binary systems, phase diagrams, thermodynamics, hardness, electroconductivity.

INTRODUCTION

Given their diverse applications, Ag-Zn alloys have been studied from various aspects [1 - 9]. In recent years, the interest for this particular binary system has increased because of the many potentially lead-based metallic materials [10 - 16] used in the production of special Ag-Zn batteries [17], contact materials [18], as well as in other branches.

Previous investigations of the Ag-Zn system [19] have shown the existence of several solid phases between silver-rich (α or (Ag)-phase) and zinc-rich (or η (Zn)-phase) in the phase diagram, as follows: β-phase, which corresponds to ZnAg - the equiatomic composition and is stable at higher temperatures, ζ-phase, which is ZnAg stable at lower temperatures, and phase-g and e-phase, corresponding to intermetallic compounds - Ag5Zn8, AgZn3, respectively. Also, it can be noticed on the basis of the literature data [19 - 21] that some deviation occurs between the experimental and calculated phase diagram.

The thermodynamic calculation of the phase diagram of the Ag-Zn system and experimental investigation of thermal, structural, mechanical and electrical properties of selected alloys is presented in this paper, as a contribution to a more complete study of this binary system.

EXPERIMENTAL

Investigated Ag-Zn alloys were prepared from metal silver and zinc of 99.99 % purity by melting them in an induction furnace under protective atmosphere.

Selected alloys with 10; 20; 30; 40; and 50 at. % of silver were studied using differential-thermal analysis (DTA) and light optical microscopy (LOM), while hardness and electrical conductivity measurements were performed on samples with molar content of silver equal to 0.2; 0.4; 0.6; and 0.8.

DTA tests were carried out on the Derivatograph 1500 (MOM Budapest) device under the following conditions - air atmosphere, heating rate of 10°C/min, maximum investigation temperature of 1273 K, and Al2O3, used as reference material.

Metallographically prepared samples were recorded on an optical microscope Reichert MeF2, with magnification 300:1. Structure development was done using an etching solution of the following composition – (30 ml CH3COOH +10 ml 9 % H2O2).

Hardness measurements were performed using...
standard the Brinell method, while the measurement of electrical conductivity was done using the apparatus SIGMATEST 2069 (Foerster).

RESULTS AND DISCUSSION

The results obtained in this work are presented in two parts – phase diagram investigation using thermodynamic calculations and thermal analysis, and characterization of the investigated samples.

a) Thermodynamic calculations and thermal analysis in the Ag-Zn phase diagram investigation

Thermodynamic calculations of the phase diagram of Ag-Zn in this study was performed according to the CALPHAD method [22] using the thermodynamic software PANDAT Vs. 8.0 [23], based on the initial thermodynamic data taken from the COST531 database [24], given in Table 1. Crystal structure data of the phases in the Ag-Zn system, taken from [25], is shown in Table 2.

During the DTA measurements, endothermic peaks for characteristic phase transformations were detected for investigated Zn-Ag alloys. Their temperatures are presented in Table 4.

The results of the thermodynamic prediction were compared with experimental DTA results from this work,

as presented in Fig.1, showing good mutual agreement and also adequate accordance with literature [19].

b) Characterization of the investigated Ag-Zn samples.

The characterization of the Zn-Ag system, in the composition range with low silver content, included light optical microscopy (LOM), and hardness and electric conductivity measurements of the chosen samples.

Fig.1. Calculated Ag-Zn phase diagram with experimentally obtained DTA results (circles).
The LOM results for three investigated Zn-Ag alloys are given through the characteristic microphotographs, shown in Fig. 2.

Chosen Ag-Zn alloys with low silver content were investigated by hardness and electrical conductivity measurements, as well. The obtained results are shown in Table 5 and Fig. 3, respectively.

As can be seen from Fig.3, the hardness of the samples decreases with composition, while the situation with the electrical conductivity is opposite - significantly increasing towards pure silver corner.

**CONCLUSIONS**

The results obtained in this study indicate mutual compatibility of experimental and calculated phase transformation temperatures existing in investigated system for Ag-Zn alloys. A good agreement with existing literature phase diagrams of Ag-Zn is noticed. The obtained data may be useful for further completion of the Zn-Ag thermodynamic and phase diagram data, and also for other investigations of Zn-Ag-based systems [26 - 28].

**Acknowledgements**

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ABSTRACT

In this paper the process of producing steel slabs by continuous casting in the Steel Mill Makstil in Skopje is presented. The technological process of slab’s production is described and the assortment of steel slabs in the Steel Mill is given. Also, the most frequent defects of slabs (internal and surfaces) are analysed. Special attention was given to the solidification processes in the continuous casting of slabs. Mathematical modeling of solidification processes during the slab’s forming was performed. For this purpose, numerical and analytical methods were applied. The temperature field in the steel solidification area, as well as the liquid phase length were defined. The temperature field was determined by using the finite element method and also by a new analytical method - isothermal method, applying Green’s function. In this way, liquid, solid and two-phase area throughout the solidification process were defined. On the basis of direct measurements of the real temperature in the solidification process of the slabs, a comparison of the results, obtained by mathematical modelling and the real ones, was carried out. The comparison points out that the applied numerical and analytical methods display satisfying results in terms of appropriate determination of the solidification process of the steel slabs. The obtained knowledge can be used to optimize the continuous casting process and to improve the quality of the continuous casting steel slabs.

Keyword: solidification, mathematical modeling, steel, slabs, isothermal method.

INTRODUCTION

The process of producing steel slabs by continuous casting is very complex. The quality of the slab depends on the steel quality and the solidification conditions [1, 2]. Properly guided casting process and good solidification conditions are accomplished with maintaining of the parameters of the continuous casting process in the optimal intervals. In practice, the technological parameters of the continuous casting process usually show slight variations [3, 4].

The analysis of the slab solidification process in industrial environment consists of following of current casting processes and the given technological parameters of the processes [5-7]. Afterwards, the quality of the produced slabs was analysed and a relation between the quality and production conditions was established.

The variation of the technological parameters of the continuous casting process in very narrow intervals significantly reduces the investigation possibilities and limits it on an analysis of the given data and the established relations between the process parameters and the slab quality. The most relevant of the followed parameters are casting speed, inflow temperature of the liquid steel in the mould and the conditions of heat transfer [8-14]. The temperature filed formed during the casting and solidification of the slab is a result of the aforementioned parameters [11, 15, 16]. It is known that the shape and the size of the two-phased area of the slab in the solidification process have influence on the slabs
quality [6, 17-19].

In the aim of determining the optimal conditions for slab producing, which provide good quality, the temperature field in the slab continuous casting process was analysed.

**OVERVIEW OF THE PROCESS OF CONTINUOUS CASTING OF STEEL SLABS**

The processes of the producing steel slabs by continuous casting in the Steel Mill in Skopje are done on radial-curved continuous casting installation, with overall length of 23 m. The installation has three casting lines with a radius of 10 m, with a capacity of 85000 t steel per year. The capacity of the ladle is 110 t.

The mould is rectangular in shape, with a height of 1200 mm. The produced slabs can have 4 different widths and thicknesses. On the end of the mould the motion of the slabs is made possible by 9 draw beams. The purpose of the draw beams is contact and secondary cooling, which results in reduction of thermal strain in the slab. Straightening of the slab is done in the eight zone. After the draw beam, the slab is cooled by water jets. The cooling process is regulated automatically. The capacity of the water jets is 27 l/h. Water consumption in the mould is approximately 300 m$^3$/h, similarly to the draw beam zone.

**EXPERIMENTAL**

From the various types of steel produced by continuous casting, here, the manganese and carbon steels were analysed. The carbon steels are divided in two groups - with carbon content up to 0.1 % and above 0.1 %.

The analysed slabs had the following dimensions - width 1540 mm and thickness 250 mm. The total number of castings was 105; 46 of type I, 30 of type II and 29 of type III [20]. During the processes, the following parameters were monitored:

- content of some of the elements in the steel - C, Si, Mn, P, S, Cu, Al and N, as well as the ratios Mn/S and C/10 + S, expressed in %.
- parameters of the temperature regime - the temperature of the steel during the pouring in the ladle ($T_p$), in the ladle ($T_L$), during the inflow in the tundish ($T_T$), during the inflow in the mould ($T_M$); expressed in °C.
- most important technological parameters of the process - casting speed (w), expressed in m s$^{-1}$, and the quantity of water spent for primary cooling ($Q_M$) and secondary cooling ($Q_S$), expressed in litre water/kg steel;

- duration for some of the operations - duration of the out-of-furnace treatment of the steel ($\tau_{O}$), duration of the casting of the steel from the tundish to the mould ($\tau_M$) and duration of the casting ($\tau_C$), expressed in seconds.

For direct measurements of the temperature (in situ) in characteristic points of the slabs Pt-RhPt thermocouple was used. For the other researches, mathematical modeling was performed, by applying numerical and analytical methods. Some of the results were done by mathematical-statistical analysis - distribution and regressive analysis. Mathematical modeling was performed by finite element method and also by a new analytical method - isothermal method, applying Green’s function.

<table>
<thead>
<tr>
<th>Chemical composition, mass %</th>
<th>Type of steel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
</tr>
<tr>
<td>0.8 ≤ Mn ≤ 1.5 [%]</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.14 - 0.21</td>
</tr>
<tr>
<td>Si</td>
<td>0.15 - 0.36</td>
</tr>
<tr>
<td>Mn</td>
<td>0.80 - 1.39</td>
</tr>
<tr>
<td>P</td>
<td>0.009 - 0.025</td>
</tr>
<tr>
<td>S</td>
<td>0.016 - 0.034</td>
</tr>
<tr>
<td>Cu</td>
<td>0.12 - 0.24</td>
</tr>
<tr>
<td>Al</td>
<td>0.005 - 0.0085</td>
</tr>
<tr>
<td>N</td>
<td>0.007 - 0.011</td>
</tr>
</tbody>
</table>

Table 1. Chemical composition of steel.
RESULTS AND DISCUSSION

The efficiency of the continuous casting process is estimated with an analysis of the steel output for all followed castings. A mathematical-statistical analysis was done. During the disperse analysis a small amount of castings with low output percentage was excluded, produced as a result of rough defects in the casting process. Part of the obtained result is presented in Table 2, where the values for the deviations, as well as minimal, maximal and mean values for the steel output are given. The distribution of the mean values of the output is shown on Figs. 1, 2 and 3.

As can be seen from the Table 2 and the Figs. 1, 2 and 3, the minimum output of steel is about 88 %. The mean values for the output are from 96.89 % (for type I steel) to 95.33 % (for type III steel). Understandably, the distribution of the mean values for the output is located on the right.

![Graph](image)

Fig. 1. Distribution of the output of steel for type I of steel casting.

![Graph](image)

Fig. 2. Distribution of the output of steel for type II of steel casting.

![Graph](image)

Fig. 3. Distribution of the output of steel for type III of steel casting.

Afterwards, a regressive analysis was done. As independent variables the aforementioned parameters were used, 20 in total, and the dependent variable was the percentage of steel output. Using the regressive analysis dependences in polynomial form, for all three types of steel, were obtained.

\[
y_1 = -282.87 + 9.85 \cdot C + 140.51 \cdot S - 305.44 \cdot (C/10 + S) + 0.04 \cdot T_p + 0.06 \cdot T_s + 0.146 \cdot T_f - 0.001 \cdot T_g - 0.31 \cdot Q_m \\
\]

(1)

\[
y_2 = 284.48 + 207.22 \cdot C + 2638.3 \cdot S - 2471.9 \cdot (C/10 + S) + 0.05 \cdot (Mn/S) - 0.065 \cdot T_s + 0.01 \cdot T_p - 0.05 \cdot T_f - 0.001 \cdot T_g \\
\]

(2)

\[
y_3 = 754.76 - 59.16 \cdot N_t - 0.07 \cdot T_p - 0.01 \cdot T_f - 0.177 \cdot T_g + 8.19 \cdot Q_s - 0.167 \cdot T_f - 0.014 \cdot T_c - 3.091 \cdot Q_m \\
\]

(3)

The regressive analysis provided interesting data about the influence of some parameters on the steel output. On the manganese steel (type I) the parameters of the temperature regime showed the greatest influence \((T_p, T_f, T_g, T_m)\), as well as the primary cooling \((Q_m)\).

The chemical composition has somewhat less influence, whereas the conditions of the secondary cooling have the least influence. In the case of carbon steels (type II and III) the parameters of the temperature regime also have the greatest influence, whereas the influence of the chemical composition is less expressed. In general, the greatest influence on the steel output is the one of the parameters of the temperature regime, especially \(T_m\). The most influential from the chemical composition are C and S, as well as the relations C/10+S and Mn/S. The most important from the other parameters are the
One of the most important parameters, the casting speed, was not singled out by the regressive analysis as important for the steel output. The reason for this is the narrow interval of variations for the casting speed, which, in the investigated cases, varied from 0.0092 - 0.0133 m s$^{-1}$. This is also the case for the content of N, which influences the output of steel insignificantly, but has a crucial meaning in real processes.

**Determining of the temperature field during slab solidification by mathematical modeling with isothermal method**

The temperature field during solidification of the slab was investigated by mathematical modeling. The known temperature values in individual places of the slab, obtained with direct measurements (in situ) during the solidification of 3 slabs, were used as starting points for the modeling and for determining the time constants [21]. The temperature field on the longitudinal sections of the slabs was determined by numerical method - method of finite elements [22-24]. On the basis of the slabs determined temperature field on the 2D sections, the spatial areas of the liquid, solid and two-phased area were defined [25, 26].

Then, the new, isothermal method was used [27]. The basis for the isothermal method is the Green’s function [28, 29]. It is derived from the mathematical description of the cooling process of steel rectangle for given initial conditions. Using the isothermal method the following parameters were determined: the liquid phase, the shape and size of the liquid phase on the longitudinal section, as well as the shape of the solidus and liquidus curves on the slabs cross-sections.

For determining of the shape of the solidus and liquidus on the longitudinal section of the slab the following expression was used [29]:

$$G(x, \tau, x') = \sqrt{\frac{1}{4\pi \tau}} \exp \left[ -\frac{(x - x')^2}{4\tau} \right]$$  \hspace{1cm} (4)

where: $\tau$ - time, $x$ - coordinate which matches the slabs thickness. The coefficient of heat-conductivity, $a$, is [21, 30]:

$$a(T) = \frac{\lambda(T)}{c_{eff}(T) \cdot \rho(T)}$$  \hspace{1cm} (5)

where: $\lambda(T)$ - coefficient of heat transfer, $c_{eff}(T)$ - effective specific heat and $\rho(T)$ - density. Characteristic for these parameters is that they are considered as functional dependences on the temperature, and not as constants; $c_{eff}(T)$ is

$$c_{eff}(T) = c - L \cdot \frac{\partial \Psi}{\partial \tau}$$ for the temperature interval

$$T_{sol} \leq T \leq T_{liq},$$  \hspace{1cm} (6)

where: $c$ - specific heat, $L$ - latent heat, $\Psi$ - formed solid phase, $T$ - temperature, $T_{sol}$ - temperature solidus, $T_{liq}$ - temperature liquidus.

For determining of the isoliquidus and isosolidus curves on the cross-section of the slab the following expression was used [20, 27]:

$$Z_{i,j} = \frac{L_1}{\pi} \left[ \frac{1 - \frac{T_{sol}}{T_0}}{64 \cdot \frac{\pi \cdot x_i \cdot \pi \cdot y_j}{L_1 \cdot L_2} \cdot C_1 \cdot C_2} \right]$$  \hspace{1cm} (7)

where: $L_1$ - slabs thickness, $L_2$ - slabs width, $L_3$ - slabs length, $T_0$ - steel casting temperature, $C_1$ and $C_2$ - time constants, which values should be previously determined. The values for $x_i$ are from 0 to $L_1/2$, and the $y_i$ values - from 0 to $L_2/2$. The $z_i$ coordinate is related to

<table>
<thead>
<tr>
<th>Castings</th>
<th>Output of steel, Y[%]</th>
<th>Root mean square deviation, S, [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>minimum</td>
<td>maximum</td>
</tr>
<tr>
<td>I</td>
<td>89</td>
<td>99</td>
</tr>
<tr>
<td>II</td>
<td>88</td>
<td>99</td>
</tr>
<tr>
<td>III</td>
<td>88</td>
<td>99</td>
</tr>
</tbody>
</table>

Table 2. Values for the steel output, Y, and root mean square deviation, S.
the slabs length - from 0 to \( L_x \).

The values of the time constants are determined using the expression [20]:

\[
C_i = \frac{1 - \frac{T_{liq}}{T_0}}{\frac{64}{\pi^3} \sin \frac{\pi \cdot x_i}{L_1} \cdot \sin \frac{\pi \cdot y_i}{L_2} \cdot \sin \frac{\pi \cdot z_i}{L_3}}
\]  

(8)

The time constants can also be calculated using the solidification constant [21]:

\[
\delta = c \cdot \sqrt{T_{sol}}
\]  

(9)

where: \( \delta \) - shell thickness, \( c \) - solidification constant, \( \tau_{sol} \) - solidification time.

The values of the time constants should be determined for each meter along the length of the slab. The constants values obtained using the expressions (8) and (9) were compared with the values obtained by direct measurements of the temperature field during the solidification. The shape of shell thickness on the longitudinal wider section of the slab for all 3 cases is presented on Fig. 4.

With the exception of the beginning, the values of the shell thickness obtained by the Greene’s function coincide to the real, measured values. Because of that, they were inputted into the isothermal model. The appliance of the isothermal methods provides analytical solutions which satisfy the differential equation - Greene’s function. The solution should satisfy the given starting conditions, such as the liquid phase length and the mould’s dimensions. The areas for liquid, two-phased and solid phase on the cross-sections of the slab were determined, beginning from the liquid steel’s surface in the mould after each meter. 2D cross-section on the mould’s outlet with solidus and liquidus curves is presented on Fig. 5. On Fig. 6 all of the solidus curves are shown, from the mould’s outlet, to 9 m of the slabs length, on each meter of its length.

On Fig. 7 the longitudinal section of the wider side of the slab \( (L_{2x}) \) is presented, with defined areas for the liquid, solid and two-phased area. The liquid phase extends to 4.72 m of length, whereas the two-phased area has a length of 10.32 m.

All of the solidus curves, calculated for one quarter of the slabs cross-section, from the mould’s outlet, to 9 m of the slabs length, on each meter, presented on the whole cross-section surface, are presented on Fig. 8.

The determining of the slabs temperature field has an increased accuracy of 4.3 % because all of the thermophysical parameters are entered into the model, not as constants, but as functional dependences on the

![Fig. 4. Shell thickness obtained by different approaches: 1 - direct measurements, 2 - calculated using the expression (9), 3 - calculated using the expression (8).](image1)

![Fig. 5. Solidus and liquidus curves on 1/4 of the slabs cross-section on the mould's outlet; 1-solidus, 2- liquidus curve.](image2)
temperature. Also, the isothermal method, in comparison to the other methods, has an option for 2D graphical presentation of the solidus and liquidus curves on slab’s cross-sections, or 3D presentation, with connecting of the curves.

**Relation between the production conditions, the temperature field and the quality of the slabs**

In the aim of establishing a relation between the production conditions, the temperature field during the solidification and the quality of the slabs, the processing of 600 castings was followed and an statistical analysis of the appearance of defects in the slabs was done [31]. From the analysed castings, 17.3 % were without defects, and 82.7 % had some type of defect present. A total of 353 t of steel was removed by flame gouging. However, it can be said that the slabs have satisfying quality, because 353 t is about 0.6 % of the overall weight of the slabs. An overview of the registered defects is presented on Fig. 9. The most common are the cracks: spider cracks, longitudinal, corner, transverse and edge cracks. These defects make 66.8 % of the overall defects. Bubbles are also a common type of defect - they occur in 25.6 % of the cases.

The quality of the produced slabs is directly related to the chemical composition of the steel and the parameters of the continuous casting process. The greatest influence, from all of the followed parameters, have the conditions of the heat transfer, the steel’s inflow temperature in the mould and the casting speed, which influences the temperature field formed during the solidification.

The analysis of the defects in dependence on the casting speed has shown that the defects occur more frequently at higher casting speeds [31]. Thus, the corner cracks have increased for 3.5 times during casting speeds of 0.013 m s$^{-1}$ compared to casting speeds of 0.008 m s$^{-1}$. The temperature of the liquid steel also influences the increase of different types of cracks, especially the
corner cracks, which have increased 6 times with the increase of the liquid steel’s temperature of 18°C. With more intense primary cooling it is notable the increase of the longitudinal and spider cracks. The intensifying of the primary cooling of 25 %, the total sum of defects increases for almost 3 times, and the intensifying of the secondary cooling of 25 % - increases the total sum of defects for 1.5 times.

Comparing the total sum of defects in relation to the size and shape of the liquid phase it can be said that at larger lengths the defects occur less frequently. Thus, castings with a length of the liquid phase of 11.7 m have 25 % less defects than castings with a liquid phase 10.32 m long. Castings with a smaller length of the liquid phase are characterised with lamination and corner cracks, whereas castings with longer liquid phase are characterised with axial porosity and structure forming with three characteristic zones.

The role of the mathematical modelling of the temperature field is in the proper choice of technological parameters which will provide optimal conditions for steel solidification and heat transfer \[32, 33\]. The structure which provides good quality of the slabs has a zone of columnar grains as small as possible and a zone of small unoriented grains as large as possible. This is provided by a wide two-phased area, which is formed at low temperature gradients and less intensive secondary cooling.

**CONCLUSIONS**

The mean values for the steel output are from 95.33 %, for carbon steel with content of C > 0.1 % to 96.89 %, for manganese steel.

The greatest influence on the steel output have the parameters of the temperature regime, especially the steel’s inflow temperature in the mould, then the chemical composition and the conditions of the heat transfer. The steel output is mostly influenced by the content of C and S, as well as the relations C/10+S and Mn/S.

The temperature field of the slab during solidification is determined by mathematical modeling, with application of the numerical and the new analytical, isothermal method. The areas of the liquid, solid and two-phased zones were determined.

The isothermal method, in comparison to other methods, is accurate enough, with the exception of small deviations at the beginning of the solidification process. The option for graphic presentation of the results makes the isothermal method suitable for determining of the slab’s temperature field in stationary conditions.

Various types of defects occur in 82.7 % of the analysed slabs. The cracks - spider cracks, longitudinal, corner, transversal and edge cracks make 66.8 % of the defects. Bubbles are also a common defect - they occur in 25.6 % of the cases.

The defects are more frequent at higher casting speeds, higher temperatures of the liquid steel and more intense primary cooling.

The role of the mathematical modeling of the temperature field is the choice of the technological
parameters which will provide optimal conditions for slab solidification and production of quality steel slabs.

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