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ABSTRACT

Nanotechnology and engineered nanostructures (ENSS) are becoming part of everyday life, starting from industrial application, even in food products, to gene therapy. Thus, tons and tons of nanoparticles (NPs) enter the environment and indirectly or directly - into the biological systems, including the human body. There are many controversial papers that describe interactions of the ENSs with biological systems and raise concern that intentional or unintentional human exposure to certain types of ENSs, may lead to significant health, i.e. toxicological effects. Because of our insufficient and contradictory knowledge about the health effects associated with the ENSs exposure, the aim of this paper is to summarize and systemize the already confirmed data and the latest found facts about ENSs and their health effects and to discuss the future opportunities and tasks in the field of nanotoxicology.

Keywords: engineered nanosized structures, nanotoxicology.

INTRODUCTION

Development of the industrial sector based on application of ENSs and nanotechnologies is a fast-growing activity. Scientific achievements in many areas of nanotechnology have been successfully transferred into numerous practical applications in the electronic, food, (bio)pharmaceutical, chemical and cosmetic industry, etc. Nanotechnology promises to exceed the impact of the “industrial revolution” with a projection of $1 trillion market by 2015 [1 - 3].

Nanomaterials and/or nanosized structures were studied in many products such as composites, sensors and chemical catalysts, nutraceutical, cosmeceutical, drug, cell and gene delivery systems, medical and electronic devices. However, due to their unique size and other physicochemical characteristics, they have raised a concern for their influence on human health and ecological systems. Research in this field is given a high priority and several reports on the toxicological properties of the ENSs with many documented deleterious effects, particularly in animals, already exist [4 - 6].

The specific physicochemical properties (Fig. 1) that make the nanosized structures useful are the same that may hazard the human body and the environment. Size distribution, surface area, porosity, shape, charge density, electrophoretic mobility, strength, flexibility, crystallinity/ solubility, stability/(bio)degradability, bio(muco)adhesivity, biocompatibility, etc., can all affect the biodistribution of the ENSs and human health.
Human exposure to ENSs can be direct or indirect - through contamination of the environment, with the main entries in the human body via the intestinal tract, lungs and skin. Generation of reactive oxygen and nitrogen species (ROs) and action by dissolved ions (in a case of metal and metal oxide NPs) were accepted as common mechanisms of cytotoxicity. Cellular plasma membrane, lysosomes, mitochondria, nucleus, and intracellular structural (cytoskeleton) and globular proteins were identified as important targets (Fig. 2) [7].

**NANOPARTICLES AND ENGINEERED NANOSTRUCTURES**

NPs include all engineered and ambient spherical particles smaller than 100 nm. They are variably called ultrafine particles (UFPs) by toxicologists from the U.S. Environmental Protection Agency, Aitken mode and nucleation mode particles by atmospheric scientists, and engineered nanostructured materials - by material scientists [8 - 11]. UFPs include ambient and laboratory-generated NPs that are not produced in a controlled, engineered way. Engineered NPs include only spherical NPs specifically engineered in the laboratory, while other ENSs are labelled according to their shape as nanotubes, nanofibres, nanowires, nanorings, etc. (Fig. 1).

ENs generated in working conditions can reach high exposure concentrations, up to several hundred micrograms per cubic meter. Even very low concentrations of nanosized materials in the air present very high particle number concentrations. For this reason and because of their different physicochemical properties as compared to larger sized particles of the same components, they have been considered as the most dangerous fraction for the human health. ENSs are so tiny that small quantities (expressed in terms of mass) could have major toxic effects because of their large surface which is often correlated with higher biological reactivity (e.g. formation of free radicals). Insoluble and low soluble ENSs usually end up in the bloodstream after crossing all the respiratory or gastrointestinal protective mechanisms and then are distributed in the various organs and accumulated at specific sites. They can travel along the olfactory nerves and penetrate directly into the brain, just as they can pass through the cell barriers [12 - 14].

In general, the toxicological data specific to ENSs remain insufficient due to the closely specialized-limited number of studies, the short exposure period, the dif-

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![Fig. 1. Nanosized structures: physicochemical properties, surface modifications and (dispersion) state.](image-url)
Different properties of the nanostructures tested and the often-unusual exposure route in the working environment, among other factors. Depending on the type of nanostructure, nephrotoxicity, effects on reproduction, genotoxicity and cytotoxic effects, mainly in animal studies, have been reported so far. Some nanostructures caused granulomas, fibrosis and tumorous reactions in the lungs [9 - 11]. Therefore, the population potentially exposed to ENSs should be prudent and apply safety measures of source elimination, exposure control and individual protection, both during the production and use of nanotechnology-based products. The most common materials in the descriptions of 580 of them are silver (139), followed by carbon (including fullerenes) (44), zinc (including zinc oxide) (28), titanium (including titanium dioxide) (28), silica (27) and gold (13) [15].

**Classes of manufactured nanostructures and toxic effects**

**Carbon nanotubes (CNTs):** Multi-walled (Fig. 3a) and single-walled carbon nanotubes (MWCNTs and SWCNTs) are constituted of a unique graphitic sheet or of two or more sheets nested together in a tubular multilayer structure. They possess extraordinary properties: high electrical and thermal conductivity, great strength and rigidity, energy storage and field emission [1, 2]. CNTs can be synthesized by three main methods: laser ablation, arc discharge (both these methods are based on the evaporation of graphite due to high temperatures) and chemical vapor deposition; evaporated carbon condenses successively in the form of CNTs and other structures, producing longer and less graphitized forms than the material obtained by the other methods. The arc discharge method has proved to be an interesting method for the mass production of CNTs. Also, other alternative methods were reported such as pyrolysis and electrolysis of molten lithium salts [2].

Fullerenes belong to a special carbon class of materials with spherical cages of 28 to more than 100 carbon atoms. They can be subjected to extreme pressures and regain their original shape when the pressure is released. These molecules are not modified and do not combine with each other. However, during manufacturing, certain carbon atoms can be replaced with other atoms and form bondable molecules, thus producing a hard but elastic material. The surface chemical composition can be modified and different organic chains can be added or incorporated into these CNTs. Since fullerenes are empty structures with dimensions similar to several biologically active molecules, they can be filled with different substances and find medical applications [16].

The last member of the series of fused polycyclic aromatic hydrocarbons is the graphene (Fig. 3b) [17]. For several years scientists thought that planar graphene could not exist in a free state since it was unstable, compared to curved structures like CNTs and fullerenes. However, Novoselov et al. have experimentally isolated a single graphene layer generating wide interest in many areas of material science and engineering [18]. Researchers have been looking for possible applications of graphene in bio-sensing devices and biomedical aims, such as drug delivery and cancer therapy. Graphene provides larger specific surface area than other CNTs and forms strong interactions with drugs being a good candidate for high drug loading.

The toxicity of these nanostructures is related to the potential presence of metal impurities (i.e. by-products of the synthesis) as well as to the surfactants used to disperse them in aqueous media. Harmful and pathogenic effects can arise due to their ability to enter the respiratory tract, deposit in the lungs, redistribute from the site of deposition, escape from the normal phagocytic defenses and modify the protein structure. Thus, they can potentially activate inflammatory and immunological responses, affecting normal organ functions. Several studies report on the toxicological effects of the CNTs.
and fullerene-based nanostructures and they are focused, mainly, on pulmonary and skin toxicity [19].

Scarce literature data describing in vitro toxicity of graphenes suggest that the latter can be either benign or cytotoxic depending on the layer number, lateral size, stiffness, hydrophobicity, surface functionalization and dose. Potential mechanisms of toxicity considered are the generation of reactive oxygen species (ROs) in target cells, direct physical toxicity due to the interactions with the membrane lipids or indirect toxicity due to the adsorption of biological molecules [20]. The interactions between the dispersed graphene or graphene oxide sheets and target cells have been studied in monolayer cultures of lung epithelial cells [21], fibroblasts [22] and neuronal cells [23], where dose-dependent oxidative stress and slight loss of cell viability at high concentrations were observed. In addition, in vivo studies (in mice) demonstrated systemic biodistribution and biopersistence, following intravenous delivery of graphene oxides. At higher doses, granulomas in the lungs, liver, spleen and kidney were observed as well as deposition and retention in the lungs with production of lung injury and inflammation (Table 1) [24, 25]. It is still unknown whether graphene-family materials have the potential to induce sarcomas since they can have large surface areas, smooth topography and may be biopersistent similarly to tumorigenic solid-state implants.

Inorganic NPs of metals and their oxides: Insoluble inorganic NPs can be composed of pure metals or their oxides, or various inorganic products and alloys (Au, Ag, Co, Cr, ZnO, TiO$_2$, CeO$_2$, SiO$_2$, CrO$_2$). Only their nanometric dimensions distinguish them from the same products normally found on a larger scale. Because of their unique properties related to their nanometric scale, these particles are precisely produced. At this scale, they display mechanical, electrical and other properties that do not exist when in larger dimensions [6]. For example, titanium dioxide UFPs (Fig. 3c) ultrafine particles that fall within a nanosize range are commonly used as photocatalysts to clean air and water, as antibacterial agents on glass and steel, and as components of many cosmetics and sunscreens [26, 27], while silicon dioxide (SiO$_2$) NPs (Fig. 3d) are widely applied in the fields, such as the chemical industry, medicine, cosmetics and agriculture [28].

Research results showed consistency in the sensitivity of aquatic, fish cell and human cell models to Ag and CeO$_2$ particles of different size; with the observed sensitivity sequence from highest to lowest is: nano-Ag > micro-Ag = nano CeO$_2$ > micro CeO$_2$ [29]. For some inorganic nanostructures, when the particle size is further reduced and approaches the Fermi wavelength of electrons (i.e., the electron de Broglie wavelength at the Fermi level 0.5 nm for Au and Ag), the continuous density of states breaks up into discrete energy levels leading to dramatically different optical, electrical and chemical properties. These particles, smaller than 2 nm, are usually called nanoclusters and they become molecular species from which size-dependent strong fluorescent emission can often be observed upon photoexcitation in the UV-visible range. For this reason, they have been widely used for bioimaging and chemical sensing [30]. For example, 1.9 nm-gold NPs (gold core diameter), with a highly water soluble organic shell making the particles both useable at high concentrations (up to 1.5 g Au/cc) and well tolerated by animals even at high concentrations (LD50 > 1.4g Au/kg), are used for production of a novel nanotechnology X-ray contrast agent for in vivo use, AuroVist™ (www.nanoprobes.com).

Toxicity of these NPs has been evaluated by several research groups indicating that apoptosis can be induced by generation of ROs, which oxidative and inflammatory
nature may then drive genotoxic and cytotoxic outcomes [28, 31 - 34]. This was confirmed when interactions of Ag NPs with human fibrosarcoma and human skin/carcinoma cells were studied [35]. The cytotoxicity of Ag NPs was also evaluated by MTT metabolic activity assay and membrane integrity assay in rat alveolar macrophages cell culture [36], while concentration-dependent genotoxicity was confirmed with the human lymphoblast TK6 cell micronucleus assay [37]. However, no genetic toxicity in bone marrow was observed.

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when rats were exposed to Ag NPs by inhalation (90 days) (Table 1) [38]. When secreted NO levels were measured to investigate the correlation of nitrosative-oxidative stress and cytotoxicity induced by Ag NPs, it was confirmed that ultimately, the phagocytosis of Ag NPs stimulated inflammatory signaling through ROS generation in macrophages, followed by induced secretion of TNF-α, that may cause damage of cell membrane and apoptosis [39]. It has been reported also that Au NPs can catalyze nitric oxide, which reacts rapidly with O2 producing harmful peroxynitrite species that can disrupt lipids, DNA and proteins [40]. Ability of Au NPs to contribute in genotoxicity is a subject of intensive research [41], while with ZnO NPs, significant DNA damage in cells has been observed [42]. Penetration of nanosized TiO2 (5 - 20 nm) into the skin and its interaction with the immune system has been also demonstrated [43]. Other studies report that exposure to TiO2 NPs resulted in pulmonary inflammation and edema, accumulation of macrophages and pneumonocyte apoptosis [44, 45]. Genotoxicity in cultured cell lines for TiO2 NPs was also observed [46, 47], but there were also studies showing no DNA damage [48, 49].

Quantum dots and semiconductors: The quantum dots, called semiconductor nanocrystals or artificial atoms, represent a special form of spherical nanocrystals from 1 to 10 nm in diameter, with unique size-dependent optical and electrical properties. Most of the research has been focused on semiconductor quantum dots, which display distinctive quantal effects, depending on the dimensions. They are used as fluorescent probes in diagnostic medical imaging and in therapeutics, because of their optical properties and their capacity to form covalent bonds with peptides, antibodies, nucleic acids or other low-weight molecules [6]. The first authors who demonstrated in vivo that CdSe/ZnS quantum dots coated with mercaptoacetic acid, could bond to blood transferrin were Chan and Nie in 1998, cited by Smith et al. [50]. This fluorescent complex was absorbed selectively by cancer cells. According to some authors, the toxicity of certain quantum dots could be linked to the release of cytotoxic ions, oxidative mechanisms and other less well-elucidated phenomena [51, 52]. Quantum dots contain toxic components, such as Cd (from Cd chalcogenide-based quantum dots) or Pb (from Pb chalcogenide-based quantum dots). Cd2+ and Pb2+ could be released from quantum dots and then kill the cells. Thus, a direct way to avoid the possible toxicity of quantum dots is to make them well coated to become biologically inert. The coating materials can be low or nontoxic organic molecules/polymer (e.g. PEG) or inorganic layers (e.g. ZnS and silica). Few studies show direct, extracellular cytotoxicity of water-soluble CdSe and CdSe/ZnS quantum dots, because of Cd2+ release from the NPs due to poor purifications and/or simple surface cappings/coatings [51]. Quantum dots coated by simple molecules, such as mercaptoacetic acid, mercaptopropionic acid, 11-mercapto-undecanoic acid, 2-aminoethanethiol, are more toxic than the ones coated with silica. The silica layer is different from the amphiphilic polymer layers or small molecular ligands; it can be very thick (up to several micrometers) and therefore reduces the possible leaking of interior toxic Cd or Pb under physiological environments. There is no clear toxic effect observed if additional PEG molecules were attached to the silica exterior surface [51, 53].

Zero-valent metals (Fe(II)salts): The usually used ferrite (Fe3O4) NPs were synthesized from a reaction solution of FeCl2 and FeCl3, and an adjusting solution of NH4OH. They have been utilized as supermagnetic NPs for in vivo or in vitro biomedical applications, such as the contrast agents for magnetic resonance imaging, hyperthermic media for tumors treatment, magnetotargeting carriers for chemotherapeutic drugs and immunoassay [54]. Not much is known about the toxicity of ferrite NPs at the cellular and molecular levels. Research of Ahamed et al. [55] showed that nickel ferrite NPs induced oxidative stress in A549 cells by induction of ROS and depletion of glutathione.

Insoluble organic NPs: Insoluble organic NPs are usually composed of various organic substances, often insoluble polymers (e.g. polystyrene, polycyanoacrylate, polyacrylamide, polyacetamide, polymethacrylic acid, etc.), to which different organic (alkyl) radicals can be grafted. Under specific conditions, some of the substances can also be made soluble. Often, only their nanometric dimensions distinguish organic NPs from the same products normally found on a larger scale. Like all other NPs, they display catalytic, chemical or other properties that do not exist in larger dimensions. To this
group, nanocapsules, nanospheres and nanoshells, based on a wide variety of insoluble organic polymers, belong as well. Some of these structures are developed with an aim of integration with other substances, often medications. The surface of these NPs can also be modified to interact specifically with certain sites of the body [6].

The (cyto)toxicity of these NPs is usually correlated with the rate of biodegradation of the polymer backbone and main products of biodegradation. Adhesion to the cell membrane can also increase cytotoxicity by local release of biodegradation products in high concentrations. For example, investigation of the liver toxicity of poly(alkyl cyanoacrylate) NPs showed slight modifications in the hepatic function after chronic administration of NPs and these effects have been found reversible when the treatment was stopped. Because the mononuclear phagocyte system is concerned, there is a potential danger for physical blockade of this tissue (Table 1) [51].

BIODISTRIBUTION AND ADVERSE HEALTH EFFECTS OF ENSs AFTER DIFFERENT ROUTES OF EXPOSURE

Skin exposure (Fig. 4a): Penetration of the skin barrier is size-dependent with NPs more likely to enter more deeply into the skin. However, in a broken skin, entry of even larger (0.5-7 µm) particles was observed and there is a hypothesis that skin when flexed can make the epidermis more permeable to NPs [57, 58]. No direct relation between other physicochemical properties and biodistribution of NPs into and via systemic circulation through the skin has been found, so far [59]. There are literature data, however, pointing to mechanical skin irritation and sensitisation with involvement of the macrophages, Langerhans cells or other cells. On exposure to the skin, particles of different surface characteristics attract different arrays of opsonins, which travel together with the NPs to different places at different times through the lipid layers within the cells of the stratum corneum and the appendage route (hair follicles, sweat glands). Internalization inside the cells may easily trigger the inflammatory cell response [59 - 61]. For example, in a study of Yanagisawa et al., exposure to polystyrene NPs under skin barrier dysfunction exacerbated atopic dermatitis-like skin lesions in NC/Nga mice, in a size-dependent manner [62]. In addition, skin inflammation via over expression of CC-chemokines was observed, even in the absence of allergens in atopic subjects. However, in a study of Park et al., in which human skin equivalent model was used to deduce the toxicity of polystyrene and TiO₂ NPs, no phototoxicity, acute cutaneous irritation or skin sensitization was observed [63].

Oral ingestion (Fig. 4b): From the respiratory tract via the mucociliary escalator, ENSs can be subsequently ingested into the gastrointestinal tract or they can be directly ingested with water, food or as drug delivery systems. After oral ingestion, depending dominantly on the size, surface charge and mucoadhesivity, particles could reach the colon or translocate from the lumen of the intestinal tract via the M cells in the Peyer’s patches and isolated follicles of the gut-associated lymphoid tissue, and/or via the normal intestinal enterocytes (Fig. 1) [64, 65]. The literature data suggest that the smaller the particle diameter, the faster they can permutate the mucus to reach the colonic enterocytes, whereas positively charged particles exhibit poor oral bioavailability through electrostatic repulsion and mucus entrapment [66].

Nanostructures entering the lymphatic may induce a secretory immune response, while those entering the systemic circulation can be distributed to different organs (e.g. kidney, lung, liver, spleen, brain, etc.). For example, in rats dosed orally with radiolabelled functionalized C60 fullerenes, 98 % were cleared in the faeces within 48 hours, while the rest was eliminated via urine, indicating uptake of the particles into the blood [67]. Also, uptake of larger TiO₂ particles (150 - 500 nm) into the blood and distribution to the liver was observed [68]. Those particles, reaching the colon, can disrupt the epithelial barrier function by apoptosis of enterocytes, thus triggering mucosal inflammation and inducing inflammatory bowel diseases [69]. Others, reaching organs other than the gut or crossing the blood-brain barrier, may induce oxidative stress locally (e.g., depletion of reduced and oxidized glutathione, inhibition of superoxide dismutase activity, increase in catalase activity, etc.) and provoke toxic effects, including liver damage, bile-duct hyperplasia, nephrotoxicity, neurotoxicity, spermatoxotoxicity, etc [70, 71]. For example, after oral administration of TiO₂ in mice, slight brain lesion with fatty degeneration in the hippocampus was observed. In the kidneys, serious swelling in the renal glomerulus
was detected, while in the liver tissue, the hydropic degeneration around the central vein was prominent and a spotty necrosis of the hepatocytes was found (Table 1) [72]. In studies, in which acute toxicity of SiC NPs was evaluated after their oral administration in Wistar rats, stases and haemorrhages in the heart, liver, kidney, lungs and spleen were observed [73,74]. Significant dose-dependent changes in the serum alkaline phosphatase and the cholesterol values, and moderate liver damage were also reported, when silver NPs in Sprague-Dawley rats were orally administered. In addition, significant decrease in the total protein was observed when high dose was administered, while in the high and middle-dosed rats, red blood cells, haemoglobin and hematocrit were increased and coagulation time decreased. Interestingly, gender-related difference in the accumulation of the silver NPs in the kidneys was observed, with two fold higher concentration in the female kidneys (Table 1) [75]. Because of these effects, a more demanding regulation that includes both nonclinical and clinical studies exists for the NPs designed as drug or nutraceutical carriers.

**Inhalation (Fig. 4c,d):** Physicochemical properties of the inhaled particles and the materials themselves, especially size distribution, surface charges and surface chemistry, are important for the pathogenic effects into the lungs, as they influence both the deposition and the clearance rates [76, 77]. The main mechanism for deposition of inhaled ENSs in the respiratory tract is diffusion due to the displacement when the particles collide with the air molecules. The clearance of deposited particles in the respiratory tract is manifested by physical translocation of the particles by different mechanisms and chemical dissolution. The efficacy of this clearance mechanism depends highly on the efficiency of the alveolar macrophages to “sense” deposited particles, to move to the site of their deposition and to phagocytise them. Phagocytosis of the deposited particles takes place within a few hours, so by 6 - 12 hours after deposition, essentially all of the particles are phagocytised by the alveolar macrophages [78]. There is little evidence for paracellular transport of ENSs in the healthy lung, but it may be present when permeability is increased [79].

![Fig. 4. Biodistribution of ENSs after skin exposure (a), oral ingestion (b), inhalation (c) and nose breathing (d).](image-url)
The size was confirmed as the key parameter in the deposition of nanostructures into the lung. The smaller the particles, the deeper they can travel into the lung [80]. So, in the alveoli, particles smaller than 2.5 µm can be found, while inhaled UFPs (an aerodynamic diameter < 100 nm), deposited mainly in the alveolar region, are subject to easy and rapid translocation through the systemic circulation to other vital organs [59]. When fractional deposition of the NPs in the lung is up to 70%, the larger of them are being recognized, phagocytised by alveolar macrophages and translocated into the interstitium [81, 82]. On the other hand, 5-nm particles showed an equal deposition of app. 30% in all three regions (nasopharyngeal, tracheobronchial and alveolar region), 20-nm particles had the highest deposition efficiency in the alveolar region (~50%), whereas in the tracheobronchial and nasopharyngeal regions, the deposition efficiency was app. 15% [83]. Kim et al. suggested that 80% of the 20-nm particles were deposited in the respiratory system [84].

As a result of macrophage phagocytosis of nanostructures in the deep lung and subsequent macrophage activation, chemokines, cytokines, ROS, C reactive protein and other mediators are released, resulting in sustained inflammation and eventually fibrotic changes. Those nanostructures, which are biopersistent for years in the alveoli (e.g. asbestos or silica) or contain mutagenic substances, are of high risk for developing cancer, due to their ability to interact with the epithelial cells and to enter the lung tissue. The same effects were observed with experimental instillation of TiO2 and carbon black [1, 85]. In the study of Heinrich et al., in which Wister rats were exposed to ultrafine TiO2 NPs for 24 months at an average concentration of 10 mg/m³, development of pulmonary tumours was observed [86]. With high chronic doses of particles with low solubility, bronchoalveolar hyperplasia, metaplasia, fibrosis and tumorigenesis were observed (Table 1).

The cascade of subsequent events and inflammation leads also to cardiovascular events and nervous system toxicity manifestations [87]. Exposure to ambient air pollution was shown to be associated with coagulation, vascular thrombosis, an increase in blood pressure and a decrease of heart rate, accelerated atherosclerosis, life-threatening arrhythmia and triggering of myocardial infarction [88-90]. For example, exposure to nanosized titanium aerosols have been associated with arteriolar constriction, while inhalation of fine TiO2 NPs - with an impaired arteriolar dilatation [91, 92]. The loss of capacity for microvascular dilatation can decrease tissue perfusion and in this way, compromise its function. In addition, pulmonary exposure to diesel particles in the ultrafine range, potentiated myocardial ischemia in patients with pre-existing coronary heart disease and provoked acute increase in diastolic blood pressure within 2 h of exposure to the particles [93].

Considering the brain toxicity, extrapulmonary translocation of the NPs through the olfactory nerve was reported to be the most probable pathway for NPs to the brain [94-97]. The research data in which biodistribution of elemental carbon and silver NPs were studied point to accumulation in the rat olfactory bulb after inhalation [95, 96]. In addition, the specific network of sensory nerve endings, between the nose and the olfactory bulb, is also involved in the transport of ENSs directly to the brain, via the olfactory nerve tract. Elder et al. suggested that the particle size plays the most important role in neuronal uptake and translocation of the ENSs [97]. For example, the solid particles deposited on the olfactory mucosa, have to be smaller than 200 nm in order to be transported through the cribriform plate. Using a predictive particle deposition rat model it was estimated that app. 11.5% of the amount deposited on the olfactory mucosa was translocated to the olfactory bulb [98]. Research data point that intranasally instilled TiO2 NPs could be also translocated into the central nervous system of mice via the olfactory nerve tract and accumulated in the olfactory nerve layer, olfactory ventricle, cerebral cortex, thalamus and CA1 and CA3 regions of hippocampus. After 30 days of instillation of TiO2 suspension into the mice’s nasal cavity, the highest content of Ti in the hippocampus was observed when compared with the olfactory bulb and cerebellum, while in the cerebral cortex, the lowest quantity was detected. In addition, an increased neuronal cells count in olfactory bulb, and irregular arrangement of the neuronal cells in the olfactory nerve layers and hippocampus, were observed (Table 1) [94]. Additional neuronal translocation pathways for ENSs via the trigeminal nerve and tracheobronchial sensory nerves, have been also reported.
by Hunter and Day in their study in rat animal model [99]. They demonstrated translocation of the intranasally instilled rhodamine-labelled nanospheres (20 - 200 nm) to the trigeminal ganglion inside the cranium via uptake into the ophthalmic and maxillary branches of the trigeminus nerve, that supplies sensory nerve endings throughout the nasal mucosa. In another study, the same ENSs were intratracheally instilled in pigs. Neuronal translocation to the ganglion nodosum in the neck area that is networked into the vagal system was reported [100]. Determination of the effects of the translocated particles in the brain is important, also because some of them may develop parkinsonism 17 years earlier than the average population [101].

Air borne NPs have been also found to penetrate into the systemic circulation following inhalation, reaching other extrapulmonary organs, such as the liver, spleen, kidney, etc [57, 76, 102, 103]. For example, pulmonary exposure to diesel particles with ultrafine range, resulted in aggravation of the cisplatine-induced effects on serum urea and creatinine, urine N-acetyl-β-D-glucosaminidase activity and renal glutathione concentration in an acute renal failure animal model [104]. In addition, high accumulation of silver NPs in the basal membranes of the medulla and cortex in the kidneys of female Sprague-Dawley rats, was reported without significant deteriorations in the kidney function and histopathology. In a study of the whole body exposure, when rats were subjected to chronic inhalation of silver particles (90 day), lung and liver were reported as major targeted organs. Also, bile duct hyperplasia, dilatation of the central vein and increased foci were observed [96].

Parenteral injection (Fig. 1): ENSs easily reach liver after intravenous administration, accumulate and usually are retained there for a relatively long period of time. Using intravenous injection, Douglas et al. studied the biodistribution of polymer-coated or uncoated poly(butyl 2-cyanoacrylate) NPs in rabbits [105]. About 60 % of the NPs were located in the liver and the spleen and app. 30 % remained in the bloodstream. The coating had no significant influence on NPs biodistribution. When biodistribution of two types of radiolabelled ($^{111}$In) functionalized SWCNTs after intravenous administration was followed, rapid first-order clearance from the blood compartment, through the renal excretion route (3 - 3.5 hours), was observed, without any toxic side effects or mortality. Radioactivity in all examined organs after 30 min of administration was detected, with higher levels of radioactivity found in the liver, muscle, skin, kidney, lung and blood. Similarly, when TiO$_2$ NPs (36 - 48 nm) were intravenously administered at high doses to mice, after 14 days of treatment, accumulation in the liver, lung, kidneys, spleen and heart was observed, with different degrees of damage in these organs, except in the heart (Table 1) [106].

**EU RESEARCH ON EFFECTS OF NANOSTRUCTURES ON HUMAN HEALTH AND ENVIRONMENT**

Since human health and environmental safety are of primary importance, the European Community pays special attention to the assessment of the risks and health effects of ENSs. In the frame of the NMP Theme of the FP7 program, each R&D project funded by the European Commission should contain a specific safety work package. One highly effective coordinative action, that brings together the best European experts in nanotoxicology, nanocotoxicology and nano-risk assessment is NANOIMPACTNET (www.nanoimpactnet.eu). NANOIMPACTNET coordinates testing strategies and methods, screening tools, risk assessment tools and methodologies for more than 800 members of the research community, as well as to over 1000 companies developing or using nanomaterials. All this work is aiming towards the goal of implementing the EU’s Action Plan for Nanotechnology.

The main goal of another project, NANOINTERACT (www.nanointeract.net), was to develop a platform and a toolkit for understanding the interactions between the NPs and the living world. Research was performed for understanding how ENSs interact with the living systems, from the first contact, via absorption and localization, to the final onset of functional impact. One of the main achievements of the NANOINTERACT has been the description of the nanoparticle-protein corona as a biological entity that interacts with the living system and cellular machinery. It also showed a first evidence of NPs modulating the rate of protein fibrillation in solution.

The NANOSAFE2 project (www.nanosafe.org)
was focused on a smaller number of ENSs for their safe industrial production and it has addressed mainly the exposure during manufacturing processes and nanomaterials exposure in the environment. Screening techniques for CNTs, ZnO, carbon black, crystalline silica, with size of around 50 nm, have been developed. The project was related to development of advanced technologies for limiting exposition to ENSs in factories and leaks into the environment, with design of safe production equipment, dynamic confinement, individual protection devices and filtration. As an outcome of the NANOSAFE2 project, a database on ENSs toxicology was created.

DIPNA (www.dipna.eu) was an integrated platform focused on verification of the ENSs possible toxicity and ecotoxicity. The main goal of DIPNA was to provide information on in vitro assays for detection of ENSs effects on human cells, instruments and methods for environmental NPs detection, as well as recommendations for nanotoxicologists and researchers. The impact of cerium, gold, cobalt and iron oxide NPs, in liquid suspension and in dry state, on various types of human cells was tested in vitro in order to identify biomarkers of nanotoxicity and design assays.

The NANOSH project (www.ttl.fi/partner/nanosh) included research on the toxic effects of NPs that were relevant to the occupational environment. Thirty five different nanomaterials have been characterized and published in a NANOATLAS book. Investigations of genotoxicity have provided evidence that both TiO$_2$ NPs and CNTs have a potential to induce genotoxicity in vivo and in vitro. It was shown that TiO$_2$ NPs induced pulmonary inflammation (both in vivo and in vitro systems) when coated with amorphous silica, suggesting that the surface properties of the nanomaterials had important influence on the effects.

HINAMOX project (www.hinamox.eu) was focused on investigations of safety of the metal and metal oxide NPs (TiO$_2$, ZnO, CuO, CeO$_2$, Al$_2$O$_3$), with an aim to establish protocols for nanosafety testing of metal nanoparticles.

PROSPECT (www.nanotechia-prospect.org) was a public/private partnership project supported by OECD and related to better understanding of the ENSs impact on humans and the environment. The programme provided a direct contribution to the global safety assessment of nanomaterials, described by the OECD Working Party on Manufactured Nanomaterials. The project contributed to the scientific foundations for adapting or creating test methods that enabled ecotoxicological hazard assessment of the nanomaterials, as well as to the establishment of quantitative relation between the structure and activity. The target particles (CeO$_2$ and ZnO) are part of a list of 14 nanomaterials identified as commercially relevant for the global economic impact of nanotechnology.

The CELLNANOTOX project (www.fp6-cellnanotox.net) was focused on research of the interaction between NPs, and lung and intestine, as primary sites following the penetration of NPs into the blood circulation, with the liver, kidney and the immunological system, as secondary sites of interaction. The project explored the mechanistic aspects of interactions, uptake and recycling of selected NPs by different cellular systems.

ENSSATOX (www.ennsatox.eu) was a project concentrated on studying the hazard effects and activity of the nanostructures within a range of biological models of increasing complexity and organization in aquatic systems. The project has started from the hypothesis that the biological activity and environmental impact of NPs are directly dependent on their structure and functionality, and that the biological membrane is playing a very important role in the nanotoxicity, as a boundary of the living cells that nanostructures should cross and as a host of many physiological processes (respiration, nerve conduction), which can be disturbed by the structural disruption.

The main goal of the project NANOMMUNE (www.nanommune.eu) was, through a multidisciplinary approach, to establish an array of red-out systems for determination of toxicity, not only of current ENSs, but also for prediction of hazardous effects of new ENSs that
are being developed, thus enabling a sustainable growth of the nanotechnology-based-industry. This project was focused on the immune system, which has the capacity to respond to invasion by pathogens and foreign particles. The core concept underpinning the project was that the recognition versus non-recognition of ENSs by immune-competent cells will determine the distribution, as well as the toxic potential of the novel nanomaterials.

The aim of the project NanoReTox (www.nanoretox.eu) was to develop novel and robust protocols for safety testing of nanomaterials. It is especially related to metals, metal oxides and metalsulphides. The project intends to examine the molecular and cellular reactivity of well-characterized NPs by comprehensively addressing five key questions: how does the environment, into which nanoparticles are released, affect their physicochemical properties and bioreactivity; how does it affect their ability to interact with and/or penetrate mammalian and aquatic cells and organisms; is there a hierarchy of activity; which combinations of conditions are most likely to pose a risk to human health and the environment; and how can this information be incorporated into a risk assessment model.

The project NEPHH (www.neph-fp7.eu) was looking at human health and environmental implications of nanotechnology-based materials from holistic life-cycle perspectives. The nanomaterials selected by the NEPHH project, were polymer composites, reinforced with silicon-based laboratory-made and industrial NPs. NEPHH aimed to increase the understanding of the mechanisms of toxicity of nanosized dust generated during cutting, fracture, breakage or cracks of nanoreinforced end-use products and also to determine acceptable exposure limits.

The NEURONANO project (www.neuronano.eu) used a knowledge-based approach to address the questions of whether NPs smaller than 40 nm, could potentially enter the brain by crossing the blood-brain barrier, and whether some ENSs may induce oxidative stress in living systems. NEURONANO aimed to establish a simple screening and risk assessment matrix for NPs in neurodegenerative diseases.

The INLIVETOX project (www.inlivetox.eu) developed a novel modular microfluidics-based in vitro test system, modelling the response of cells and tissues to the ingestion of NPs (gold, silver, TiO₂). The project aimed to answer how the target tissues (the gastrointestinal tract, the liver) individually respond to NPs and how the interactions between the different tissues modulate their responses.

The aim of the NANEX project (www.nanex-project.eu) was to develop a catalogue of generic and specific (occupational, consumer and environmental release) exposure scenarios for ENSs, taking in account the entire lifecycle of nanomaterials. NANEX collected and reviewed available exposure information, with focus on three very relevant ENSs: high aspect ratio nanomaterials (e.g. CNTs), mass-produced nanomaterials (e.g. ZnO, TiO₂, carbon black) and specialized nanomaterials that were only produced on a small scale (e.g. Ag NPs). The exposure information included both quantitative (measurement results) and qualitative contextual exposure information (risk management measures).

The aim of the NANOTEST project (www.nanotest-fp7.eu) was to develop alternative testing strategies and high-throughput testing protocols, using in vitro and in silico methods essential for the risk assessment of NPs used in medical diagnostics.

The NANOPOLYTOX project (www.nanopolytox.eu) was designed to improve the understanding of the potential environmental/health impact of nanotechnology-based products, at different stages of their life-cycle.

The ENRHES project (http://ihcp.jrc.ec.europa.eu/enrhes) performed a comprehensive and critical scientific review on the health and environmental safety of fullerenes, CNTs, metal and metal oxide nanomaterials. The review considered sources, pathways of exposure, the health and environmental outcomes of concern, in a context illustrating the state-of-the-art in the field, and informing the regulatory bodies on the potential risks of ENSs.

CONCLUSIONS

ENSs are becoming a part of everyday life improving human health and life style. However, when entering in the organism by various means and via different pathways, they agglomerate, dissolve and change their physicochemical properties as a consequence of the environmental impact on the body, thus affecting bio-
logical effects, which from beneficiary may turn into toxic. Therefore, the safety assessment of the ENSs is mandatory to recognize the risks and avoid the potential hazards.

We are witnesses that more and more data regarding toxicity of ENSs and methods of its assessment, are becoming available. This paper reports on many findings and achievements in this respect. Further studies in which the impact of different structures and their physicochemical properties on toxicity after different exposure pathways has to be evaluated, are still needed. Well-summarized results are especially important for the industry and sectors, where ENSs are produced or used, for providing guidance on the assessment of exposure to these materials. An improved understanding of the risks for toxicity and health effects of the ENSs will aid in future development and exploitation of a variety of nanomaterials. It is of a paramount importance, nanotechnology and nanotoxicology to cooperate closely in order to provide useful information and to avoid misinformation about the toxicity potential of nanostructures. Material scientists, physicians, pharmacists and toxicologists should be included in nanotechnological developments and risk assessments in early stages, taking into consideration available and produced data, various structures, the dose-response relationship, in vivo and in vitro experiments and interactions between cells from different tissues and nanostructures. Projects that promote and coordinate research in the field of nanotoxicology, including development of alternative in vitro methods for toxicity evaluation, and that contribute to establishing/managering of databases and information systems of nanostructures toxicity should be continually sponsored, while the dialogue, critical discussions and networking between all stakeholders, industry, academia and regulatory bodies, must be continually promoted.

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SYNTHESIS AND CHARACTERIZATION OF DIBLOCK COPOLYMERS BASED ON POLY (ETHYLENE GLYCOL) AND POLY (4-VINYL PYRIDINE) VIA ATOM TRANSFER RADICAL POLYMERIZATION

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ABSTRACT

Atom transfer radical polymerization (ATRP) was applied for the preparation of block copolymers based on poly (ethylene glycol) monomethyl ether and poly (4-vinyl pyridine) (MeOPEG-b-P4VP). This was achieved using chloro-terminated PEG as a macroinitiator. Further, the ATRP was performed using 4-VP as a second forming block in the presence of CuCl/PMDETA as a catalyst system. The successful formation of MeOPEG-b-P4VP block copolymers was proved by 1H NMR with the presence of all characteristic signals arising from PEG and 4-VP units. The GPC results showed the preparation of well-defined block copolymers with low dispersity, which confirms the controlled character of radical polymerization. The thermal properties of thus prepared copolymers were characterized by TGA analysis.

Keywords: atom transfer radical polymerization, block copolymers, poly (ethylene glycol), poly (4-vinyl pyridine).

INTRODUCTION

In the recent years, block copolymers have received considerable attention due to their ability to self assemble in solution forming a range of different morphologies and sizes including lamellar, hexagonal-packed cylindrical, and body-centered cubic micellar structures, depending on the relative volume fractions of the blocks [1-3]. Therefore, the design of block copolymers with well-defined architecture, controlled molecular mass, polydispersity and chain composition is a very important research field. Controled/living radical polymerization is a method which allows the synthesis of wide range of well-defined polymers/copolymers and this can be achieved by three main methods: nitrooxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer polymerization (RAFT) [4]. Among them, atom transfer radical polymerization is the most effective and used method since its introduction by Wang and Matyjaszewski [5-6]. The ATRP process uses an alkyl halide as an initiator and a metal in its lower oxidation state with complexing ligands. The process involves transfer of the halide from the dormant polymer chain to the metal complex, thus establishing a dynamic equilibrium between active and dormant species. ATRP method is applied for the polymerization of large number of monomers as styrene and its derivatives, acrylates and...
methacrylates [7]. The controlled chain growth with ATRP is very useful for the preparation of well-defined block copolymers because the growing polymer chain contains a stable halogen terminated ω-end that can act as an initiator for chain extension [8].

Recently, 4-vinylpyridine (4VP) was employed to prepare block copolymers via ATRP due to its ability to form self-assembly supramolecular structures [9 - 10] and complexes with metal ions [11]. The block copolymer of 4VP has been already prepared via ATRP method [12 - 15]. However, there are some limitations in the polymerization of 4VP by ATRP due to its strong coordination effect with the metal catalysts component in the polymerization system. Therefore, multidentate ligands with strong coordination ability and protic solvent have to be applied to minimize the contamination of the catalyst [16].

This work is focused on the synthesis of block copolymers based on poly (ethylene glycol) monomethyl ether and poly (4 - vinyl pyridine) via atom transfer radical polymerization. For this purpose a novel chloro-terminated MeOPEG macroinitiator obtained by reaction of MeOPEG with thionyl chloride is applied for the polymerization of the second 4VP block.

EXPERIMENTAL

Materials
Poly(ethylene glycol) monomethyl ether (MeOPEG, Merck, Mn - 1900 g/mol) was dried under vacuum at 40°C for 24 hour before use. Toluene (Sigma Aldrich, 99,8 %) was distilled. 4-vinylpyridine (Acros Organics, 95 %) was passed through a neutral alumina (Al₂O₃) column and distilled. Thionyl chloride (Acros Organics, 99 %), CuCl (Aldrich, 98 %), Pyridine (Sigma Aldrich, 99,8 %) and 1,1,4,7,7-pentamethyldiethylenetriamine (PMDTA, Across Organics, 98 %) were used as received.

Synthesis of MeOPEG-Cl macroinitiator
20 g poly(ethylene glycol) monomethyl ether (MeOPEG, 0,025 mol) and pyridine (1.30 ml) were added to a three-neck flask equipped with a magnetic stir bar, a condenser and a calcium chloride drying tube and stirred. To this mixture, 20 ml toluene was added under stirring at 87°C. Then, thionyl chloride 1.3 ml (0.0625 mol) was added slowly to the reaction mixture. The resulting mixture was stirred for 15 h at 87°C. The solid obtained was removed by filtration. The solution was concentrated by rotary evaporation in order to remove the residual thionyl chloride. The product was recovered by precipitation in cold diethyl ether, followed by filtration. Pale-yellow product was dried at 40°C under vacuum.

Synthesis of MeOPEG-b-P4VP block copolymer
The MeOPEG-b-P4VP copolymer was synthesized by atom transfer radical polymerization (ATRP) of 4-VP and MeOPEG-Cl macroinitiator using technique described by Matyaszewski at al. [6]. Polymerization was performed in a 50 ml flask, equipped with a magnetic stir bar and septum. MeOPEG-Cl (3g) was added to 17 ml i-propanol and heated at 60°C in order to dissolve the macroinitiator and deoxygenated by passing N₂ through the mixture. Then, the ligand (1,1,4,7,7-PMDTA, 0.330 ml) was added and the solution was stirred and deoxygenated with N₂ for 30 min, followed by addition of CuCl (0.155 g). The reaction mixture was stirred while become homogenous and green. At last, deoxygenated 4-VP (17 ml, preheated at 60°C) was added. Polymerization was performed at 60°C for 48 h. The diblock copolymer MeOPEG-b-P4VP was purified by passing through Al₂O₃ column to remove the copper catalyst and then precipitated in cold diethyl ether, followed by filtration. The product was dried at 40°C under vacuum.

Methods
Size exclusion chromatography (SEC)
SEC analysis was performed on Waters 600 liquid chromatograph equipped with a 410 refractive index detector and styragel HR columns HR 1, HR 2, and HR 4; and a UV detector-Waters 2487; in dimethylformamide (DMF). Polyethylene glycol standards were used for calibration.

The relative molecular mass (Mᵣ, SEC) and polydispersity index (Mₘ/Mᵣ) of the block copolymer were determined in tetrahydrofuran (THF) (flow rate : 1mL min⁻¹) at 40°C with a Waters liquid chromatograph equipped with a 410 refractive index detector and Phenogel columns (three columns 50 Å, 100Å, 104Å). Polystyrene standards were used for calibration. Molecular mass was calculated on Clarity software.

Fourier Transform Infrared Spectroscopy (FTIR) was done on Perkin-Elmer Spectrum GX spectrometer.

¹H NMR spectra of the MeOPEG macroinitiator and MeOPEG-b-P4VP copolymer were recorded with
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a Brucker spectrometer (400 MHz) in CDCl₃.

**Thermogravimetric Analysis (TGA)**
TGA analyses were performed on TA Instruments Q 500. The temperature was increased from 30 to 700ºC at a heating rate of 20ºC/min under nitrogen atmosphere.

**RESULTS AND DISCUSSION**

**Synthesis of MeOPEG-Cl macroinitiator**
Poly (ethylene glycol) monomethyl ether (Me-OPEG) (Mn = 1900 g mol⁻¹), which has a hydroxyl end group, was converted to an appropriated ATRP macroinitiator for the polymerization of 4-VP. This was achieved by reaction of MeOPEG with thionyl chloride according to scheme 1 thus leading to the formation of suitable chloro-terminated ATRP macroinitiator.

![Scheme 1. Chlorination of MeOPEG with thionyl chloride.](image)

Thus prepared MeOPEG-Cl macroinitiator was characterized by FT-IR, ¹H NMR and SEC analyses.

Initially, the MeOPEG-Cl macroinitiator was characterized by FT-IR analysis. IR spectra of pure MeOPEG and MeOPEG-Cl macroinitiator showed all characteristic signals for the MeOPEG units at: 2878 cm⁻¹ (C-H stretching); 1095 cm⁻¹ characteristic for -C-O-C- stretching vibration and 1469 cm⁻¹ for C-H banding vibration. The chlorination of MeOPEG-Cl macroinitiator is clearly evidenced by the appearance of a new band at 665 cm⁻¹ which is characteristic for C-Cl bond (Fig. 1).

Further, MeOPEG-Cl was characterized by ¹H NMR spectroscopy. ¹H NMR spectrum of MeOPEG-Cl macroinitiator showed all characteristic for PEG units signals at 3.38 ppm (3H, -O-CH₃) and 3.45-3.83 ppm (4H, -CH₂CH₂O⁻), (Fig. 2).

The number average molecular mass and molecular mass distribution of MeOPEG-Cl macroinitiator was determined by SEC. As seen from Fig. 3, SEC peak of MeOPEG-Cl macroinitiator was shifted toward higher molecular masses (Mn = 2050 g mol⁻¹, PDI = 1.078) in comparison to the pure MeOPEG (Mn = 1949 g mol⁻¹, PDI = 1.069) indicating the successful chlorination of MeOPEG macroinitiator, (Fig. 3).

![Fig. 1. FT-IR spectra of MeOPEG and MeOPEG-Cl macroinitiator.](image)

![Fig. 2. ¹H NMR spectrum of MeOPEG-Cl macroinitiator.](image)

![Fig. 3. SEC analysis of pure MeOPEG and chlorinated MeOPEG-Cl.](image)
Synthesis of MeOPEG-b-P4VP block copolymer

P4VP is a pH sensitive polymer which is soluble in water at pH lower than 4.7 and became insoluble in water at higher pH (> 4.7). Therefore, block copolymer of P4VP will respond to pH changes in the aqueous solution and self-assemble into different supramolecular structures [17].

The synthesis of MeOPEG-b-P4VP block copolymer by ATRP was performed in 2-propanol at 60ºC using MeOPEG-Cl macroinitiator in the presence of V4P and PMDETA/CuCl catalyst system according to Scheme 2.

The 1H NMR spectrum of the MeOPEG-b-P4VP block copolymer shows the peaks for MEOPEG’s terminal (a, 3H, -CH\_3) protons at 3.38 ppm and at 3.45-3.83 ppm (b, 4H, -CH\_2-CH\_2-O-) from the main PEG chain. The P4VP characteristic protons at 1.20 - 2.00 ppm (c, 3H), and its aromatic ring at 6.00 - 6.90 ppm (d, 2H) and 7.70 - 8.90 ppm (e, 2H) assigned to the ortho- and meta-protons, respectively, were observed as well, (Fig. 4). This result demonstrated the successful synthesis of PEG-b-P4VP block copolymer.

The molecular masses and molecular mass distributions of diblock copolymers were further investigated by SEC. Fig. 5 presents the SEC curve of the diblock copolymers PEG-b-P4VP block copolymer by using MeOPEG-Cl macroinitiator. SEC curve of diblock copolymer showed narrow and unimodal elution peak, which is clearly shifted toward higher molar mass (Mn = 6470 g mol\(^{-1}\), PDI = 1.13) in comparison to the MeOPEG-Cl macroinitiator (Mn = 2050 g mol\(^{-1}\), PDI = 1.078), (Fig. 5).

Thermal stability of MeOPEG-Cl macroinitiator and MeOPEG-b-P4VP block copolymer were examined by thermal gravimetric analysis in the range from 30ºC to...
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TGA analysis showed that MeOPEG-Cl macroinitiator and MeOPEG-b-P4VP block copolymer undergo thermal degradation above 300ºC, (Fig. 6). The maximal degradation temperature for the both were around 400ºC - 405ºC, which indicated that the second P4VP block did not impair the thermal stability of the MeOPEG-b-P4VP block copolymer obtained.

CONCLUSIONS

MeOPEG-b-P4VP block copolymers were successfully prepared by atom transfer radical polymerization. For the first time, MeOPEG-Cl macroinitiator, obtained by reaction of MeOPEG and thionyl chloride, was applied for polymerization of 4VP by ATRP. The synthesis of well-defined MeOPEG-b-P4VP block copolymers was proven by ¹H NMR spectroscopy with the presence of all typical for the both block signals. SEC analysis also confirms the formation of block copolymers by increasing of MeOPEG-b-P4VP molecular mass in comparison to the MeOPEG-Cl macroinitiator keeping low polydispersity index.

Acknowledgements

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The printing substrate and its characteristics have a significant impact on print quality. Print quality includes desired colour reproduction and satisfactory reproduction of image elements. This study analyzes the transparent polymer material substrates, printed by a screen printing technique. The paper primary focus is on the analysis of colour differences between obverse and reverse side of the printing substrate, and in addition, on line quality and the dot roundness analysis. Considering the results, it can be concluded that substrate thickness has influence on the colour reproduction in reverse printing when observing through a transparent substrate. Also, the differences between line area and perimeter in obverse and line area and perimeter – in the reverse printed side increases with the printing substrate thickness increase and dot roundness observed from the reverse side has a more irregular shape.

Keywords: polyethylene films, obverse and reverse printing, colour reproduction, line quality, dot roundness.
of light by a film that results in a cloudy appearance or poorer clarity of objects when viewed through the film. Light may be scattered by particles suspended in the substance, such as pigment particles or contaminants, or by an imperfect surface caused by dirt, oil, or a fine texture. Haze is an important appearance attribute which can be quantified and then used to assess the objects such as liquids, glass, plastics, painted panels, and even metals [6]. More technically, haze is the percentage of light transmitted through a film that is deflected more than 2.5° from the direction of the incoming beam. This property is used to describe transparent and translucent films, not opaque films. Haze is greatly influenced by material selection and product design. Additives and coatings usually contribute to increased haze. Also, thicker films will be hazier than thinner films. Additional variables, like process temperatures in the different stages of film-making, can further affect haze, so they are tightly controlled [7]. Reverse printing, i.e. printing on the underside of a transparent film, is mostly used in the production of packaging for food as snacks, juices, biscuits, ketchup, etc. In this technique the ink is printed on the inner layer of substrate and it does not become in direct contact with human skin, weather conditions and other substrates because in most of cases the ink is sandwiched between substrates by a lamination process. Reverse printed and laminated materials such as BOPP (biaxial oriented polypropylene), CPP (Cast Polypropylene), LDPE (Low density polyethylene) makes the perfect double, triple or quadruple layer films used for food packaging. Beside laminated products reverse printing is also used with an LDPE film for bottle label, overwrap film for books, bundling and pallets, towels and tissues, film for bakery goods, meat, coffee, frozen foods, liquid packaging (milk cartons and bag-in-box applications), bags and shoppers, packaged beverages industries and others. In case of a reverse printing substrate, characteristics can affect the image quality in many ways [8]. The colour reproduction can be characterized using the CIE L*a*b* colour coordinates. CIE L*a*b* coordinates enable colour differences estimation between samples, or between samples and standards, or in this research between reverse and obverse image of the same sample. Colour differences determination is based on calculations of the differences of colour space coordinates (ΔL, Δa, Δb) [9]. There are many systems that use different formulas (models) for colour distance calculation, wherein the gain values can be classified into several groups: \( ΔE_{ab} < 0.2 \) (the difference is not visible), \( ΔE_{ab} \) between 0.2 and 1 (the difference is noticeable), \( ΔE_{ab} \) between 1 and 3 (the difference can be seen), \( ΔE_{ab} \) between 3 and 6 (the difference is easy to see) and \( ΔE_{ab} \) over 6 (obvious colour difference) [10]. Colour distance \( (ΔE_{ab}) \) is defined by the equation [11]:

\[
ΔE_{ab} = \sqrt{ΔL^2 + Δa^2 + Δb^2}
\]

In equation (1) ΔE_{ab} is the colour difference value, L* is the brightness value, a* is red/green colour value, b* is yellow/blue colour value.

Quantitative assessment of the colour reproduction is not enough for defining overall print quality. It is proven that print quality does not represent monotonous function of hue, saturation and value [12, 13]. Quality attributes as contrast, sharpness, macro non-uniformity are not connected to a colour reproduction but certainly have an affect on print quality. They are directly connected with line and dot quality that represent the component of any image [14]. Important print quality attributes are: contrast, sharpness, noise/graininess, edge raggedness, effective resolution, text quality, macro uniformity, macro non-uniformity, gloss uniformity, etc. [13]. Many researchers have questioned and acknowledged the importance of quality attributes. However, they did not reach an agreement which of them were the most important. Engeldrum in his work states that observers most likely will not be able to perceive more than five quality attributes simultaneously [15].

Line quality reproduction depends on numerous factors, including the printing plate (screen and the process of illumination), ink and substrate [16]. Some of the quality components are line width and its variations, raggedness and sharpness. Line raggedness indicates deviation of printed lines from ideal geometric shape and is the undesired line property that leads to print quality reduction. Line raggedness can be characterized by measuring area and perimeter of lines and comparing these values with ideal ones. Excessive line raggedness causes low sharpness of the prints and can cause text to become unclear or bold [11].

Printed dot fidelity is determined by evaluating dot area and its roundness [17]. Dot roundness represents the shape of the dot relative to a perfect circle. The ideal circular dot should be the one whose area is \( \pi/2 \) that of
the corresponding square pixel. If the dot is not perfectly round, its deviation can cause uneven ink coverage. Dot roundness is defined as [18]:

\[
\text{Roundness} = 4\pi \left( \frac{A}{p^2} \right)
\]

(2)

where \(A\) is the area of the dot and \(p\) is its perimeter. The roundness is equal to 1 for circle, and is less than one for any other closed figure. The closer the roundness is to 1, the better is the quality of the dot. Fleming et al. stated that their analyses and interpretation are general and applicable to any printing processes where image quality is governed by the smallest printable dot [19]. In screen printing, due to the technique itself, it is not expected that roundness reaches values as high as 1.

It should be pointed out that the aim of this study is to investigate the influence of transparent polyethylene film thickness on print quality. The analysis primarily included the colour reproduction, but important quality attributes such as line quality and dot roundness, were also examined. Colour reproduction was analysed by spectrophotometric measurements, and secondary image quality parameters evaluation was performed by the method of digitally analysed scanned imprint images in specified programming languages.

EXPERIMENTAL

This research included four different thicknesses of polymer material of the same composition. The material used was PE-LD low density polyethylene (0.910 - 0.925 g cm\(^{-3}\)). Used thicknesses were 30, 35, 38 and 110 \(\mu\)m. The samples were printed with the screen printing technique. Test image, used in research, was created using Adobe Illustrator CS5.5 software. The test image dimension was 210 x 297 mm and contained different elements used for print quality control. Elements used for obtaining the results were 2.54 x 2.54 mm solid tone patches, lines 2 pt width and dots with 0.6 mm diameter. Screen with thread count of 120 threads per cm was used for printing plates, which were made conventionally using linearized positive films. As a photo sensitive coating Sericol Dirasol 22 emulsion was used. Exposure was performed 90 seconds with a RUVA lamp (40W), where the distance from the lamp to screen measured 20 cm. Printing speed amounted to 15 cm per second, squeegee hardness - 85 Shore Type A, while snap-off distance measured 4 mm. Ink used for printing was Sericol Polyscreen yellow colour PS-043/1 (Mid Chrome). Fixation of printed samples was carried out on room temperature in duration of 4 hours. After fixation, the printed sheets were digitalized by Mustek 1200 ub plus flat scanner for further analysis. The scanning resolution was set as 600 spi and all auto functions were turned off.

CIE L*a*b* colour coordinates on the obverse and reverse side of a printed sample were obtained using diffuse spectrophotometer Konica Minolta cm-2600d (Illuminant D65, Standard Observer 8º, geometric condition d/8, measurement area 11 mm).

Line reproduction was assessed by measuring area and perimeter of 2 points thick lines and comparing these values with area and perimeter values of an ideal image created using a computer in resolution of 600 ppi.

Dot roundness was obtained by measuring printed dots with 0.6 mm diameter. All values of importance were calculated using ImageJ software, implemented in Java for the creation, visualization, editing, processing, and image analysis [20].

RESULTS AND DISCUSSION

Colour reproduction

The influence of substrate thickness on the change of the sample features by screen printing technique was experimentally determined. First the CIE L*a*b* coordinates of the samples on the obverse printed side were determined with a spectrophotometer. Five measurements were performed for each sample, and was used the mean value as the result. The same process was performed for the reverse side of printing, and the obtained results are shown in Table 1, where the film thickness used in the printing process for every sample is specified.

On the basis of the obtained results the colour difference values of the obverse side of the printed sample and the reverse side measured through the transparent film, are determined. The obtained results show that there is a change in colour. These changes are small and can be listed in two groups of values - a group of values for colour difference where the difference is noticeable (\(\Delta E_{ab}\) between 0.2 and 1), and a group where the colour difference between obverse and reverse side results is visible (\(\Delta E_{ab}\) between 1 and 3). An increase of colour difference with an increasing of film thickness is noticeable which shows that film thickness affects colour, i.e. with the increase of film thickness the film has a greater haze and it brings changes to colour coordinates readings.
To determine the dependence of colour difference between two sides of the transparent polyethylene film sample on the thickness of the film, a mathematical model, based on a simple linear regression, was developed (Bivariate Linear Regression). Simple linear regression focuses on explaining/predicting one of the variables on the basis of information for the other variable. The regression model thus examines changes in one variable as a function of changes or differences in values of the other variable. The relationship between dependent (criterion) variable and independent (predictor) variable explored by the linear regression is described by the general linear model. The mathematical equation for the general linear model using population parameters is [21, 22]:

\[
Y = \beta_0 + \beta_1 X + \varepsilon
\]

where:
- \( Y \) - dependent variable,
- \( X \) - independent variable,
- \( \beta_0 \) - an adjustment constant due to scale differences in measuring \( X \) and \( Y \) (the intercept or the place on the \( Y \) axis through which the straight line passes. It is the value of \( Y \) when \( X = 0 \)).
- \( \beta_1 \) - the change along the \( Y \) scale expected for every unit changed in fixed values of \( X \) (represents the slope or degree of steepness).
- \( \varepsilon \) - an error component for each individual measurement, the portion of \( Y \) score that cannot be accounted for by its systematic relationship with values of \( X \).

Constants \( \beta_0 \) and \( \beta_1 \), that represent the theoretical evaluation of parameters \( \beta_0 \) and \( \beta_1 \), are determined from the results of experimental research.

In Table 2 are shown the obtained results of the simple linear regression coefficients for the proposed mathematical model, equation (3) that determine the dependence of the colour difference \( \Delta E_{ab} \) between two sides of the transparent film, on the film thickness \( L \).

Statistical analysis of the colour difference results of printed transparent polyethylene film with a simple linear regression model analysis revealed the existence of a statistically reliable mathematical model of dependence of the colour difference from film thickness, with simple linear regression coefficient \( R^2 = 0.966 \).

Table 1. Average values of CIE L*a*b* coordinates and \( \Delta E_{ab} \).

<table>
<thead>
<tr>
<th>Film thickness</th>
<th>Sample side</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>( \Delta E_{ab} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 ( \mu )m</td>
<td>Obverse</td>
<td>77.66</td>
<td>20.45</td>
<td>83.23</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>77.39</td>
<td>20.91</td>
<td>83.60</td>
<td>0.65</td>
</tr>
<tr>
<td>35 ( \mu )m</td>
<td>Obverse</td>
<td>77.47</td>
<td>20.88</td>
<td>83.88</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>77.25</td>
<td>21.41</td>
<td>83.40</td>
<td>0.75</td>
</tr>
<tr>
<td>38 ( \mu )m</td>
<td>Obverse</td>
<td>77.71</td>
<td>20.09</td>
<td>82.96</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>77.50</td>
<td>20.38</td>
<td>83.78</td>
<td>0.89</td>
</tr>
<tr>
<td>110 ( \mu )m</td>
<td>Obverse</td>
<td>77.26</td>
<td>20.75</td>
<td>82.48</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>76.46</td>
<td>21.77</td>
<td>81.75</td>
<td>1.48</td>
</tr>
</tbody>
</table>

Table 2. Simple linear regression coefficients for the obtained mathematical model that determine the dependence of the colour differences \( \Delta E_{ab} \) between two sides of the transparent film print, on the film thickness \( L \).

<table>
<thead>
<tr>
<th>( \Delta E_{ab} ) = 0.43 + 0.01 \cdot L (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple linear regression coefficient</td>
</tr>
<tr>
<td>Std. Error of the Estimate</td>
</tr>
<tr>
<td>( b_0 = 0.43 )</td>
</tr>
<tr>
<td>( b_1 = 0.01 )</td>
</tr>
<tr>
<td>( r^2 )</td>
</tr>
<tr>
<td>( s )</td>
</tr>
<tr>
<td>( t )</td>
</tr>
<tr>
<td>( t )</td>
</tr>
<tr>
<td>0.966</td>
</tr>
<tr>
<td>0.08358</td>
</tr>
<tr>
<td>0.080</td>
</tr>
<tr>
<td>5.411</td>
</tr>
<tr>
<td>0.001</td>
</tr>
<tr>
<td>7.570</td>
</tr>
</tbody>
</table>
Line reproduction

Line analysis, as an essential attribute of print quality, was performed by measuring the surface area and perimeter lines. The results obtained by measuring the 2 pt thick lines from both sides of the printed sample are shown on Fig. 1. The smallest difference is with the thinnest film of 30 μm, and the difference increases with the increasing of film thickness, so the biggest difference is with the thickest film of 110 μm.

In this graph, the differences between the line areas from both sides of the film can be seen. It is necessary to examine the relations between differences of the line areas on the obverse and line areas on the reverse side of print, then between the line areas on the obverse side of the print and the ideal line as well as the difference between line areas on the reverse side and the ideal line. The results are shown in Fig. 2.

Results in Fig. 3 show 2 pt (0.7 mm) line perimeter values. The smallest difference between the line perimeters is on the 30 μm thick film sample and it gradually increases with increasing film thickness, so that the biggest difference between the obverse and reverse side of a film is on the 110 μm thick film.

In this graph, differences between the line perimeters from both sides of the film can be seen. It is necessary to examine the relations between differences of line perimeters on the obverse and line perimeters on the reverse side of print, then between the line perimeter on the obverse side of the print and the ideal line, as well as the difference between line perimeters on the reverse side and the ideal line. The results are shown in Fig. 4.

Dot reproduction

In addition to analysis of line area and perimeter, the quality of dot reproduction, which is determined on the basis of its roundness, is a more important factor for determining the print quality. Roundness of a dot was analyzed with ImageJ software. Dots with 0.6 mm in
Fig. 3. Graphic representation of line perimeter values.

Fig. 4. Graphic representation of line perimeter movements with increasing of film thickness.

A-B – difference between reverse side line perimeter and obverse side line perimeter
A-I – difference between obverse side line perimeter and ideal line perimeter
B-I – difference between reverse side line perimeter and ideal line perimeter

Fig. 5. Graphic representation of dot roundness values.
diameter were measured. Measurements were performed with five dots from the same sample and average values are presented in Fig. 5.

Dot roundness, according to the results, decreases on the reverse compared to the obverse side of the print. There the dot gets a more irregular shape, far away from the ideal circle. The resulting changes, or distortion of dot roundness from the reverse, compared to the obverse side of print, are very small but they do exist and increase from the thinnest film, where the difference is minimum, to the thickest 110 µm film, at which point the dot has the most irregular shape. That growth is shown in Fig. 6.

CONCLUSIONS

The aim of this paper is to point out the influence of the substrate thickness on the reverse print on transparent polymeric materials. Low-density polyethylene films were printed with the screen printing technique, and the print was examined through the transparent substrate. With the aim of determining the influence of the substrate, the basic attributes of print quality were analyzed: reproduction of colour, lines and dots.

Light that is scattered upon passing through a film or sheet of a material can produce a hazy or smoky field when objects are viewed through the material, like with the reverse printing. Thin films make lower light scattering and with the increase of the film thickness, light scattering becomes higher. These changes of substrate thicknesses influence print quality attributes, i.e. the thicker the film, the greater the differences, between the attributes measured from the obverse and the reverse side of print are.

Colour reproduction was analysed by spectrophotometric measurements and a colour difference on the reverse side compared to the obverse print side, was noticed. Although the differences are small and unnoticeable to the inexperienced eye, it is very important to note that they exist and that they are increasing with the increase of substrate thickness.

Assessment of quality attributes was performed by the analysis of digitalized print images in an appropriate programming language. Quality attributes that were analyzed are line quality and dot roundness.

Line quality was estimated on the basis of line area and line perimeter. Line area and line perimeter for all samples clearly deviate from the ideal. Comparison of the line areas and perimeters on the obverse and the reverse side, shows a difference that becomes greater with the film thickness increase.

Dot roundness, according to the results, decreases from the reverse of the print side, as compared to the printed side. Dots are getting an irregular shape, far away from the ideal circle. However, in this case the difference between the roundness of a dot from the printed side, and the roundness of a dot from the reverse side increases with the increase of the substrate thickness.

Considering all results, we can conclude that the substrate with its thickness affects the quality of print. With the aim of further knowledge, influence of transparent film thickness on other important quality attributes such as text legibility and macro nonuniformity, should
be examined. It would also provided an opportunity to examine the influence of other material properties such as surface tension, surface roughness, dampening and contact angle on the print quality.

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STUDY OF THE APPLICATION IN THE BREWING OF ENZYME PREPARATION, CONTAINING LAMINARINASE AND LICHENASE, PRODUCED FROM TRICHODERMA SP. 405
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ABSTRACT

The β-glucanase enzymes find wide application in the brewing. It was obtained a enzyme preparation with laminarinase and lichenase activity, produced from Trichoderma sp. 405 and was investigated its application in the technological process of brewing wort preparation. It was found that the studied enzyme preparation has a hydrolytic effect on the β-glucans and the hemicelluloses of the used ingredients. From economical point of view the obtained enzyme preparation, added at a dose of 0.04 % compared to the used ingredients, leads to receiving of brewing wort, containing β-glucans suitable for healthy lifestyle.

Keywords: laminarinase, lichenase, β-glucans, enzyme preparation, brewing, brewing wort.

INTRODUCTION

The β-glucanase enzymes pertain to the group of hemicellulases. They catalyze the degradation of β-D-glucans. Among the microorganisms, synthesizing β-glucanases, are the strains of genus Trichoderma - Trichoderma reesei [1], T. harzianum [2], T. viride [3], T. koningii T 199 [4], T. sp. GXC [5], T. asperellum [6]. The group of β-glucanase enzymes include also the laminarinase and the lichenase. The laminarinase [E.C. 3.2.1.39] attacks 1,3-β-D-glycosidic bonds into 1,3-β-D-glucans. Its substrate is the polysaccharide laminarin [7]. The lichenase [E.C. 3.2.1.73] hydrolyses β-D-glucans, containing 1,3- and 1,4-bonds. Its substrates are the lichenin and the β-D-glucans in the cereals. The content of 1,3 and 1,4-β-glucans in the endosperm cell walls of the various cereals is different. Linear 1,3-;1,4-β-glucans have been isolated from seed endosperm of barley, oats, rye, wheat, millet, ryegrass. The content of β-glucans of different Bulgarian oats varieties ranges from 2,71 % to 4,26 % [8], in different Bulgarian barley varieties is in the range of 3,15 % - 6,08 % [9], in traditional USA oats varieties is around 4,4 - 4,9 % and in some special selected USA oats varieties reaches to 7,5 - 7,8 % [10]. The content of β-glucans in barley ranges from 1,5 - 2,5 % [11] to 3,0 - 4,5 % [12]. The β-glucans are the main component of barley and malt cell walls [7, 11, 13]. It is considered that they contain approximately 75 % β-1,3-1,4-glucans, 20 % arabinoxylans (noted as pentosans) and 5 % proteins, with traces of ferulic acid. According to Bamforth et al. [14, 15] the internal layer of barley and malt cell walls to the endosperm is composed from dense layer of β-glucans, connected with proteins and the external layer contains xylans, arabinose residues and ester linked acetic and ferulic acid among them (Fig. 1).

Beer is traditionally made from malt, hops, yeasts and water, but the technology is based mainly on the action of the enzymes, activated during the brewing. In the process participate 4 main categories enzymes: α- and β-amylases, (carboxy)peptidases and β-glucanases. All
of them act synergistically.

For brewing is necessary that the brewing wort contains β-glucans as low as possible, i.e. the β-glucans have to be completely degraded. When they are not fully degraded they exert negative influence on the brewing wort and the beer - increased viscosity and deteriorated filtration [16 - 21]. The β-glucans are partially cleaved by the action of β-glucanases and as a result is observed the release of high molecular mass β-glucans from complex compounds with proteins and other substances, as well as a cleavage of the β-glucans with high molecular mass to low molecular mass β-glucans, including glucose [22].

Usually the β-glucanases, which are used in the brewing, are isolated from Trichoderma reesei, Aspergillus niger, Penicillium emersonii and Bacillus subtilis [18]. It was established better filtration velocity of the brewing wort when enzyme preparations with β-glucanase activity were added in the production process of beer and brewing wort [23]. More effective degradation of glucans and viscosity decreasing of brewing wort and beer were established when enzymes with endo-β-1,3(4)-glucanase and xylanase activities were used in the production process of beer [10].

The aim of this research is to create a technological scheme for receiving an enzyme preparation, containing β-glucanase (laminarinase Е.С.3.2.1.39 and lichenase Е.С.3.2.1.73), and to study its application in the brewing.

EXPERIMENTAL

It was used Trichoderma sp. 405, bought from the National bank for industrial microorganisms and cell cultures - NBIMCC.

A spore inoculation product was obtained from the strain producer cultivated on potato-dextrose agar (PDA- Biokar Diagnostics) slants. Mandel’s sowing media was inoculated with the spore inoculating material. Mandel’s fermentation media was inoculated with the sowing material [24]. The Mandel’s fermentation media content is: NH4Cl 1.00 g l -1; urea 0.30 g l -1; KH2PO4 2.00 g l -1; (NH4)2SO4 1.40 g l -1; MgSO4.7H2O 0.30 g l -1; CaCl2.2H2O 0.40 g l -1; Corn extract 10.00 ml l -1; Glucose 20.00 g l -1. The Mandel’s fermentation media content is: NH4Cl 1.00 g l -1; urea 0.30 g l -1; KH2PO4 2.00 g l -1; (NH4)2SO4 1.40 g l -1; MgSO4.7H2O 0.30 g l -1; CaCl2.2H2O 0.40 g l -1; Corn extract 0.1 %; Wheat bran 1 %. The cultivation of Trichoderma sp. 405 was carried out by the method of deep fermentation in 500 ml flasks on a shaker “Inkubations - Schüttelschrank BS-4 B.Braun” (220 rpm) for 144 hours at 28°C.

The activity of both enzymes was obtained spectrophotometrically by measuring the reducing groups, which are released when hydrolyzing their substrates - laminarin and lichenin, respectively. An Unicam SP 1800 Ultraviolet spectrophotometer was used. For determination of enzyme activities was applied Somogyi-Nelson’s method [25, 26]. One international unit (IU) of laminarinase activity is the amount of enzyme which catalyses the transformation of 1 μmol of reducing sugars in 1 cm3 per minute at 40°C in a citric phosphate buffer of pH 5.00. One international unit (IU) of lichenase activity is the amount of enzyme which catalyses the transformation of 1 μmol of reducing sugars in 1 cm3 per minute at 40°C in an acetate buffer of pH 4.00.

The protein contents in the liquid culture in mg ml-1 was obtained by the spectrophotometric method (OD280/OD 260) [27].

The lyophilization was carried out in a freeze-drying installation „HOCHVAKUUM” TG-16. The freezing process of the liquid culture was done at -35°C. The lyophilization’s duration was 28 hours. The cooling temperature of the desublimator was -75°C and the temperature of the plates was -35°C. The enzyme activities were recovered by adding 10 ml distilled water to the lyophilized liquid culture and then they were analysed by the above mentioned Somogyi-Nelson’s method [25, 26]. The residual moisture content of the lyophilized enzyme preparation was determined according to Bulgarian State Standard-1109-89- modified method by using an electronic scale “Sartorius thermo-control” with infrared heating of the samples.

The total mesophilic aerobic microorganisms (CFU g-1) of the lyophilized enzyme preparation is determined according to ISO 4833:2003 [28]; Escherichia coli and coliforms (CFU g-1) of the lyophilized enzyme preparation are analyzed according to ISO 21528-2: 2004 and ISO 4832: 2006 [29, 30]. The determination of Staphylococcus aureus (CFU g-1) of the lyophilized enzyme preparation is according ISO 6888-1: 1999 [31], and the determination of Salmonella sp. (CFU g-1) of the lyophilized enzyme preparation – according to ISO 6579: 2002 [32].

The gamma-irradiation of the samples lyophilized enzyme preparation was performed with the following
parameters: radionuclide Cs$_{137}^+$; type of radiation - gamma rays; activity of Gamma-irradiation installation- „GAMA-1300”, dose rate 1,75 Gy min$^{-1}$; radiation doses: 0, 5 and 10 kGy; operating temperature - 20°C - 22°C.

To study the application of the lyophilized enzyme preparation in obtaining of the brewing wort are conducted laboratory runs according to infusion regime in the production of 10% bright beer when 30% of the malt is replaced by 30% unmalted barley. The enzyme preparation was dosed in the beginning of the process in amounts presented in Table 1 and the doses are confirmed with its activity and with the activities of other industrial preparations (from 776 to 12700 IU g$^{-1}$ and recommendatory doses from 150-250 to 350-450 g t$^{-1}$ grist) [23].

The brewing wort is obtained on laboratory automatic apparatus of the German company “Bender & Hobein” by infusion method of the Department of Technology of Beer and Beverages of the Institute of Cryobiology and Food Technology. In this method the malt grist was mixed with water in a ratio 1:4 and after cytolytic, proteolytic and amylolytic degradation is adjusted to a certain volume and then is filtered. The obtained laboratory brewing worts are analysed by the following methods of the EBC Analysis Committee [33]: the time for saccharification is checked with iodine solution [34]; the speed of draining is determined taking into account the past milliliters brewing wort for a certain period of time [34]; the yield of the extract is determined by calculating the amount of the extracted substances from 100 g malt in the result of the mashing process [34]; the brewing wort extract is determined according to the measured relative mass of a certain quantity brewing wort and according to an official table is reported as g extract in 100 g brewing wort [33]; the determination of the brewing worts and beer pH values is made with pH-meter [33]; the brewing wort and beer colour is determined spectrophotometrically ($\lambda = 430$ nm) [33]; the brewing wort viscosity is measured with viscometer Höppler [33]; the soluble nitrogen is determined spectrophotometrically ($\lambda = 215$ nm and $\lambda = 225$ nm) [35]; the β-glucans determination is performed according to the method of Erdal [36].

RESULTS AND DISCUSSION

Technological scheme for receiving an enzyme preparation with laminarinase and lichenase activities

It was developed a scheme for obtaining a lyophilized enzyme preparation with laminarinase and lichenase activities, produced from Trichoderma sp. 405, which combines several technological stages, presented schematically in Fig. 2.

Characterization of the received enzyme preparation

The total yield after vacuum-freeze drying of 1 l liquid culture is 7,815 g lyophilized enzyme preparation. The obtained lyophilized enzyme preparation is a powder product with uniform consistency and yellowish-brown colour. The laminarinase activity of the filtered liquid
culture, determined immediately after the fermentation is 0,520 IU ml⁻¹, and the lichenase activity - 0,107 IU ml⁻¹. After vacuum-freeze drying the laminarinase and lichenase activities of the lyophilizate, determined immediately after the lyophilization, are respectively 65,26 IU g⁻¹ and 13,59 IU g⁻¹. It was found that the obtained lyophilizate is with average residual moisture content of 8,65 %. This ensures the structural and microbiological stability of the product during its storage.

The results from the microbiological analysis of the received lyophilized enzyme preparation show absence of pathogenic microorganisms - *Escherichia coli* and coliforms (CFU g⁻¹ enzyme preparation), *Staphylococcus aureus* (CFU g⁻¹ enzyme preparation) and *Salmonella sp.* (CFU g⁻¹ enzyme preparation) were not isolated. The total mesophilic aerobic microorganisms of the lyophilized enzyme preparation is 10⁶ CFU g⁻¹, i.e. this result is above the norm for total mesophilic aerobic microorganisms according to the norms of Bulgarian State Standards and ISO. This can be explained by the fact that the filtering of the liquid culture and the subsequent preparation of the samples before the lyophilization process are performed in non-sterile conditions. In order to reduce the reported high number of total mesophilic aerobic microorganisms the lyophilized enzyme preparation was subjected to a gamma-irradiation with low doses with 5 kGy and with 10 kGy, respectively.

After irradiation with 5 kGy and 10 kGy the lamina-
rinase and lichenase activities remain high. It was found that the irradiation with 5 kGy is more favorable, because the reducing of laminarinase and lichenase activities is less compared to the samples, irradiated with 10 kGy. The percentage of preservation of the enzyme activities is presented in Table 2. The results for total mesophilic aerobic microorganisms are shown in Table 3. From the analysis it can be concluded that the irradiation with 5 kGy is enough to ensure considerable preservation of the enzyme activities of the lyophilized enzyme preparation and its necessary microbiological purity, which makes possible to use it in contact with food products.

**Study of the application of the obtained enzyme in the brewing**

It was studied the effect of the lyophilized enzyme (subjected to gamma-irradiation with 5 kGy) with laminarase and lichenase activities 60,13 IU g⁻¹ and 12,43 IU g⁻¹, respectively, in the wort preparation. Laboratory runs according to infusion regime in the production of 10 % bright beer, when 30 % of the malt is replaced by 30 % unmalted barley, were conducted.

In Table 4 are presented some physico-chemical parameters of the malt used in the laboratory runs and in Table 5 - some physico-chemical parameters of the barley used in the laboratory runs. With these ingredients it is expected to obtain beer with relatively good quality.

Table 6 shows the parameters of the brewing wort. The used quantities of enzyme influence the filtration speed, the extract values and the viscosity. The time for saccharification for the first three samples is similar. The speed of draining of the brewing wort in the variants is respectively 0,77 %, 2,77 % and 3,41 % higher than that of the control sample. The extract of the obtained brewing worts is in the range of 10,20 - 10,31 % for the control sample and the first two variants. In Variant 3 the increasing of the extract is with 0,44 % relative to the control sample. The pH values meet the requirements for the technology of bright beers. They vary in a narrow range 5,78 - 5,81. The brewing worts viscosity with dosed enzyme is the same 1,57 mPa s and it is 0,04 mPa s lower than that of the control sample.

In Fig. 3 are presented the received results for the yield of the extract. The values are in the range of 72,98 - 76,50 %. The yield in Variant 1 is 0,24 % higher than that of the control sample, in Variant 2 - 0,88 % higher than that of the control sample and in Variant 3 - 3,52 % higher than that of the control sample.

In Fig. 4 are shown the colour changes of the laboratory brewing worts, measured spectrophotometrically. The control sample and Variant 1 have almost the same colour. Probably the enzyme colour and the doses in Variants 2 and 3 affect the colour of the brewing worts. In Variant 2 the increasing is 1,3 times and in Variant 3 - 2,7 times.

Table 2. Preservation of laminarinase and lichenase activities of the lyophilizate, determined immediately after lyophilization and after its gamma-irradiation with 5 kGy and with 10 kGy.

<table>
<thead>
<tr>
<th>Analysis phase</th>
<th>Laminarinase activity preservation, %</th>
<th>Lichenase activity preservation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Immediately after lyophilization of the liquid culture (0 kGy)</td>
<td>98,07</td>
<td>98,15</td>
</tr>
<tr>
<td>After gamma-irradiation of the lyophilizate with 5 kGy</td>
<td>90,37</td>
<td>89,81</td>
</tr>
<tr>
<td>After gamma-irradiation of the lyophilizate with 10 kGy</td>
<td>86,32</td>
<td>86,11</td>
</tr>
</tbody>
</table>

Table 3. Total mesophilic aerobic microorganisms of the lyophilized enzyme preparation after gamma-irradiation.

<table>
<thead>
<tr>
<th>Total mesophilic aerobic microorganisms, determined of the lyophilized enzyme preparation</th>
<th>Established result</th>
<th>Norm for Total mesophilic aerobic microorganisms according to Bulgarian State Standards and ISO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before gamma-irradiation</td>
<td>10⁶ CFU g⁻¹</td>
<td>10³ CFU g⁻¹</td>
</tr>
<tr>
<td>After gamma-irradiation with 5 kGy</td>
<td>0 CFU g⁻¹</td>
<td>10³ CFU g⁻¹</td>
</tr>
<tr>
<td>After gamma-irradiation with 10 kGy</td>
<td>0 CFU g⁻¹</td>
<td>10³ CFU g⁻¹</td>
</tr>
</tbody>
</table>
Table 4. Analysis of the malt used for the laboratory runs.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
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</thead>
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<tr>
<td>Moisture, %</td>
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</tr>
<tr>
<td>Time for saccharification, min.</td>
<td>10</td>
</tr>
<tr>
<td>Extract, % ADM, - fine grist</td>
<td>79.4</td>
</tr>
<tr>
<td></td>
<td>- roughly grist</td>
</tr>
<tr>
<td>Extract difference, %</td>
<td>1.4</td>
</tr>
<tr>
<td>Colour, EBC</td>
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</tr>
<tr>
<td>Viscosity, mPa.s</td>
<td>1.47</td>
</tr>
<tr>
<td>Soluble nitrogen, - mg/100 ml</td>
<td>76.6</td>
</tr>
<tr>
<td></td>
<td>- mg/100 g</td>
</tr>
<tr>
<td>Total protein, % ADM</td>
<td>10.4</td>
</tr>
<tr>
<td>Kolbach Index, %</td>
<td>40.9</td>
</tr>
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</table>

Table 5. Analysis of the barley used for the laboratory runs.

<table>
<thead>
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<th>Parameters</th>
<th>Values</th>
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<tbody>
<tr>
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<td>Uniformity over sieve, %:</td>
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<td>- 2.8 mm</td>
<td>70.5</td>
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<tr>
<td>- 2.5 mm (2.5 + 2.8 mm)</td>
<td>94.9</td>
</tr>
<tr>
<td>- 2.2 mm</td>
<td>4.3</td>
</tr>
<tr>
<td>- below 2.2 mm</td>
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</tr>
<tr>
<td>Impurities, %</td>
<td>0.1</td>
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<tr>
<td>Total protein, % ADM</td>
<td>11.3</td>
</tr>
</tbody>
</table>

Table 6. Parameters of the laboratory brewing worts.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Control sample</th>
<th>Variant 1</th>
<th>Variant 2</th>
<th>Variant 3</th>
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</thead>
<tbody>
<tr>
<td>Saccharification, min.</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>Filtration speed, l h⁻¹.m⁻²</td>
<td>16.99</td>
<td>17.12</td>
<td>17.46</td>
<td>17.57</td>
</tr>
<tr>
<td>Extract, %</td>
<td>10.20</td>
<td>10.23</td>
<td>10.31</td>
<td>10.64</td>
</tr>
<tr>
<td>pH</td>
<td>5.80</td>
<td>5.78</td>
<td>5.81</td>
<td>5.78</td>
</tr>
<tr>
<td>Viscosity, mPa.s</td>
<td>1.61</td>
<td>1.57</td>
<td>1.57</td>
<td>1.57</td>
</tr>
</tbody>
</table>

Fig. 4. Colour of the obtained brewing worts.

Table 6. Parameters of the laboratory brewing worts.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Control sample</th>
<th>Variant 1</th>
<th>Variant 2</th>
<th>Variant 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saccharification, min.</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>Filtration speed, l h⁻¹.m⁻²</td>
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<td>17.46</td>
<td>17.57</td>
</tr>
<tr>
<td>Extract, %</td>
<td>10.20</td>
<td>10.23</td>
<td>10.31</td>
<td>10.64</td>
</tr>
<tr>
<td>pH</td>
<td>5.80</td>
<td>5.78</td>
<td>5.81</td>
<td>5.78</td>
</tr>
<tr>
<td>Viscosity, mPa.s</td>
<td>1.61</td>
<td>1.57</td>
<td>1.57</td>
<td>1.57</td>
</tr>
</tbody>
</table>

Fig. 5. β-Glucans content in the obtained brewing worts.
Fig. 5 presents the effect of the input enzyme preparation on the contents of β-glucans. In the control brewing wort they are in an amount of 168 mg l⁻¹. The enzyme preparation has clearly underlined effect on them and breaks them down 4.1 times in variant 1, 2-12 times in variant 2 and 3-11 times in variant 3. Independently of the measured low laminarinase and lichenase activities, the obtained enzyme, although it is not purified, can be considered suitable for use for the preparation of brewing wort.

CONCLUSIONS

Based on the results for the brewing wort preparation, it can be concluded that the enzyme prepared with laminarinase and lichenase activities, produced from Trichoderma sp. 405, has a hydrolytic effect on the β-glucans and the hemicelluloses of the used ingredients, more pronounced in decreasing of the β-glucans content and less in increasing of the brewing wort filtration speed.

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EXAMINATION OF THE INFLUENCE OF THE GRINDING DEGREE AND STABILIZING AGENT ON THE RHEOLOGICAL PROPERTIES OF AQUA-COAL FUEL SUSPENSIONS

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ABSTRACT

It has been established that 50 - 60 minutes of Angren and Shargun coal’s grinding are sufficient to obtain particles of size not less than 50 µm, the amount of which is more than 80 % of the total mass. A considerable increase of the structural viscosity value and the stability of the aqua-coal fuel suspensions (ACFS) are observed under the studied conditions. It has been shown that the optimal concentrations of plasticizing reagents such as NaOH or Ca(OH)$_2$ are 1,0 % and 0,75 % from the total mass of ACFS based on Angren lignite. There are 38 - 40 % and 43 - 49 % of solid phases, respectively, in the ACFS.

For Shargun black coal the same plasticizing agents with similar concentrations have been applied. As a result there is 52 - 54 % of solid phase in the total mass of ACFS. The results show that the use of NaOH or Ca(OH)$_2$ as the plasticizing agent reduced the structural viscosity of lignite and black coal ACFS from 2,52 to 1,28 Pa s and from 2,52 to 1,34 Pa s, respectively. The value of viscosity of ACFS has thus been reduced practically two times in the studied conditions.

Keywords: aqua-coal fuel suspensions, stability, fluidity, humidity, viscosity, stabilizing, agent, grinding degree.

INTRODUCTION

It is known that the stabilization of a suspension is determined by surface forces occurring in the thin layers, which round the particles of dispersed phase [1]. The role of the stabilizing agents (soda ash, sodium pyrophosphate, iron chloride and aluminium chloride, alkaline salts of organic acid and sulfate alkaline solution, etc.) is that when agents are adsorbed on the particles of the dispersed phase they form films around them which reduce surface tension, block immediate contact and hinder the process of the particles coagulation. In the past some resins and their fractions, different soups, etc. have been applied as stabilizers but currently synthetics with complex composition are used as surface active substances (SAS). Huge numbers of substances have been researched for stabilization of ACFS [2 - 5]. For lignites from deposits the necessity for individual selection of chemical agent appears along the task for reduction of rheological properties and achievement of the necessary stability in static and dynamical conditions. Usually, the plasticizing agents are introduced into the suspension as water solution, so the chemical composition of water affects significantly their efficiency.

EXPERIMENTAL

The Angren lignite grade of 2BSC (brown, slab, coarse), grade of 2BNFSC-1 and 2BNFSC -2 (brown nut, fine, seed, chip) and the Shargun black coal grade of 1SCCNF (soft coking coarse, nut, fine) of Uzbekistan were the objects of our studies [6 - 12]. The presence of oxygen containing carboxyl and hydroxyl (phenolic) groups and humic acids are typical for the Angren lignite. It is known that humic acid in coal has a protective effect on clay and coal particles showing their subsidence.
Their content is about 5% in the Angren coal. NaOH and Ca(OH)₂ were taken as stabilizing agent for ACFS. The structural viscosity of ACFS dependence on concentration of alkali has an extremal character with a minimum.

The coal samples were ground in a ball mill model BML (ball mill laboratorial) to different contents of solid phase in ACFS - coal particles of size not less than 50 µm. The grinding time was determined by the yield of fine fraction of coal (less than 50 µm). The grain size composition was determined with sieves according to GOST 2093-82. Rheological characteristics were evaluated by determining structural viscosity on a BCH-3 rotary viscometer. The mass fraction of solid phase was defined by drying at 1050C (GOST 11014-84).

RESULTS AND DISCUSSION

The aqua-coal suspension is a micro heterogeneous system that consists of two or more phases and it depends on the quantity of the dispersion medium. As a result one of the phases forms a medium divided into particles of dispersed phases. Usually the interval of particles size can be changed from some nanometers to 100 µm and more. Fundamental physicochemical signs

<table>
<thead>
<tr>
<th>Grinding duration min.</th>
<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Residue, % R₅₀ less than 50 µm</td>
<td>R₂₀₀ less than 200 µm</td>
<td>μc, Pa s</td>
<td>τ₀, Pa</td>
<td>Stability, day</td>
</tr>
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<td>The Angren lignite grade of 2BSC</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>56-58</td>
<td>96-97</td>
<td>1.87</td>
<td>29</td>
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<tr>
<td>20</td>
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<td>1.89</td>
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<td>2</td>
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<td>~ 99</td>
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<td>5</td>
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<tr>
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<td>~ 99,3</td>
<td>2.52</td>
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<tr>
<td>50</td>
<td>86-88</td>
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<td>2.58</td>
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<td>60</td>
<td>90-92</td>
<td>~ 99,9</td>
<td>2.58</td>
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<td>The Angren conditioned commodity grade of 2BNFSC-1</td>
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<tr>
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<td>89-91</td>
<td>~ 99,9</td>
<td>1.90</td>
<td>26</td>
<td>36</td>
</tr>
</tbody>
</table>

*The content of solid phase of ACFS for Angren lignite grade of 2 BSC is 38,8 - 40,0 %, the grade of 2 BNFSC-1 is 43,6 - 45,0 %, the grade of 2 BNFSC-2 is 47,8 - 49,2 %, and for Shargun black coal grade of 1 SCCNF is 51,8 - 53,6 % from total mass, respectively.
such as heterogeneity, a notable presence of a separating surface between the phases and dispersion (atomism) are general for all dispersed system. The role of the factors becomes more considerable when the particles size and their content in liquid medium are decreased in order to demonstrate the aggregative and sedimentation stability of fine system.

Table 1 shows the results for the grinding duration on the grinding degree and properties (structural viscosity, dynamic stress of shift and stability) of ACFS. It can be seen from Table 1, that with the increase of the grinding duration the yield of coal particles of fraction size less than 50 µm (R50) rises.

In this connection the structural viscosity of ACFS and its stability are increased. It is established that 50 - 60 minutes of grinding are sufficient for obtaining ACFS with an 80 % content of coal fraction less than 50 µm (R50). The plasticizing agents are added to elongate storage term of ACFS by increasing of solid phase in the suspension.

The plasticizing agents (lignosulphonates, CAR (coal alkali reagents), NaOH, Ca(OH)₂, etc.) contribute mostly alkaline medium in the ACFS.

Increase of alkali content to 2 % leads to exfoliation of the flurry with formation of a hard residue. In the literature [3] for this fact the following explanation was given. The water-alkali reacts with lignite in the first stage and converts humate sodium into a water phase in the form of sodium salts:

\[ \text{NaOH} + (\text{HO} - \text{Humic})_{\text{coal}} \rightarrow (\text{NaO} - \text{Humic})_{\text{water}} + \text{H}_2\text{O} \]

It is known that humic acid and its sodium humate inserted as CAR reduce the rheological character of ACFS [13 - 16]. The sodium humate and the calcium humate are active substances, having plasticizing activity. In this study, the possibility to use a CAR analog - alkaline agents of NaOH and Ca(OH)₂ for ACFS has been studied. The resulting sodium humate and calcium humate have been formed directly at their adding into the ball mill and in the coal grinding process that allowed to simplify the process of introduction and batching of the agents. The process occurred exactly at little concentrations of alkali and leads to coagulation of humic acid, the passage of the true solution of the sodium humate into a colloid solution - a gel of humic acid, which stabilizes the aqua-coal fuel suspensions and reduce their viscosities.

\[ (\text{NaO} - \text{Humin})_{\text{water}} + (\text{HO} - \text{Humin})_{\text{coal}} \rightarrow (\text{HO} - \text{Humin})_{\text{gel}} + (\text{NaO} - \text{Humin})_{\text{coal}} \]

Fig. 1. Dependence of the structural viscosity of ACFS obtained on the basis Angren lignite (grade of 2 BSC), from the amount of inserted sodium hydroxide (a) and calcium hydroxide (b).
Fig. 1 shows that the dependence of the structural viscosity of ACFS on concentration of inserted alkali has an extreme character. Results showed that the optimum amount of alkali plasticizing agents - NaOH was 1.0 % for obtaining an ACFS with Angren lignite, containing 38 - 40 % of solid phase in the suspension, as well as, a certain amount of Ca(OH)₂ agent - 0.75 % including 43 - 49 % of solid phase in the suspension.

The application efficiency of alkali agents was studied in the ACFS, obtained from the Angren lignite and the Shargun black coal (Table 2). The data on the influence of the stabilizing agents NaOH and Ca(OH)₂ on the rheological characteristics of ACFS which were obtained from local types of coal are given in Table 2. They show that the application of NaOH or Ca(OH)₂ as plasticizing agents for lignite and black coal reduces the structural viscosity of lignite and black coal’s ACFS from 2.52 - 1.28 Pa·s to 2.52 - 1.34 Pa·s, respectively.

<table>
<thead>
<tr>
<th>№</th>
<th>Coal samples</th>
<th>Content of solid phase in the ACFS, %</th>
<th>Chemical agent</th>
<th>Amount of agent %</th>
<th>Rheological characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>μₙ, Pa·s</td>
</tr>
<tr>
<td>1</td>
<td>Angren lignite grade of 2BSC</td>
<td>36</td>
<td>without addition</td>
<td>-</td>
<td>2.52</td>
</tr>
<tr>
<td>2</td>
<td>Angren lignite grade of 2BNFSC -1</td>
<td>42</td>
<td>without addition</td>
<td>-</td>
<td>2.2</td>
</tr>
<tr>
<td>3</td>
<td>Angren lignite grade of 2BNFSC -2</td>
<td>45</td>
<td>without addition</td>
<td>-</td>
<td>2.1</td>
</tr>
<tr>
<td>4</td>
<td>Shargun black coal of 1SCCNF grade</td>
<td>52</td>
<td>without addition</td>
<td>-</td>
<td>1.84</td>
</tr>
<tr>
<td>5</td>
<td>Angren lignite of 2BSC grade</td>
<td>36</td>
<td>NaOH</td>
<td>1.0</td>
<td>1.28</td>
</tr>
<tr>
<td>6</td>
<td>Angren lignite of 2BNFSC -1 grade</td>
<td>42</td>
<td>NaOH</td>
<td>1.0</td>
<td>1.16</td>
</tr>
<tr>
<td>7</td>
<td>Angren lignite grade of 2BNFSC -2</td>
<td>45</td>
<td>NaOH</td>
<td>1.0</td>
<td>1.1</td>
</tr>
<tr>
<td>8</td>
<td>Shargun black coal grade of 1SCCNF</td>
<td>52</td>
<td>NaOH</td>
<td>1.0</td>
<td>1.06</td>
</tr>
<tr>
<td>9</td>
<td>Angren lignite grade of 2BSC</td>
<td>36</td>
<td>Ca(OH)₂</td>
<td>0.75</td>
<td>1.34</td>
</tr>
<tr>
<td>10</td>
<td>Angren lignite grade of 2BNFSC -1</td>
<td>42</td>
<td>Ca(OH)₂</td>
<td>0.75</td>
<td>1.22</td>
</tr>
<tr>
<td>11</td>
<td>Angren lignite grade of 2BNFSC -2</td>
<td>45</td>
<td>Ca(OH)₂</td>
<td>0.75</td>
<td>1.18</td>
</tr>
<tr>
<td>12</td>
<td>Shargun black coal grade of 1SCCNF</td>
<td>52</td>
<td>Ca(OH)₂</td>
<td>0.75</td>
<td>1.15</td>
</tr>
</tbody>
</table>
Notably the value of ACFS viscosity decreases practically two times.

The initial ash of coal did not have a considerable influence on the reduction of the structural viscosity, which allowed to use the alkaline agents for the low-ash lignite and black coal. It should be noted that currently the use of an inexpensive and cost-effective agent with which to obtain a stable ACFS, is quite actual. That is why, usage of plasticizing agents as inexpensive and available as Ca(OH)$_2$ for ACFS can be perspective and economically beneficial factor (the cost of Ca(OH)$_2$ is 50 - 60 times lower than the cost of NaOH, etc.).

Thus, it is established that for production of lignite and black coal of ACFS the application of calcium hydroxide - Ca(OH)$_2$ as plasticizing agent, simplifies and reduces the price of the production process with simultaneous increase of the slurry fuel stability and calorific value.

CONCLUSIONS

It has been established that 50 - 60 minutes of Uzbekistan Angren and Shargun coal grinding is sufficient to obtain particles of a size not less than 50 µm, which assemble more than 80% from the total mass. A considerable increase of the structural viscosity and the stability of the aqua-coal fuel suspensions (ACFS) has been observed in these conditions.

It has been shown that in order to obtain ACFS on the basis of Angren and the Shargun coal the optimal concentration of plasticizing agents - NaOH or Ca(OH)$_2$ should 1,0 % and 0,75 % from the total mass, with the content of solid phase 38 - 40 % and 43 - 49 %, respectively. Similar plasticizers with homothetic concentration were applied during the stabilization of Shargun black coal with amount of solid phase 52 - 54 % from the total mass of ACFS. The results testify that the application of NaOH or Ca(OH)$_2$ as plasticizing agents for lignite and black coal, reduce the structural viscosity of lignite and black coal ACFS from 2,52 - 1,28 Pa s to 2,52 - 1,34 Pa s, respectively. The value of ACFS viscosity has reduced practically two times.

REFERENCES

13. V.E. Gubin, V.V. Gubin, Piping transport of oil and

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SPECIFICITIES OF THE RECIRCULATING METHOD FOR CENTRAL KYZYL KUM PHOSPHORITES PROCESSING TO QUALIFIED PHOSPHORIC FERTILIZERS
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ABSTRACT

With the purpose of obtaining concentrated grades of phosphoric fertilizers, the decomposition of phosphorus concentrate from phosphorites of the Central Kyzyl Kum with evaporated wet processing with phosphoric acid by the recirculating method in liquid phase, has been investigated. The results of the research have shown, that the expansion coefficient of the phosphorus concentrate is 83,34 - 90,29 %. In addition the filtration rate by liquid phase has been found. The degree of distribution of the phosphate constituent parts components has been given. The process of neutralization of the acid monocalcium phosphate, obtained from phosphorus concentrate with a 25 % water solution of ammonia (NH₃) and limestone (CaCO₃), has been studied. Products, containing 53,01 - 55,36 and 50,51 - 51,19 % P₂O₅ with 4,13 and 1,92 MPa static strength, respectively, have been obtained. The latter can be recommended as a double superphosphate by the State Standard grade A.

Keywords: phosphorus concentrate, evaporated wet processing, expansion coefficient, filtration rate.

INTRODUCTION

In the world's practice some traditional technologies based on acid treatment (nitric acid, sulfuric acid, phosphoric acid and hydrochloric acid) of phosphate raw materials to phosphorus containing fertilizers such as nitrophosphate, ammophos, simple superphosphate, double (triple) superphosphate and precipitate exist. Traditional acid decomposition is conducted by energy-,material- and capital intensive efforts with foundations of large tonnage - phosphogypsum, calcium chloride, and calcium nitrate wastes. Moreover, in the presented technologies there are significant and strict requirements for quality of the phosphate raw material. Their values have to be controlled for: content of P₂O₅ from 24,5 to 39,4 %; CaO from 39,5 to 52,5 %; MgO from 0,1 to 3,5 %; total Fe₂O₃ and Al₂O₃ have to be from 1,5 to 3,3 %; CO₂ from 1,3 to 1,8 %, residue should be 10 - 20 % on mesh sieve № 0071. Conditioned raw phosphates of Khibini, Florida, Moroccan, Syrian deposits meet the requirements, and are suitable for acid processing. As opposed to them, the phosphorites of Central Kyzyl Kum are poor raw materials regarding content of P₂O₅ (16 - 17 %), carbonate impurities (21 - 41 %), high values of calcium modulus (CaO:P₂O₅ > 2), chlorine (0,1 %) and organic impurities. In addition this raw material is characterized by thin intergrowth of phosphate minerals with calcite [1]. Therefore, attempts to enrich them with flotation have not lead to positive results [2, 3].

The most efficient method of enrichment can be selective removal of calcareous impurities out of the phosphorites by the nitric acid method [4] or thermal burning for CO₂ removal [5]. The latter is implemented in the Kyzyl Kum phosphorite plant where ore reduction, dry separation with obtaining phosphorite flour, deslimation and washing of raw chlorine, burning for the decomposition of carbonates and CO₂ removal, are used.

As a result of this process, washed and burned concentrate, that contains (mass %): 27,26 P₂O₅, 53,36 CaO, 1,3 Al₂O₃, 0,51 Fe₂O₃, 0,6 MgO, 1,91 F, 2,41 CO₂, 0,04 CI, CaO:P₂O₅ = 1,96, is obtained. Since 2006, the Kyzyl Kum phosphorite plant has been producing annually up
to 400 thousand tons of washed and burned phosphorus concentrate. This concentrate is only supplied the Open Joint Stock company (OJSC) “Ammofos-Maxam” for production of ammonium phosphate (10 % N and 46 % P₂O₅, suprefos (8 - 15 % N and 20 - 24 % P₂O₅) and ammonium sulfate phosphate (15 - 19 % N and 4 - 23 % P₂O₅) [1]. These are products belonging to complexed fertilizers. They have to be applied before planting, with planting and into dressing. Phosphoric fertilizers are most efficient when they are applied with the autumn plough [6]. Simple superphosphate and double superphosphate are ordinary phosphoric fertilizers. They are good quality phosphorous containing fertilizers, suitable for application in any soil and under all crops. However, simple superphosphate with content 16 - 19 % P₂O₅: 51 - 54 % P₂O₅; 50 - 52,5 % P₂O₅ unacceptable 39 - 50,7 % P₂O₅; 2,0 - 5,9 N; 13 - 14 CaO and 55,5 - 57,55 % P₂O₅; 55 - 56,3 % P₂O₅ unacceptable 49,2 - 52,7 % P₂O₅ respectively. Their hygroscopicity was at level with the standard samples of superphosphate.

Studies of double superphosphate produced on the basis of phosphorites from Central Kyzyl Kum were reported [8, 9]. The deficiencies found in the mentioned studies are low-degree of efficiency of the phosphate raw material, application of high-priced ammonia and low content of P₂O₅ in the product.

In our view one of the rational ways is decomposition of phosphate raw material with evaporated wet processing phosphoric acid on recirculation in liquid phase. The present method includes phosphate raw material decomposition with a redundant norm of evaporated wet processing phosphoric acid, necessary for formation of monocalcium phosphate, a saturated solution of monocalcium phosphate, separation of insoluble residues, monocalcium phosphate crystallization and separation from the mother solution, monocalcium phosphate neutralization, sulfuric acid extraction of mother solution, separation of gypsum and return of the phosphoric acid to decompose the next phosphate raw material. The main advantage is the recirculating processing of the phosphate occurs in one cycle, which does not require the camera ripening and long storage after ripening for production of the traditional double superphosphate [1, 7].

There are data on processing of different kinds of phosphate raw material into phosphorus-containing fertilizers with nontraditional cycle methods [10 - 12]. A possibility for double superphosphate production on the basis of decomposition of Apatite and Kingisepp phosphorus concentrate with evaporated wet processing phosphoric acid, containing 40 - 45 and 55 - 65 % P₂O₅ has been shown. The norm of the phosphoric acid was varied within the ranges 400 - 600 % from a stoichiometry of monocalcium phosphate and at temperatures of 60 and 110 - 130°C for 1 - 2 hours. The crystallization process was carried out at temperature of 40 - 60°C for 90 minutes. After neutralization of the acid monocalcium phosphate with ammonia and limestone, granulated double superphosphate was obtained, containing (mass %): 51 - 54 P₂O₅; 50 - 52,5 P₂O₅ unacceptable 39 - 50,7 % P₂O₅; 2,0 - 5,9 N; 13 - 14 CaO and 55,5 - 57,55 % P₂O₅; 55 - 56,3 % P₂O₅ unacceptable 49,2 - 52,7 % P₂O₅ respectively. Their hygroscopicity was at level with the standard samples of superphosphate.

Phosphate ore of Chili say deposit (17,7 % P₂O₅) was calcited apriory at 600 - 650°C for prevention of foaming and improvement of filtration rate [13]. The cycle method processing of this raw material was conducted with application of a 450 - 550 % norm of phosphoric acid (stoichiometric norm to monocalcium phosphate) concentration 40 - 41 % P₂O₅. It was revealed that after 7 cycles process stabilization of the composition of the circulating phosphoric acid was established. As a result a double superphosphate, containing 50,4 - 51,0 % P₂O₅; 46,7 - 47,0 % P₂O₅ unacceptable 0,75 - 1,2 % P₂O₅ free 2,3 - 2,9 N, 0,75 - 1,2 % P₂O₅ free 2,3 - 2,9 H₂O, that corresponds to the requirement of State Standard 16306-80 for double (triple) superphosphate grade A, was obtained.

Research on the decomposition of unconditioned Karatau phosphorites such as deposits of Kokjon and Koksu showed [14], that the degree of decomposition of the raw material reached 99 - 99,5 %. However due to content of insoluble residue (SiO₂, etc.) in the raw material, the latter was removed off the technologic process. The basic technological parameters were the following: norm of phosphoric acid to Ca(H₂PO₄) stoichiometry 450 - 500 %; concentration of acid - 40% P₂O₅; decomposition temperature - 95°C; crystallization temperature - 40°C.

Currently there are no reports concerning the granular phosphorites of Central Kyzyl Kum by a cyclic method in order to treat them to phosphoric fertilizers. That is why this is the aim of the present research.
In this study results of laboratory research on the decomposition of washed and burned phosphorus concentrate from phosphorites of Central Kyzyl Kum, with redundant norm of evaporated wet processing phosphoric acid (stoichiometric norm to monocalcium phosphate), with subsequent separation into solid and liquid phase by filtration, have been given. The liquid phase has been cooled and removed to obtain commodity a monocalcium phosphate, which will neutralize with ammonia and limestone.

EXPERIMENTAL

Materials

Washed and burned phosphorus concentrate (WBP), containing (mass %): 25,77 P₂O₅ total; 3,43 P₂O₅ acceptable by 2 % of citric acid; 2,94 P₂O₅ acceptable by 0,2 M of ethylene diamine tetraacetate (EDTA); 52,70 CaO total; 17,34 CaO acceptable by 2 % of citric acid; 1,20 MgO; 0,63 Fe₂O₃; 1,15 Al₂O₃; 2,67 SO₃; 3,43 CO₂; 6,88 insoluble residue and evaporated wet processing phosphoric acid (WPA) with composition (mass %): 41,20 P₂O₅; 25,77 P₂O₅ containing (mass %): 25,77 P₂O₅; 1,15 Al₂O₃ in initial phosphorite; 25

Formulas for calculations

The computational norm of WPA to stoichiometric monocalcium phosphate was ranged within norms of 300, 350, 400 % calculated by:

\[ N_{WPA} = \frac{0,3944 \cdot \omega(P_{2}O_{5, wpa}) - 100 - m_{wpp} \cdot 0,3944 \cdot \omega(P_{2}O_{5, wpa})}{m_{wpp} \cdot \omega(CaO, wpp) - m_{wpp} \cdot 0,7 \cdot \omega(SO_{3, in wpp}) - 0,7 \cdot \omega(SO_{3, in wpp})} \times 100\% \]  
(1)

where 0,3944 is ratio of molar mass of CaO; P₂O₅ in Ca(H₂PO₄)₂; \( \omega(P_{2}O_{5, wpa}) \) is the mass fraction of P₂O₅ in wet processing phosphoric acid; \( m_{wpp} \) is mass of the initial phosphorite; \( \omega(P_{2}O_{5, in wpp}) \) is the mass fraction of P₂O₅ in initial phosphorite; \( \omega(CaO, wpp) \) is the mass fraction of CaO in initial phosphorite; 0,7 is ratio of molar mass of gypsum CaO; SO₃ in initial phosphorite and wet processing phosphoric acid; \( \omega(SO_{3, in wpp}) \) is the mass fraction of total SO₃ in initial phosphorite; \( \omega(SO_{3, in wpp}) \) is the mass fraction of free SO₃ in wet processing phosphoric acid.

The filtration rate was calculated according to:

\[ \beta = \frac{m_{\text{liquid phase}}}{t \cdot S}, \text{kg} / m^2 \cdot \text{hour} \]  
(2)

where, \( m_{\text{liquid phase}} \) - mass of liquid phase, kg; \( t \) - time from moment filling of funnel to flow of liquid phase off surface of solid phase, h; \( S \) - area of funnel surface \( (S = \pi \cdot r^2) \), m².

The results for the expansion coefficient were calculated \( (K_{exp}) \) by the formula:

\[ K_{exp} = 100 - \left( \frac{\omega_{1P_{2}O_{5, in wpp}} - \omega_{1P_{2}O_{5, in in wpp}}}{\omega_{2P_{2}O_{5, in wpp}} \cdot m_{\text{in dried filter cake}} \cdot 100\%} \right) \]  
(3)

where \( \omega_{1P_{2}O_{5, total}} \) - the mass fraction of total and water-soluble form P₂O₅ in dried filter cake; \( m_{\text{in dried filter cake}} \) - mass of dried filter cake, g; \( \omega_{2P_{2}O_{5, in total}} \) - the mass fraction of P₂O₅ in initial phosphorite, g; \( m_{\text{in initial WBP}} \) - mass of initial phosphorite, g.

The degree of distribution of the components in the acid undecomposed phosphate cake, acid monocalcium phosphate (MCP) and fugate (mother solution) were determined, according to:

\[ R = \frac{(m_{1} \cdot \omega_{1}(\text{com}) \text{ in undeccare, MCP,moth.sol})}{(m_{2} \cdot \omega_{2}(\text{com}) \text{ total})} \times 100\% \]  
(4)

where \( m_{1} \) - mass of acid undecomposed phosphate cake, acid monocalcium phosphate and fugate (mother solution), respectively, g; \( m_{2} \) - total mass of pulp, g; \( \omega_{1}(\text{com}) \) - mass fractions of P₂O₅, CaO, MgO, Fe₂O₃, Al₂O₃ and SO₃ in the acid undecomposed phosphate cake, acid monocalcium phosphate and fugate (mother solution), respectively; \( \omega_{2}(\text{com}) \) - total mass fraction of P₂O₅, CaO, MgO, Fe₂O₃, Al₂O₃ and SO₃, incoming with WPA and phosphorite.

The processing neutralization of the acid monocalcium phosphate with limestone and ammonia was performed by the equations:

\[ CaCO₃ + 2H_{2}PO₄ \rightarrow Ca(H₂PO₄)₂ + CO₂ + H₂O \]  
(5)

\[ 3NH₄ + 2H₃PO₄ \rightarrow NH₄H₂PO₄ + (NH₄)₂HPO₄ \]  
(6)

EXPERIMENTAL PROCEDURE

Laboratory experiments were carried out in a temperature-controlled reactor (500 ml) equipped with a stirrer, with controlled speed. Temperature was kept at 95°C by the thermoregulator in the thermostat. For conduction of the experiment, a weighed amount of acid with reactor, were placed in the thermostat. On obtaining
of the predetermined temperature, we started to measure phosphate raw material at portions for 10-15 min. After the feeding was finished, the time of the decomposition process was 60 min. Further, the obtained pulp was divided into solid and liquid phases by filtration under vacuum of 500 mm of mercury in a Buchner funnel. Determination of the degree of decomposition of the phosphorus concentrate was investigated simultaneously in the process of filtration at the mentioned norm of evaporated wet processing phosphoric acid (300, 350 and 400 %). During the filtration, the acid solid residue was washed several times carefully with distilled hot water to remove any soluble substances. The washed and wet filter cake was dried in an electric oven at 90-95°C until reaching a constant mass. The dried filter cake was subjected to chemical analysis by conventional procedures [16, 17] for determination of total and watersoluble $P_2O_5$.

In the separation process of pulp into solid and liquid phases, the filtrate was cooled within 2 hours at 40°C. As a result, the acid monocalcium phosphate crystallized. The monocalcium phosphate crystallization occurred as described in [15]. It should be noted, that the crystallization time with increasing the norm of the acid from 300 to 400 %, increased. For example, if crystals of monocalcium phosphate at 300 % were formed within 2 hours, the crystals of monocalcium phosphate at 350 % formed within 3 hours. Moreover, at norm of 400 % a seeding agent, which was finished product with size ≤1 mm, in quantity of 1 - 1,5 % from total mass of filtrate was added in order to speed up crystallization.

The described observation in all likelihood is explained by unsaturation of the liquid phase (filtrate) for calcium ions (CaO$^{2-}$). The obtained monocalcium phosphate product was separated from the filtrate with a laboratorial centrifuge CLS-5 (made in Russia). The rotating velocity was 3000 rpm. The centrifugation time was 15 min. Acid undecomposed phosphate cake, acid monocalcium phosphate (with some free form of $P_2O_5$) and fugate (mother solution) were obtained during the research. These were named symbolically as phosphate constituent parts. Chemical analysis of the acid undecomposed phosphate cake, acid monocalcium phosphate and fugate (mother solution) were performed by conventional procedures [16-17]. Also a degree of distribution was defined in connection with the content of components in them.

The neutralization of the acid monocalcium phosphate with 25 % water solution of ammonia (NH$_3$) and limestone (CaCO$_3$) was carried out in laboratory conditions. The composition of the limestone is (mass %): 54,45 CaO; 1,62 MgO; 0,24 Fe$_2$O$_3$; 0,30 Al$_2$O$_3$; 0,86 SO$_3$; 43,83 CO$_2$; 0,89 insoluble residue.

The reaction mixture at the process neutralization of the acid monocalcium phosphate with 25 % water solution of ammonia in chinaware, was heated up to 90 - 95°C. The ammoniated pulp had movability, which helped to exercise the processes of granulation and drying without specific difficulties. A CO$_2$ emission was observed when the acid monocalcium phosphate reacted with limestone, that suggest interaction of the limestone with free phosphoric acid.

**Methods for analysis**

The obtained mixture of the, reaction was moistened with water, and then it was granulated and dried in chinaware at 90 - 95°C.

Dried samples were analyzed for the content of various form of phosphorus, nitrogen and calcium by the respective procedures [16, 17]. The assimilated form of $P_2O_5$ was determined with 2 % citric acid and 0,2 M of EDTA by the colorimetric method. The assimilated form of CaO was determined only with 2 % citric acid. Nitrogen content was obtained by sublimation (Kjeldal). The pH of the products was assessed in 10 % water suspension. In addition, the strength of the granules of 2 - 3 mm in diameter obtained as products - phosphorus-containing fertilizers, were determined using the special device MIP-10-1 according to Standard [18].

**RESULTS AND DISCUSSION**

The laboratory results from the chemical analyses of the acid undecomposed phosphate cake, the acid monocalcium phosphate and the fugate (mother solution) are shown in Table 1.

The results of the research show that at norms of 300, 350 and 400 % from stoichiometry for formation of monocalcium phosphate, the content of the total form of $P_2O_5$ is 35,06, 32,45 and 31,78 %, in the acid undecomposed phosphate cakes, respectively. There are water-soluble and free forms of $P_2O_5$ containing 33,36; 30,32; 28,06 and 25,14; 22,17; 19,90 %, respectively, at norms of 300; 350 and 400 %.
monocalcium phosphate is from 44.97 to 45.79 %; from the cake. All the same, the chemical composition of acid
0.82 to 0.98 % and from 1.51 to 1.81 %, respectively, in%
phosphorus concentrate from phosphorites of Central Kyzyl Kum with phosphoric acid.
Acid undecomposed
Acid monocalcium-
Mother solution

Table 1. Chemical composition of the phosphate constituent parts, obtained by basis decomposition of the phos-

<table>
<thead>
<tr>
<th>Name of phosphate constituent parts</th>
<th>Chemical composition, %</th>
</tr>
</thead>
</table>
|                                    | P₂O₅total. | P₂O₅water-
|                                    |             | soluble |
| Acid undecomposed phosphate cake   | 35.06       | 33.36    |
|                                    | 25.14       | 12.53    |
|                                    | 0.95        | 0.79     |
|                                    | 1.55        | 7.66     |
|                                    | 32.46       | 30.32    |
|                                    | 22.17       | 13.37    |
|                                    | 0.99        | 0.89     |
|                                    | 1.64        | 9.56     |
|                                    | 31.78       | 28.06    |
|                                    | 19.90       | 14.04    |
|                                    | 1.02        | 0.96     |
|                                    | 1.76        | 11.24    |
| Acid monocalcium-phosphate         | 44.97       | 43.40    |
|                                    | 22.81       | 6.74     |
|                                    | 1.46        | 0.88     |
|                                    | 1.65        | 0.21     |
|                                    | 45.40       | 44.20    |
|                                    | 24.72       | 6.26     |
|                                    | 1.13        | 0.83     |
|                                    | 1.46        | 0.15     |
|                                    | 45.79       | 44.65    |
|                                    | 21.21       | 5.84     |
|                                    | 0.77        | 0.72     |
|                                    | 1.23        | 0.11     |
| Mother solution                    | 40.72       | -        |
|                                    | -           | 2.10     |
|                                    | -           | 0.80     |
|                                    | 0.66        | 1.84     |
|                                    | 0.012       |          |
|                                    | 42.46       | -        |
|                                    | -           | 2.02     |
|                                    | -           | 0.98     |
|                                    | 0.68        | 1.87     |
|                                    | 0.008       |          |
|                                    | 42.33       | -        |
|                                    | -           | 1.97     |
|                                    | -           | 1.11     |
|                                    | 0.71        | 1.89     |
|                                    | 0.01        |          |

Table 2. Degree of distribution of the chemical components.

<table>
<thead>
<tr>
<th>Name of the phosphate constituent</th>
<th>Chemical composition, %</th>
</tr>
</thead>
<tbody>
<tr>
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<td>P₂O₅</td>
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<td>Acid undecomposed phosphate cake</td>
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<tr>
<td></td>
<td>27.76</td>
</tr>
<tr>
<td></td>
<td>23.15</td>
</tr>
<tr>
<td>Acid monocalcium-phosphate</td>
<td>25.74</td>
</tr>
<tr>
<td></td>
<td>24.25</td>
</tr>
<tr>
<td></td>
<td>22.75</td>
</tr>
<tr>
<td>Mother solution</td>
<td>36.92</td>
</tr>
<tr>
<td></td>
<td>47.99</td>
</tr>
<tr>
<td></td>
<td>54.10</td>
</tr>
</tbody>
</table>

MgO, Fe₂O₃ and Al₂O₃ are changed from 8.41 to 11.34 %; from 12.43 to 14.04 %; from 0.99 to 1.05 %; from 0.82 to 0.98 % and from 1.51 to 1.81 %, respectively, in the cake. All the same, the chemical composition of acid monocalcium phosphate is from 44.97 to 45.79 %; from 6.74 to 5.84 %; from 1.46 to 0.77 %; from 0.88 to 0.72 %; from 1.65 to 1.23 %, for P₂O₅, CaO, MgO, Fe₂O₃ and Al₂O₃ at norms of 300, 350 and 400 %, respectively. Besides, a considerable amount of 21.21 - 22.81 % P₂O₅free is contained in the acid monocalcium phosphate. The
Table 3. Influence of the norm of phosphoric acid on the degree of decomposition of the raw phosphate and the filtration rate of the liquid phase.

<table>
<thead>
<tr>
<th>Norm of WPA from stoichiometry, %</th>
<th>Washed and dried filter cake, %</th>
<th>Expansion coefficient, %</th>
<th>filtration rate, kg/m²·h, by liquid phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>P₂O₅total.</td>
<td>P₂O₅water-soluble.</td>
<td>K_Exp</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>9,19</td>
<td>2,53</td>
<td>83,34</td>
</tr>
<tr>
<td>350</td>
<td>6,85</td>
<td>2,02</td>
<td>86,81</td>
</tr>
<tr>
<td>400</td>
<td>4,39</td>
<td>1,04</td>
<td>90,29</td>
</tr>
</tbody>
</table>

mother solution has also total forms of P₂O₅ and CaO in its composition in the range of 40,72 - 42,33 % and 1,97 - 2,10 %, respectively.

The degree of distribution was calculated in consideration of the content of the components in the acid undecomposed phosphate cake, acid monocalcium phosphate and mother solution. The results are shown in Table 2. Table 2 shows that the data for the degree of distribution change, depending on the norm of wet processing phosphoric acid - 300, 350 and 400 % from stoichiometry. So, with increasing the norm of phosphoric acid, from 37,34 to 23,15 % P₂O₅; from 69,86 to 65,37 % CaO; from 39,55 to 29,20 % MgO; from 42,70 to 35,63 % Fe₂O₃; from 38,66 to 29,84 % Al₂O₃ pass into the acid undecomposed phosphate cake and from 36,92 to 54,10 % P₂O₅; from 9,93 to 16,09 % CaO; from 28,25 to 55,76 % MgO; from 30,33 to 45,98 % Fe₂O₃; from 39,18 to 56,02 % Al₂O₃ pass into the mother solution. The rest goes into the acid monocalcium phosphate.

As shown in Table 2, the whole amount of SO₂ is precipitated mainly in the acid undecomposed phosphate cake in the form of gypsum - CaSO₄. The acid undecomposed phosphate cake and the mother solution are subjected to sulfuric acid processing.

Influence norm of phosphoric acid on degree of decomposition of phosphate raw and filtration rate of liquid phase are studied. The results are shown in Table 3.

The data from the Table show that there is a dependence between the filtration rate and the expansion coefficient. This is explained by the fact that with increasing of the amount of liquid phase some active hydrogen goes, respectively, in the pulp.

Reasonably, the low degree of decomposition of the raw phosphate is explained by neutralization of the phosphoric acid of Central Kyzyl Kum phosphorite by impurities such as MgO, Fe₂O₃, Al₂O₃, etc. The products of the neutralization of the acid monocalcium phosphate are shown in Table 4. As the data in the Table show, the products obtained by neutralization of the acid monocalcium phosphate by 25 % water solution of ammonia (NH₃), present themself as concentrated phosphorus containing fertilizers, with a considerable amount of nitrogen. The basic components are varied from 53,01 to 55,36 % P₂O₅ by 52,29 to 54,52 % P₂O₅ soluble by citric acid, from 51,80 to 53,87 % P₂O₅ soluble by EDTA, from 44,73 to 47,07 % P₂O₅ water-soluble, as well as

Table 4. Chemical composition of the concentrated phosphoric fertilizers, obtained by phosphoric acid processing of the phosphorus concentrate from phosphorites of Central Kyzyl Kum.

<table>
<thead>
<tr>
<th>Norm of WPA from stoichiometry, %</th>
<th>pH of 10 % suspension</th>
<th>Chemical composition, mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>P₂O₅total.</td>
</tr>
<tr>
<td>Acid Ca(H₂PO₄)₂, neutralized with 25 % water solution of NH₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>5,23</td>
<td>53,01</td>
</tr>
<tr>
<td>350</td>
<td>5,13</td>
<td>54,43</td>
</tr>
<tr>
<td>400</td>
<td>4,87</td>
<td>55,36</td>
</tr>
<tr>
<td>Acid Ca(H₂PO₄)₂, neutralized with CaCO₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>2,79</td>
<td>51,19</td>
</tr>
<tr>
<td>350</td>
<td>2,75</td>
<td>50,62</td>
</tr>
<tr>
<td>400</td>
<td>3,04</td>
<td>50,51</td>
</tr>
</tbody>
</table>
from 9.51 to 9.89 % nitrogen. This type of products, with high content of two components, can be named nitrogen-phosphorus fertilizers.

The products obtained by neutralization of acid monocalcium phosphate by limestone (mass %): 50.51 - 51.19 P₂O₅; 49.28 - 49.79 P₂O₅ acceptable by citric acid; 48.15 - 48.67 P₂O₅ acceptable by EDTA; 40.65 - 43.43 P₂O₅ water-soluble; where ratio of P₂O₅ acceptable by citric acid: P₂O₅ total = 97.26 - 97.56 %; P₂O₅ acceptable by EDTA: P₂O₅ total = 95.08 - 95.33 %; P₂O₅ water-soluble: P₂O₅ total = 80.48 - 84.84 %. There are water forms of P₂O₅ and CaO in the products. This indicates the presence of the product monocalcium phosphate, which is a basic product of double superphosphate. The difference between the total and the water form of P₂O₅ in the product, gives approximately the content of assimilated form of phosphate - dicalcium phosphate. The difference between of the acceptable and water form of P₂O₅ in the product, is indicative of the content of tribasic calcium phosphate.

Therefore, this type of products can be applied as ordinary phosphoric fertilizers, that completely correspond to the requirements of State Standard for double (triple) superphosphate grade A [18].

With the purpose to investigate the mechanical properties of the obtained products, we studied their static strength. The results are presented in Table 5.

A rise of strength scatter (3.48 - 4.13 MPa) in the products, obtained by neutralization of monocalcium phosphate with ammonia, in comparison to granulated fertilizer obtained with limestone (1.92 - 2.23 MPa), is observed. This is explained by the presence of Fe³⁺ and Al³⁺ in the evaporated wet processing phosphoric acid, which form a strong complex compound at the neutralization with ammonia [19].

Therefore, the offered approach includes both processing with sulfuric acid for extraction of the undecomposed phosphate cake and mother solution, and neutralization of the acid monocalcium phosphate,

Table 5. Static strength of phosphorus containing fertilizers.

<table>
<thead>
<tr>
<th>Norm of WPA from stoichiometry, %</th>
<th>P₂O₅ total, %</th>
<th>N total, %</th>
<th>Static strength of granules with size 2-3 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>kg/granules</td>
</tr>
<tr>
<td>Acid Ca(H₂PO₄)₃, neutralized with 25 % aqueous solution of NH₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>53.01</td>
<td>9.51</td>
<td>1.76</td>
</tr>
<tr>
<td>350</td>
<td>54.43</td>
<td>9.78</td>
<td>1.95</td>
</tr>
<tr>
<td>400</td>
<td>55.36</td>
<td>9.89</td>
<td>2.09</td>
</tr>
<tr>
<td>Acid Ca(H₂PO₄)₃, neutralized with CaCO₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>51.19</td>
<td>-</td>
<td>0.97</td>
</tr>
<tr>
<td>350</td>
<td>50.62</td>
<td>-</td>
<td>1.07</td>
</tr>
<tr>
<td>400</td>
<td>50.51</td>
<td>-</td>
<td>1.13</td>
</tr>
</tbody>
</table>

Fig. 1. A block scheme for obtaining of double superphosphate by the cyclic method.
to obtain nitrogen-phosphorus fertilizers and double superphosphate. More details can be found in Fig. 1.

CONCLUSIONS

The results of the carried research show the suitability for application of the liquid cyclic method for processing of low-grade phosphorites of Central Kyzyl Kum to highly concentrated nitrogen-phosphorus and double (triple) superphosphate fertilizers. It is proved, that under the treatment, the phosphorus concentrate from phosphorites of Central Kyzyl Kum with a redundant norm of evaporated wet processing phosphoric acid (300, 350, 400 % stoichiometric norm to monocalcium phosphate), the phosphate mineral is not uncovered completely. That is why we propose to mix it with mother solution, and to subject it to sulfuric acid processing, in order to return back produced phosphoric acid for the decomposition process. However, research on the sulfuric acid processing of the undecomposed phosphate cake and mother solution, would be the subject of our future work.

Therefore, a possibility for obtaining two types of phosphoric fertilizers on the basis of the suggested approach, which is suitable for introduction into the soil in different agrochemical data, is created.

REFERENCES

INVESTIGATION OF POROSITY EFFECTS IN THE EMISSION OF POLLUTANTS IN POROUS BURNERS

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ABSTRACT

Furnaces are the devices, providing heat to industrial operations such as chemical reactions, extraction of metals, production of ceramic, etc. The main challenge of furnaces is the emission of massive air pollutants. However, the porous burners produce less pollutants, compared to the rest of them. In this paper, the finite volume method is used to investigate the effects of porosity on the production of pollutants in the porous burner. The simulation results show that temperature distribution in the low porosity burner is more uniform than in the high porosity one. In addition, increasing the porosity the maximum temperature of the flame increases, and thus reduces the conversion of fuel to carbon monoxide and increases production of nitrogen oxides. Therefore, the average porosity leads to reduction of the total emission of pollutants.

The simulation results are in good agreement with experimental data.

Keywords: burner, porous media, modeling, pollutants.

INTRODUCTION

Environmental crisis is one of the main problems that the world is facing today. One of the strategies for controlling the air pollution is the increasing of combustion efficiency and reducing fuel consumption. So, a burner should control the combustion of fuel for producing heat.

Porous burners consume low value fuels for producing heat. This may be a solution to reduce the production of carbon dioxide. Weinberg and Howell et al. studied the porous materials and their convective, conductive and radiative properties [1, 2]. They described the flame stabilization within a porous burner and showed that the porous matrices have higher burning speeds and lower flammability limits, than open flames.

Yoshizawa et al. numerically simulated an one-dimensional porous burner by considering one-step kinetics [3]. They studied the effects of the heat transfer on the burning rate and flame structure. Barra et al. numerically studied an one-dimensional two-layered porous burner [4]. They showed that the first layer should have a low volumetric heat transfer coefficient, low conductivity, and high radiative coefficient. The second layer should have a high volumetric heat transfer coefficient, high conductivity, and medium radiative coefficient.

Yu et al. experimentally studied the thermal efficiency and the emission properties of porous burners [5]. They investigated three kinds of porous burners: metal fiber (MF), ceramic (CM) and stainless steel fin (SF). They showed that the MF and SF burners had the lowest and highest CO emissions between the three types of burners, respectively. However, the MF and SF burners had the highest and the lowest NO\textsubscript{x} emission among the burners, respectively.

Li et al. experimentally studied the liquid fuel combustion in a porous media burner [6]. They showed that the flame of porous burner is affected by the airflow velocity.

In this paper, the effects of porosity on the emission of pollutants and combustion quality in porous burners are investigated.
NUMERICAL SIMULATION OF POROUS BURNER

The porous burner system is composed of two parts: 1) a solid matrix and 2) void space, saturated by fluid. Therefore, the continuity and momentum equations are written for gas phase and the energy equations are written for both phases. In this paper, a steady state and a two-dimensional system are considered. The effect of gravity force is neglected. So, the governing equations are as follows:

The continuity equation [7]:
\[
\nabla \cdot (\rho \mathbf{v}) = 0
\]  (1)

where \( \rho \) is fluid density (kg/m\(^3\)), and \( \mathbf{v} \) is gas velocity (m/s).

The momentum equations [8]:
\[
\frac{1}{\varepsilon^2} \nabla \cdot (\rho \nu \mathbf{v}_t) = \nabla \cdot (\mu \nabla \mathbf{v}_t) - \nabla P
\]  (2)

where \( P \) is pressure (Pa), \( \nu \) is fluid viscosity (kg m\(^{-1}\) s\(^{-1}\)), and \( \varepsilon \) is porosity of the porous matrix.

Gas phase energy equation [7]:
\[
\frac{1}{\varepsilon^2} \nabla \cdot (\rho \nu h') = \nabla \left( \frac{k}{C_p} \nabla h \right) + h c_R
\]  (3)

where \( h' \) is convective heat transfer coefficient, \( k \) is thermal conductivity (W m\(^{-1}\) K\(^{-1}\)), \( C_p \) is heat capacity (W Kg\(^{-1}\) K\(^{-1}\)), \( R \) is reaction rate (kg fuel m\(^{-3}\) s\(^{-1}\)), \( h \) is specific enthalpy (J kg\(^{-1}\)), and \( h c \) is heat of combustion (J kg\(^{-1}\)).

Solid phase energy equation [9]:
\[
(1 - \varepsilon) \nabla \cdot (k \nabla T) - \nabla \cdot (q_p) = 0
\]  (4)

where \( q_p \) is radiative heat transfer per unit area (W m\(^{-1}\) K\(^{-1}\)).

Fuel diffusion [7]:
\[
\nabla \cdot (\rho \nu y_f) = \nabla \cdot (D \nabla y_f) - R
\]  (5)

where \( D \) is diffusivity (m\(^2\) s\(^{-1}\)), and \( y_f \) is mass fraction of fuel.

\[
\frac{\partial}{\partial \tau} (\rho y_p) + \nabla \cdot (\rho \nu y_p) = \nabla \cdot (D \nabla y_p) - R
\]  (6)

where \( y_p \) is mass fraction of products.

A single-step global reaction mechanism is selected for the complete combustion of fuel.

EXPERIMENTAL

Geometry of porous burner was generated using Gambit 2.0 software. The dimensions of the simulated burner are 13 cm diameter \( \times \) 110 cm length. In order to obtain grid independent results, different uniform grid numbers - 20 \( \times \) 120, 40 \( \times \) 240 and 50 \( \times \) 300 were tested for porosity of 0.5. It was noticed that the difference between the length of the concentration of the fully developed zone, predicted for 40 \( \times \) 120 and 50 \( \times \) 150 grids is insignificant (< 1 %). The length of the concentration of the fully developed zone for the tested grid points were 9.276, 9.301 and 9.305 for grids of 20 \( \times \) 120, 40 \( \times \) 240 and 50 \( \times \) 300, respectively. Thus, 40 \( \times \)

![Fig. 1. The effect of porosity on the temperature distribution in the center line of the porous burner.](image)
Fig. 2. The effect of porosity on the temperature distribution in the porous medium burner.

Fig. 3. The effect of porosity of burner on carbon dioxide production.

Fig. 4. Fully developed length of concentration and temperature vs porosity.
240 grid was used for generating the results. The model equations were solved using a commercial flow simulation software, FLUENT 6.0.1.

The temperature of the inlet stream is 300K and the velocity is 0.2 m s\(^{-1}\). The studied reaction is combustion of methane with 20% excess air as following:

\[ \text{CH}_4 + \text{Air} \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]

The above equations were solved for 7 different porosities: 0.10, 0.25, 0.40, 0.55, 0.70, 0.85, and 1.00.

RESULTS AND DISCUSSION

In order to verify the validity of the results, the temperature of the center line of the porous burner with porosity of 0.5 is compared with the experimental results, presented in the literature. As it is seen in Fig. 1, the simulation results are in line with experimental results [10].

In this paper, combustion of methane with 20% excess air in the porous burner is studied. Fig. 2 shows the effects of porosity on the temperature distribution in the porous burner. As it is seen, an increase of porosity rises the maximum temperature of the flame. Whereas, in low porosities, due to faster heat conduction, temperature throughout the porous medium is lower and more uniform than at high porosities.

Fig. 3 shows the amount of carbon dioxide produced in the length of the flame. As it is seen, increasing the porosity increases the production of carbon dioxide. In other words, combustion process performs better than in the low porosity burner. It is noticed that in the combustion process, pollutants such as CO and \(\text{NO}_x\) are produced. If the maximum temperature of the flame increases, the amount of produced carbon monoxide is reduced. In addition, by increasing the temperature, the amount of produced nitrogen oxides increases. In order to reduce the emission of the burner, the operating temperature should be at an optimum in order to reduce the production of all pollutants. Comparison of Fig. 2 and Fig. 3 shows that an increase in the porosity causes increases of the temperature especially in the maximum point. So, at the high porosities, the quality of combustion is better than at low porosities, CO production decreases, but the production of \(\text{NO}_x\) increases. Therefore, the optimum porosity for decreasing the pollutants simultaneously according to Fig. 2 and Fig. 3 is 0.5.

Fig. 4 shows the fully developed length of concentration and temperature in the different porosities. As it is seen, the porosity increasing extends the combustion process forward and increases the concentration fully developed length. In the other word, combustion takes place in the greater part of the burner, so, the efficiency of the process increases. In addition, increasing of porosity increases the length of reaching to fully developed zone for temperature. In other words, in the low porosity, temperature is more uniform than in the high porosity. So, increasing the temperature increases the production of nitrogen oxides. Therefore, an average porosity should be considered for reducing CO and \(\text{NO}_x\) production, simultaneously.

CONCLUSIONS

In this paper, combustion of methane in porous burners is numerically studied. The finite volume method is used to investigate the variation of porosity effects on improving the combustion process and decreasing the production of CO and \(\text{NO}_x\). It is observed that flame temperature increases by increasing the porosity of the burner. Increasing the temperature of the burner decreases the production of CO and increases the production of \(\text{NO}_x\). So, the use of an intermediate porosity for minimizing the emission of pollutants seems reasonable.

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ABSTRACT

The CFD simulation of a proton exchange membrane (PEM) fuel cell has been carried out to investigate the effects of different parameters influencing cell performance. The model considers the mass and momentum transfer, charge conservation and electrochemical reactions in the presence of membrane and catalyst. The predicted polarization curve is in good agreement with the measured data in the range 0 - 1 A/cm². An increase in flow velocity from 0.1 to 0.5 m/s leads to a decrease in the optimum channel width from 0.8 to 0.6 mm. Also there is a sharp decrease in current density as the channel width increases above 0.8 mm at all flow velocities. The presented CFD approach can be used for determination of the optimum fluid velocity and channel geometry of a PEM fuel cell.

Keywords: PEM fuel cell, CFD simulation, channel width, current density.

INTRODUCTION

There has been a significant progress in the studies of the proton exchange membrane (PEM) fuel cell technology in the last decade. Despite great successes, the automotive application of PEM fuel cell (PEMFC) faces many technical challenges [1, 2]. A PEM fuel cell consists of three essential compartments: polymer electrolyte membrane, an anode and a cathode [3]. At the anode the hydrogen is oxidized into electrons and protons, while at the cathode, the oxygen is reduced [4]. The wet reactant gas transfers through the gas diffusion layer (GDL) into the catalyst layer where the electrochemical reactions take place [5]. Electrodes are considered as porous media where reactant gases are distributed on the catalyst layers [6]. The PEM fuel cell is a renewable energy source and is important because of factors such as low operating temperatures, modular structure, quick start-up time, high power density, corrosion resistance and environmental benefits. On the other hand, the fuel cells technologies are still more expensive than the conventional fossil fuel-based alternatives [7].

The flow field design and scale of a bipolar plate is one of the significant issues in PEM fuel cells [8]. Maharudrayya et al. studied the pressure drop and flow distribution in multiple parallel channel configurations, used in PEM fuel cell stacks [9]. Dutta et al. obtained velocity, density and pressure contours in the gas diffusion layers [10]. They used a finite volume technique for solving model equations. Their results showed that the current direction is drastically dependent on the mass transfer mechanism in the membrane-electrode assembly. Futerko and Hsing applied finite element method (FEM) for solving governing equations in the gas diffusion layers and flow channels [11]. They studied the resistance of membranes in polymer electrolyte fuel cells. Their modeling findings illustrated the conclusion that the mole fraction of reactant gases, water content in the membrane and current density are dependent on pressure. More recently, Rodatz et al. carried out studies on the operational aspects of a PEM fuel cell stack under practical conditions [12]. Their work focused exclu-
sively on the pressure drop, two-phase flow and effect of bends. They noticed a decrease in the pressure drops at a reduced stack current. Ahmed and Sung performed a numerical model to investigate the effects of channel geometrical configuration [13].

In this work, the effects of channel geometry and fluid velocity on the performance of a single PEM fuel cell with a straight channel at co-current flow conditions are evaluated and the optimal operating conditions at different flow conditions are investigated by CFD simulation. The schematic diagram of simulated PEM fuel cell comprising a cathode, an anode, gas diffusion layers, catalyst layers and a proton exchange membrane is shown in Fig. 1.

Proposed CFD Modeling

A 3-dimensional isothermal model is developed to account for the mass, momentum and species balances in the flow channels, GDL and the catalyst layers. Electrochemical reactions in the catalyst layer and GDL parts of the fuel cell and membrane are also considered in the proposed model. Model assumptions include steady state condition, laminar flow regime, ideal gas behavior, gas phase, fixed proton conductivity of membrane, isotropic gas diffusion layer, activation over potential is constant, the membrane is not permeable for reactant gases, isothermal operation. All governing equations are summarized as follows:

Continuity equation:
\[ \rho \nabla \cdot \bar{u} = Q_{br} \]  

Momentum balance equation:
\[ \nabla \cdot \left[ -p + \frac{\mu}{\varepsilon_p} \left( (\nabla \bar{u}) + (\nabla \bar{u})^T \right) - \frac{2\mu}{3\varepsilon_p} (\nabla \bar{u}) \right] - \frac{2\mu}{3\varepsilon_p} (\nabla \bar{u}) - (\frac{\mu}{k_{br}} + \frac{Q_{br}}{\varepsilon_p}) \bar{u} = 0 \]  

Mass transfer equation:
\[ \nabla \cdot (\sigma^e \nabla \phi_e) = \pm i_{r,tot} \]  

Charge conservation equation:
\[ \nabla \cdot (\sigma^e \nabla \phi_e) = \pm i_{r,tot} \]  

where \( Q_{br} \) is source term in the catalyst layer due to reaction of reactant species and can be calculated from the following equation:
\[ Q_{br} = \sum_m \sum_i R_{r,m} M_i \]  

\( R_{r,m} \) are the electrochemical reactions of hydrogen and oxygen and water:
\[ R_{r,m} = \frac{\nu_i m_i}{n_i F} \]  

The electrochemical reactions of the sink term for water, hydrogen and oxygen are shown in Table 1.

The diffusional mass flux vector is calculated from the equation:
\[ \bar{j}_i = -\left( \rho \omega_i \sum_k D_{ik} (\nabla x_k + \frac{1}{p_A} [(x_k - \omega_k) \nabla p_A]) \right) \]  

where \( D_{ik} \) is diffusivity of mixture that can be calculated using Maxwell-Stefan equations. The Maxwell-Stefan diffusion is a model for describing diffusion in multicomponent systems:
\[ D_{ik}^{eff} = \varepsilon^{1.5} D_{ik} \]  

Table 1. Electrochemical reactions of the sink term for water, hydrogen and oxygen.

<table>
<thead>
<tr>
<th></th>
<th>H_2O</th>
<th>H_2</th>
<th>O_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>i_{r}</td>
<td>\frac{i_{r}}{2F}</td>
<td>-\frac{i_{r}}{2F}</td>
<td>-\frac{i_{r}}{4F}</td>
</tr>
</tbody>
</table>
Within porous media, electrical conductivity of electrode and membrane are estimated from the modified Bruggemann equation:[14]

\[ \sigma_{e}^{\text{eff}} = \sigma_{e} \times \varepsilon_{e}^{1.5} \]  

(9)

The source term, \( i_{v,\text{total}} \) is given by:

\[ i_{v,\text{total}} = \sum_{m} a_{i_{\text{loc}}} \]  

(10)

The current densities, \( i_{\text{loc}} \) are calculated using the Butler-Volmer equation in anode and in cathode.

\[ i_{a} = i_{0,a} \left( \frac{Y_{H_{2}}}{Y_{H_{2}O}^{\text{ref}}} \right) \left( \exp \left( \frac{\alpha_{a,a} F \eta_{\text{act}}}{RT} \right) - \exp \left( \frac{\alpha_{a,a} F \eta_{\text{act}}}{RT} \right) \right) \]  

(11)

\[ i_{c} = i_{0,c} \left( \frac{Y_{O_{2}}}{Y_{O_{2}^{\text{ref}}}^{\text{ref}}} \right) \left( \exp \left( \frac{\alpha_{c,c} F \eta_{\text{act}}}{RT} \right) - \exp \left( \frac{\alpha_{c,c} F \eta_{\text{act}}}{RT} \right) \right) \]  

(12)

where \( i_{0,a} \) and \( i_{0,c} \) are the exchange current density of the anode and the cathode at a reference temperature (25°C) and pressure (1 atm), respectively. \( \alpha_{a,a} \) and \( \alpha_{a,c} \) are the anodic and the cathodic transfer coefficients for the reaction at the anode. \( \alpha_{c,a} \) and \( \alpha_{c,c} \) are the anodic and the cathodic transfer coefficients for the reaction at the cathode. \( Y_{H_{2}O}^{\text{ref}} \) and \( Y_{O_{2}}^{\text{ref}} \) are the mass fractions of hydrogen and oxygen at a reference temperature (25 °C) and pressure (1 atm), respectively. The values of the exchange current density and the transfer coefficients are listed from Siegel et al. [15]. R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), F is the Faraday constant (C mol⁻¹), and T is the temperature (K). The activation over potential, \( \eta \) is given by:

\[ \eta_{\text{act}} = \phi_{s} - \phi_{l} - E_{\text{eq}} \]  

(13)

The relevant numerical and geometric parameters for this study are shown in Table 2 and Table 3.

### RESULTS AND DISCUSSION

The simulation results are compared with experimental data [16] in Fig. 2. The predicted cell potential is in excellent agreement with the measured data in the wide current density range of 0 - 1 A/cm².

Fig. 3 shows the effect of the channel width on the current density at a constant channel length and different flow velocities. Depending on the flow velocity, there is an optimum channel width for which a maximum current density is obtained. An increase in the flow velocity from 0.1 to 0.5 m/s leads to a decrease in the optimum channel width from 0.8 to 0.6 mm. There is a sharp decrease in

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Table 2. Operating conditions of the simulated PEM fuel cell.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet anode/cathode temperature (°C)</td>
<td>80</td>
</tr>
<tr>
<td>Inlet anode/cathode pressure (atm)</td>
<td>3</td>
</tr>
<tr>
<td>Anode/cathode flow velocity (m/s)</td>
<td>2</td>
</tr>
<tr>
<td>Relative humidity of inlet gases (%)</td>
<td>100</td>
</tr>
<tr>
<td>Mole ratio of O₂/N₂</td>
<td>0.79/0.21</td>
</tr>
<tr>
<td>Mass fraction of H₂O (anode)</td>
<td>0.7</td>
</tr>
<tr>
<td>Mass fraction of H₂ (anode)</td>
<td>0.3</td>
</tr>
<tr>
<td>Mass fraction of H₂O (cathode)</td>
<td>0.14</td>
</tr>
<tr>
<td>Mass fraction of O₂ (cathode)</td>
<td>0.2</td>
</tr>
<tr>
<td>Mass fraction of N₂ (cathode)</td>
<td>0.66</td>
</tr>
<tr>
<td>Inlet O₂ concentration (kmol/m³)</td>
<td>0.00086</td>
</tr>
<tr>
<td>Inlet H₂ concentration (kmol/m³)</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Table 3. Geometric parameters of the simulated fuel cell.

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel length, mm</td>
<td>120</td>
</tr>
<tr>
<td>Channel width, mm</td>
<td>1.0</td>
</tr>
<tr>
<td>Channel depth, mm</td>
<td>1.2</td>
</tr>
<tr>
<td>Membrane thickness, mm</td>
<td>0.036</td>
</tr>
<tr>
<td>Catalyst layer thickness, mm</td>
<td>0.012</td>
</tr>
<tr>
<td>Electrode thickness, mm</td>
<td>0.21</td>
</tr>
</tbody>
</table>
current density as the channel width increases above 0.8 mm at all flow velocities, shown in Fig. 3.

Fig. 4 shows the effect of channel depth on the current density at a constant channel length and different flow velocities. The numerical results confirm that the current density increases as the channel depth is increased at a constant flow velocity. Comparison of Figs. 3 and 4 suggests that regardless of channel width or depth, there is not a significant change in the current density at flow velocities higher than 0.2 m/s, which is quite interesting from engineering viewpoint.

For a cell potential of 0.6 V, the profile of the hydrogen mole fraction at the anode channel and gas diffusion layer at the different flow velocities, is shown in Fig. 5. This figure testifies that the hydrogen mole fraction at the anode side decreases gradually from inlet to outlet of the channel due to the consumption of hydrogen at the anode catalyst layer. As the mole fraction of hydrogen in the gas diffusion layer decreases, the strong oxidation of hydrogen can be seen. Fig. 5 a,b shows that the
average outlet mole fraction of $H_2$ increases, as the flow velocity is increased.

Fig. 6 displays the effect of channel width on the average outlet mole fraction of $H_2$ at a constant channel length for different flow velocities. The predicted results confirm that the average outlet mole fraction $H_2$ is increased, as the channel width is increased at the different flow velocities. As observed, the maximum hydrogen consumption takes place at flow velocity of 0.1 m/s. At flow velocities higher than 0.2 m/s, there is no significant change in the hydrogen mole fraction at the cell outlet.

Fig. 7 displays the effect of channel depth on the average outlet mole fraction of $H_2$ at a constant channel length for different flow velocities. The numerical results confirm that the average outlet mole fraction $H_2$ increases as the channel width is increased at the different flow velocities. As shown, the maximum hydrogen consumption takes place at a flow velocity as low as 0.1 m/s similar to what is observed in Fig. 6.

Fig. 8 compares the effect of channel depth and channel width at a fixed flow velocity of 0.1 m/s. As shown, the channel width is more effective than the channel depth, regarding the mole fraction of hydrogen at the channel outlet.

Fig. 9 displays the effect of channel width on the average outlet mole fraction of $O_2$ at a constant channel length and a constant channel depth at different flow velocities. The predicted results confirm that the average outlet mole fraction of $O_2$ increases as the channel width is increased at different flow velocities.

Fig. 10 shows the effect of channel depth on the average outlet mole fraction of $O_2$ at a constant channel length and a constant channel width, at different flow velocities. The predicted results confirm that the average outlet mole fraction of $O_2$ increases as the channel depth is increased at the different flow velocities.

Fig. 11 shows the relationship between the average outlet mole fraction of $H_2$ and the inlet fluid velocity at a cell potential of 0.6 V. It is clearly seen that an
increase in the inlet fluid velocity leads to an increase in the average outlet mole fraction of H₂. It should be noted that an increase in inlet fluid velocity causes significant hydrogen loss at the channel outlet of PEM fuel cell. The presented CFD approach can be used for determination of the optimum fluid velocity and channel geometry of a PEM fuel cell. As shown in Fig. 12, an increase in flow velocity from 0.1 to 0.5 m/s leads to a considerable increase in the current density. However, an increased flow velocity from 0.1 to 0.5 m/s leads to a significant increase in the mole fraction of H₂ at the cell outlet according to Fig. 11. Therefore, the optimum design of the PEM fuel cell can be established by the proposed CFD model.

CONCLUSIONS

A 3-dimensional CFD simulation of a PEM fuel cell according to a rigorous finite element numerical method is presented. The simulation is conducted to investigate the effect of channel geometry and fluid velocity on the performance of a PEM fuel cell. The predicted polarization curve is in good agreement with the measured data in the range 0 - 1 A/cm². An increase in flow velocity from 0.1 to 0.5 m/s leads to a considerable increase in the current density. However, an increased flow velocity from 0.1 to 0.5 m/s leads to a significant increase in the mole fraction of H₂ at the cell outlet. It is found that the channel width is more effective than the channel depth, regarding the mole fraction of hydrogen at the channel outlet. It is shown that depending on the flow velocity, there is an optimum channel width for which a maximum current density is obtained. The optimum design of the PEM fuel cell can be determined by using the proposed CFD model and economic considerations.

REFERENCES

DECISION MAKING FOR CONTROL OF COMBUSTION PROCESS OF PULVERIZED COAL

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ABSTRACT

A method and system for decision making and control (DMC) of combustion process of pulverizing fuel-air mixture in large multiburner furnace is proposed. Due to the lack of necessary information inference measurements are created on the basis on the first principle CFD model of the combustion process and a sequential image processing. Decision making procedure is based on Case Based Reasoning and Rule Based Reasoning which contains some elements of knowledge, acquired via a long time operator experience and off-line simulations on the CFD – model. Combination of off-line and on-line procedures is accepted in to two stage algorithm of DMC which improves the efficiency and safety of combustion process.

Keywords: Case Based Reasoning (CBR), combustion process, control, decision making, inference measurement, Rule Based Reasoning (RBR).

INTRODUCTION

The combustion process (CP) is still important for a great number of plants in chemical, metallurgical and power industries. Despite of the large volume of long standing investigations, the control of the CP, especially in a big size combustion chamber with a multiburner systems, continues to be at least in part the problem of operator skill. The main reason is a lack of relevant information for main characteristics of the turbulent flame. To cope with this obstacle into the last decade a lot of methods for flame measurement appear – laser, fiber-optical, video-camera, spectroscopical, colour-based [1]. This methods have a promising potential, but nowadays they are with limited commercial success because are costly, unreliable and with problematic maintenance in hard industrial conditions [1, 2].

In parallel a very extensive development of inference methods for measurement, monitoring, decision making and control, can be observed [3-5]. They are considered as an alternative or compliment solution in reengineering initiative [6]. In the present paper a new approach is presented for decision making for improvement of combustion process based on softsensing and inference control [3, 5, 7]. A novel hybrid system is proposed based on mathematical modeling, image processing and incorporating some intelligent techniques containing knowledge elements – Case Based Reasoning (CBR) and Rule Based Reasoning (RBR) [8 - 11].

As a case study, a typical plant is chosen for decision making and control of combustion process of pulverized fuel-air mixture with direct feeding. The technological and economical considerations are combined with the \( NO_x \) minimization in flue gases.
STEAM BOILER PROPERTIES

A typical scheme of a steam drum-type boiler plant with mill-fans based pulverization system is shown in Fig. 1. The combustion process is carried out in furnace 1, where through a system of main (12) and auxiliary (13) burners a mixture of pulverized coal, air (primary and secondary) and flue gases is fed. The pulverization system comprises a mill-fan (8), electro-drive (9), inertial separator (10) and dust concentrator (11). The raw coal from the bunker 3 through the feeder 4 is directed toward the drying shaft 5, where it is mixed with flue gases intaked from the top of the furnace via the duct 2. The furnace crosssection (Fig 1b) shows the placement of 8 mill-fans (A-H) with tangential organization of the combustion via central vortex.

The direct firing pulverizing system is a source for a lot of difficulties [1, 2, 4, 6]:

- The flame stability depends on the combination of many factors: mill-fans load, their technical condition, fuel/air flow ratio;
- Big number of disturbances such as changeable heating value of the coal, nonregular work of the row coal feeder, strongly variable temperature of the drying
flue gases;
  - Risk of fire in the air-fuel mixture;
  - Problems with overloading and underloading of the mill fans;
  - Relatively short operational life of the mill-fans (less than 2000 h);
  - The conventional measurements in pulverizing system are very poor. A large number of key variables are unmeasurable: fineness of the dust, flow rate of the air-fuel mixture, degree of the separator recirculation, flow rate of the additional cold air and hot air, moisture of the pulverized coal.

The number of control variables, only the throughput capacity of the fuel and secondary air, is very limited.

The pulverization system plays the main role in organization and maintaining the combustion process. Existing conventional monitoring and control systems are not able to cope with the listed above circumstance in order to ensure the flame stability, safety and effectiveness of the combustion process.

PROBLEM STATEMENT

The objective of the considered problem is to propose a relevant procedure for Decision Making (DM) and control of dust-air mixture combustion process into a multiburner furnace in order to satisfy the next multicriteria requirements:

\[ J = < J_1, J_2, J_3, J_4, J_5 > - \text{extr} \quad (1) \]

where \( J \) are partial criteria as follows:
- \( J_1 \) - Efficiency of the combustion process maximization getting up by:
  - Fuel/air ratio optimization,
  - Radiation/Convection heat balancing,
  - Fowling minimization;
- \( J_2 \) - \( NO_x \) concentration in flue gases restriction;
- \( J_3 \) - Minimization the risk of abnormal conditions owing to:
  - Slagging,
  - Flame unstability (e.g. Lost Of Ignition - LOI),
  - Local overheating of constructive elements (e.g. arousing the water tube ruptures),
  - Overloading or underloading of mill-fans,
- \( J_4 \) - Minimization of off/on and over switching of MF;
- \( J_5 \) - Minimization of Kindle Oil Burner (KDB) switches on/off.

The problem can be solved via combination of quantitative approaches (formal methods, CBR, RBR) and qualitative ones (operator expertise).

MATHEMATICAL MODELING OF THE COMBUSTION PROCESS

In this work a first principal \( k - \varepsilon \) model of the combustion process is accepted. Following [12], the CFD model could be presented in the next generalized form:

\[
\frac{\partial}{\partial x_i}(\rho u_i \varphi) = \frac{\partial}{\partial x_i} \left( \Gamma_{\varphi} \frac{\partial \varphi}{\partial x_i} \right) + S_\varphi + S_{\rho \varphi} \quad (2)
\]

where \( x_i \) is a direction of Cartesian coordinate system and \( i = 1, 2, 3 \) for 3D space, \( u_i \) are the velocity components in \( x_i \) direction; \( \varphi \) is a generalized variable, which represents all main components of the thermodynamical state of the system – velocity, \( k - \varepsilon \) characteristics, fraction contents, entalphy (temperature) and masses; \( \Gamma_{\varphi} \) is a generalized transfer index, corresponding to each particular acceptation of \( \varphi \), \( S_\varphi \) and \( S_{\rho \varphi} \) are generalized sources terms for a gas and particle phases.

More detailed description of this CFD model can be found in [12].

The next values for each discrete element of the mesh are determined: the trajectories of the dust particles; the heat received from dust particles combustion; temperature of the gas and coal particles; density of gas-fuel mixture; sequential velocities of the gas and dust correction in dependence on the temperature and density in the mesh.

The input conditions for the model are: power unit load \( N, \text{MW} \); total throughput capacity of the coal \( B_t, \text{t h}^{-1} \); working lower heating value of the coal \( Q^L_{l}, \text{kJ kg}^{-1} \); concentration of oxygen in flue gases \( O_2 \), \%; efficiency of the boiler \( \eta_b \), \%; Temperature of the cold air \( \theta_m, ^\circ C \); temperature of the hot secondary air \( \theta_H, ^\circ C \); temperature of the flue gases at the end of furnace \( \theta_g, ^\circ C \); working moisture of the coal \( W, \% \); working mass of the ash in coal \( A_w, \% \); theoretical volume of air for combustion \( V_0, m^3 \text{kg}^{-1} \); portion of regularly
blowed air $g$, %.

In order to adapt the model parameters, the relevant constructive data are used for combustion chamber, burners, mill-fans, inertial separators, etc.

Model tuning is carried out via iterative correction of model parameters (Fig. 2), using data from number of direct measurements, arranged in the following vectors:

\[
Y_1 = \left( N, B_1, B_2, V_{ac}, \theta_{ac}, V_{ah}, \theta_{ah}, O_2 \right)
\]

\[
Y_2' = \left( Q_L', \eta_B', W^w, A^w, g \right)
\]

\[
Y_3' = \left( \theta_{v'}, \theta_{gr}', V_0' \right)
\]

\[
Z_1 = \left( \theta_{afi}, \theta_{gi}, \theta_{sh}, D_{sh}, H_f \right)
\]

The data for the temperature of intake drying gases $\theta_{gs}$ must be filtered because of significant measurements errors due to fouling, slagging, aerodynamic shadows. This can be seen from the experimental data given in Table 1.

### INPUT DATA PROVIDING

Three types of input data for considered above first principle CFD model to compute the temperature, velocity and concentration fields of combustion process, are used:

From direct measurements: $\theta_{afi}, \theta_{gi}, O_2, \theta_{ac},$

<table>
<thead>
<tr>
<th>Experiment No</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>772</td>
<td>875</td>
<td>929</td>
<td>876</td>
<td>851</td>
<td>-</td>
<td>916</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>915</td>
<td>-</td>
<td>930</td>
<td>936</td>
<td>814</td>
<td>-</td>
<td>931</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>-</td>
<td>953</td>
<td>923</td>
<td>871</td>
<td>872</td>
<td>877</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>932</td>
<td>921</td>
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<tr>
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<td>854</td>
<td>-</td>
<td>932</td>
<td>868</td>
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<td>841</td>
<td>871</td>
<td>-</td>
<td>824</td>
<td>662</td>
<td>-</td>
<td>734</td>
<td>840</td>
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<tr>
<td>8</td>
<td>794</td>
<td>885</td>
<td>-</td>
<td>845</td>
<td>634</td>
<td>-</td>
<td>738</td>
<td>861</td>
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<tr>
<td>9</td>
<td>792</td>
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<td>-</td>
<td>693</td>
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<td>978</td>
<td>906</td>
<td>886</td>
<td>812</td>
<td>1009</td>
<td>-</td>
<td>920</td>
<td>-</td>
</tr>
</tbody>
</table>
From indirect measurements - \( f, \alpha, \eta, B, V, AV, shG (i=1,8) \)

From inference measurements:

a. Based on information from direct and indirect measurements: \( \eta_B, Q_L^w, W^w, A^w, A^d \);

b. Based on established design models \[13\]: \( V_0, \theta_g, \theta_gf \).

Here some of the inference measured values are considered, which contain new authors results.

Efficiency of the boiler can be found using two different ways \[4,13\]:

Direct balance method

\[
\eta Q_L^w = \frac{A}{B}, \quad A = \sum D_j \Delta i_j \tag{4}
\]

where \( D_j \) - output steam flow rates, \( \Delta i_j \) - corresponding enthalpies differences.

Indirect (inverse) balance method

\[
\eta_{IN} = 1 - \frac{1}{6} \sum_{i=2}^{6} q_i \tag{5}
\]

where \( q_i (i=2,6) \) are respectively the relative heat losses with: waste gases, incomplete combustion, unburned carbon to surrounding, and with physical heat of slag.

The heat balance can be presented additionally in the next form:

\[
\eta Q_L^w = \frac{qN}{B} = \frac{q}{F} \quad \text{where} \quad F = \frac{B}{N} \tag{6}
\]

where \( N \) is the current electrical power load, \( q \) - function, which was derived using experimental data. It is presented in Fig. 3.

According to eq. (4) and eq. (6) we have two relationships for the working lower heating value of fuel \( W_L^w \). As the right sides of the eqs. (4) and (6) are known, and \( \eta_{IN} \) is defined from eq. (5), \( Q_L^w \) can be derived using the equation:

\[
\hat{Q}_L^w (k) = \beta Q_L^w (k) + (1 - \beta) Q_{L_{FB}} (k) \tag{7}
\]

where \( \beta \) is weighting coefficient.

The relationship between the coal moisture \( W^w \) and the ash content \( A^w \) have been found in the form

\[
W^w + A^w = 94,2 - 0,0139 \hat{Q}_L^w \tag{8}
\]

The values of \( V_0, \theta_g, \theta_gf \), which are of critical importance for the developed model parameters tuning, are derived following the recommendations in \[13\].

**SIMULATION RESULTS**

The established methods for combustion chamber design \[e.g. 13\] are based on using averaged values of temperatures in each cross section of the furnace. This design patterns do not give any data for the spatial displacement of the flame, no thermograms in zones of interests or hydrodynamic characteristics of the combustion process. As it was discussed above, the problem of local information of flow, temperature and concentration fields are very important for avoiding unadmissible situations via proper control of the combustion process.

Realistic scenarios have been accepted to cover the representative operational situations with enough density. In order to obtain more detailed maps of the main characteristics of the combustion process a lot of simulation results using this different working structures, load, technical conditions and values of input variables have been received. As an illustration some of them are shown in Figs. 4-7. They are in accordance with Fig. 4, showing the horizontal and vertical cross-sections.

Some conclusions can be made from the analysis of the simulation results:

- The temperature and concentration fields are strongly nonregular, nonhomogeneous and with a lot of local peculiarities.
- The velocity field is more regular, but the corresponding maps are less informative than the temperature
Fig. 4. A scheme of horizontal (a) and vertical (b) cross-sections.

Fig. 5. Cross-section of the furnace at the burner level.

Fig. 6. Cross-section of the furnace at the top of the combustion chamber.

Fig. 7. Vertical cross-section distribution of the flame.
Kosta Boshnakov, Venko Petkov, Metodi Nikolov

distribution.

- Nonregularities of the temperature field exist both in radial and axial direction.
- The concentration fields are closely correlated with the temperature field.

All simulation results show that the digital model is very complex and can not be directly used for decision making and control.

The calculation time for each scenario is too long in comparison with the combustion time of a separate particle (3 - 4 s). Thus only after some kind of approximation of the obtained 3D fields they can be acceptable for on-line implementation.

Image processing should be applied for appropriate features selection.

PROCEDURES PROVIDING COMPONENTS FOR DECISION MAKING AND CONTROL

Feature selection

Nowadays the image processing [1, 2] allows the problem of feature selection from sophisticated images to be solved successfully. In our study it is addressed in three most important cross-sections:

Horizontal cross-sections at the burner’s level

The next features are selected in order to form the attributes for CBR:

- Deriving the center of combustion vortex from velocity distribution (Fig. 5a),
- Determination the degree of cross-section filing by flame using the isoterms (Fig. 5b),
- Average temperature at the burner level,
- Estimation of the local burner stream flame length for each working burner.

b. Horizontal cross-sections at the top of the furnace

- Deriving the center of the vortex,
- Defining the zones with highest temperatures lean against the water tube walls,
- Determination the local average gas temperatures into the inputs of intake drying shafts,
- Average temperature of the flame at this level,
- Finding the zones with the maximal temperatures,
- Extraction the isotherms with temperature > 1000°C.

c. Vertical cross-sections at the axis with the highest temperature in the top of the furnace

- Defining the place of the maximum temperature in axial direction,
- Estimation of the equivalent diameter of the fireball.

Case base for CBR formation

CBR is promising approach for reasoning on the base of analogy [8 - 10]. In this study the cases are presented in established “problem (P) solution (S)” form:

\[ C = \langle P, S \rangle \]  

Here \( P \) is accepted to be considered as a “situation” in a form

\[ P = \langle I, F, T \rangle \]  

where \( I \) is the vector of input information, \( F \) is the vector of the selected features from the image processing, \( T \) is the vector of given thresholds as requirements. Each of vectors \( I, F, T \) contains number of relevant attributes.

\( S \) is solution for MF control actions and is presented as follow:

\[ S = \langle B, V_{ac}, V_{ah}, V_{at}, T_s \rangle \]  

where \( B, V_{ac}, V_{ah} \) are the vectors of the throughput capacity of the fuel, flow rate of the cold and hot air, respectively. \( V_{at} \) is the total combustion air flow rate, \( T_s \) is the vector of the thresholds.

As in this study a two stage procedure for DMC is proposed, two corresponding case bases have been formed - simplified \( C_s( P_s, S_s ) \) and full \( C_f( P_f, S_f ) \).

Rule base for RBR formation

On the base on a long time of operational experience, existing technical instructions, and supplier’s requirements a set of particular \( RB_i \) have been derived. A small part of them is presented in Tables 2, 3 and 4.

Decision making approach

The basic acceptance in DM approach in this study are:

- CBR is used in two different variants - simplified and full;
- CB is used to create CBR local regressions corresponding to the \( kNN_i \) area of interest [8],
- Simplified procedure at the first stage of DM
allows a faster retrieval. It is concentrated mainly on the most important aspect of the combustion process – availability ($J_3$).

* At the second stage of DM, partial criteria $J_3, J_4, J_5$ can be accepted as constraints.
* To faster the calculations for an optimal distribution of the coal $B_i$ and cold air $V_{aci}$ between $MF$, the changes of control variables are carried out by actions over the opposite pairs of burners.

**Software tools**

The established tools for CBR, myCBR and jColibry, have been used in accordance with the earlier accepted adaptation and modification [9, 11].

## A SYSTEM FOR DECISION MAKING AND CONTROL (DMC) OF COMBUSTION PROCESS

An iterative two level system for DMC is proposed (Fig. 8). At the first level $L_1$ (left side of the scheme) the preliminary recommendations are deduced for:

- Current structure of the pulverizing system (number and indexing of the proposed for running mill-fans (MFs), state of the Kindl Oil burners (KOB);
Fig. 8. A system for decision making and control (DMC).
b. Distribution of coal $B$ and cold air $V_{ac}$ for each $i$ - indexed MF. To define these recommendations the subsistem $L_1$ uses an information from direct, indirect and inference measurements. After retrieval of $k$-nearest neighbours ($KNN_{i1}$) and adaptation according $R^4$ cycle for CBR [8 - 10], a primary optimal ($B, V_{ac}$), distribution is carried out. Because the initial retrieved case is changed, an iterative procedure is started via $KNN_{i2}$ retrieval. When the requirements for level $L_i$ are covered, these recommendations are sent via logical block $LB_{21}$ toward the functional level $L_2$ (right side of Fig. 8). As the case base $CB_x$ addressed to the level $L_2$ contains more attributes in comparison with $CB_y$ a new retrieval $KNN_y$ is fulfilled. A comparison of both values $C_{12}$ and $C_{21}$ directs the procedure to be executed in $MF_i$, or to continue the improvement of the preliminary recommendation given from the first level $L_j$.

The proposed decision making and control system (DMC) is situation based. It adapts the pulverizing system toward the new conditions. In a relatively simple way the proposed system can maintains the thermal fireball in the center of the combustion chamber and will improve the efficiency of the whole combustion process accordingly the accepted multicriteria $J (1)$ as well.

CONCLUSIONS

A new method is proposed for a real time decision making and control of flame position and combustion process improvement. Inference measurements are developed to add the lack values on the base of the conventional measurements. A hybrid system for decision making and control, based on first principle model of the combustion process, image processing, and building blocks containing knowledge elements - Case Based Reasoning and Rule Base Reasoning is considered. Experimental data from a multiburner combustion process are used to tune mathematical model and to acquire relevant production rules. The proposed hybrid system contains promising potential to assist the operators with different level of expertise to adjust the combustion process.

REFERENCES

ABSTRACT

The current oscillatory behavior of epoxy-coated low carbon steel at anodic polarization was investigated in 3.5% and 0.5% solutions of NaCl. It was established, that the coated steel may show current oscillations at potentiostatic anodic polarization. The oscillations are of different type, period and amplitude and are more clearly expressed in 0.5% solution. The presented results might be used in the field of electrochemistry, electronics and electrical engineering as well as in the field of oscillatory systems study.

Keywords: current oscillations, oscillatory systems, epoxy-coated steel, corrosion.

INTRODUCTION

Electrochemical systems are complicated dynamic systems, determined by plenty of non-linear mechanisms. Oscillations of the current or potential can be observed in many systems and the investigation of these complex dynamic behaviors today became a new branch of the modern electrochemistry.

The presence of oscillations in some electrochemical systems can be explained by coupling of chemical reactions and transport processes in multicomponent systems. While chemical reactions are time-dependent, the transport processes are related to change in location. By coupling of chemical reactions and surface diffusion chemical waves can be developed, which can create geometrical patterns (motifs) on the electrode surface, to induce mechanical stresses and convection and create periodical oscillations in time and space [1].

Many years ago a guess was made about a phenom-enological resemblance between electrophysiological and electrochemical oscillators and it was assumed that these two classes of nonlinear systems have a kinetic analogy in their behavior [2]. A hypothesis was proposed, that the instability as a result of coupling between the chemical reaction and diffusion could have an important role in the first biogenetic step. Studying the electrochemical oscillation systems, their coupling and network formation it would be possible to create a model about neurophysiologic networks and, in future, artificial neurons for the needs of robotics.

The study of oscillators will serve for understanding of highly organized molecular systems such as living bodies, and for understanding of mechanisms of the electrochemical reactions themselves as well. Therefore, the investigation of the electrochemical oscillatory systems, i.e. knowing of the conditions and factors, related to their oscillatory behavior and the type of the oscillations, as well as the reasons for this behavior, is very important in the investigation of the electrochemical networks.

Oscillations in current and potential in the electrochemical systems have been observed and studied for a long time [1]. Nowadays it is assumed, that they are due to the cycling forming and dissolution of the passivating layers (oxide, hydroxide or salt) or porous film. Oscil-
lations are observed on the iron and cobalt electrodes in water solutions, containing aggressive ions; on Zn electrode at cathodic and anodic polarization; stainless steel in sulfuric acid solutions with chromic acid [3]. The onset of complex oscillations is explained by the development of pitting corrosion on the passive iron surface; pure iron and steel undergo a destruction of the passive state in neutral and alcaline solutions of NaCl [4 - 7]. The current oscillations are accompanied by a cyclic increase and a decrease in the amount of SiO$_2$ covering the Si surface.

Recently, the classification of the electrochemical oscillators was vastly expanded and it is no limited only to the passivity phenomenon. In this category are included also: potential- depended adsorbtion of inhibitors; potential- depended desorption by the addition of halogenides (Cl, Br, I) or halogenide-like ions (e.g. SCN$-$); electrostatic effect at low ionic strength of the solution; electrodissolution of metals; electrodeposition of alloys; oscillatory behaviour in the oxidation of organic fuels; anodic oxidation of small organic molecules and hydrogen etc.

Electrochemical processes are based on the interaction of chemical reactions, flow of reactant and products, and electrical effects. Because of the complex nature of the interactions many industrial applications require characterization of the electrochemical properties in the space and time [8]. For example, in the fuel cells, the interaction of current-generating chemical reactions with the fuel flow and external load on the multi-electrodes can produce complex responses; a proton exchange membrane fuel cell exhibits larger power in the oscillatory state than in the corresponding stationary state [8], etc.

Usually, the electronic equipment and components are packed with polymers in order to be protected against mechanical and chemical damages, as well as against pollutions. Moreover, some of them need to be protected against electrostatic discharge or electromagnetic influence. However, all polymers are permeable to moisture. In the most metallic systems, protected by organic coatings, the absolute performance depends not so much on the quality of the coating but more on the response of the coating to defects that are either initially present or that arise in the course of service. Hence, the coating’s properties will have a direct influence on the device behavior [9, 10].

Studying the protective action against corrosion of the epoxy-coated steel with different content of quartz particles [11], it has been observed, that this system has an oscillatory properties at some conditions. In previous work [12] the influence of quartz particles in the coating on the oscillatory behavior of the system was examined. It would be interesting to investigate the behavior of the epoxy-coating, without quartz, as it would have wider application in the technics. For example the epoxy-resins are used widely in the electrical engineering as bonding compounds and as isolating and anticorrosion coatings [13]. This study would be interesting also from the point of view of a new oscillatory system, as up to now data about oscillators conductor- dielectric was not reported.

This paper presents the results of investigation of the oscillatory behavior of epoxy-coated steel in NaCl solutions during anodic polarization.

EXPERIMENTAL

The composition, the treatment of the steel specimens and samples preparation are described in details in [11]. The average dry thickness of the epoxy coating is about 150 $\mu$m.

The electrochemical measurements were performed using a potentiostat Princeton Applied Research (PAR), model 263A using the SoftCorr program. A cell for flat specimens (PAR) with a conventional three electrode arrangement was used. Saturated calomel electrode was used as a reference electrode, platinum mesh - as a counter and coated steel - as working electrode with exposed area 1 cm$^2$. All experiments were performed within the first few hours of immersion in a solution of NaCl with concentration of 3,5 % and 0,5 %. The potentiodynamic polarization curves with low sweep rate 1 mV/s were performed in order to give the possibility to any surface reaction to take place.

The polarizations curves are related to charge-transfer reaction of steel surface, exposed in coating. In the case of coatings the polarization curves are more complicated, compared to these ones for metals, because they contain data not only for exposed steel but also for the bulk electrolyte resistance and the ionic resistance in the coating pores and defects. This ohmic drop can mask the answer of the metal substrate. The major problem with the use of polarization curves to characterize coatings is that a moderate amount of damage is induced
to the coating and coating/metal interface, especially in cathodic polarization, so this surface cannot be used for further study. There are only some cases for anodic polarization curves (which are our object) with polarization in very small potential range [14].

As the task of this work is to study the instability and oscillatory behavior of the system and not to estimate corrosion behavior of the coatings, correction of this curves is not necessary and calculation of corrosion parameters will not be presented here. For the needs of present work a comparison of the form and stability of curves is more important and will be presented and discussed. Obtaining the results about the eventually destroying or growing the defects of the coating during anodic polarization would give important information concerning the behavior of the coating under constant electrical tension.

RESULTS AND DISCUSSIONS

Polarization curves

Figs. 1 and 2 show the polarization curves for epoxy coated steel in 3.5 % NaCl and 0.5 % NaCl, respectively, for different time of immersion in solution.

In 3.5 % NaCl the corrosion potential and current are changed considerably during one hour, the current grows about twice and the potential shifts in negative direction. The curves for one and three hours contact of the samples with the solution are almost the same. The anodic branch of the curves at Fig.1 has not any peculiarity and only for one hour contact with the solution has a fluctuation at 0.2 V.

Usually new epoxy-coated steel with no any defects and good barrier properties shows in the first days a positive potential. In the studied system, the starting corrosion potential of the coated metal is about 300 mV more positive compared to this one of the pure steel and in the first 1 - 2 hours is getting close to the potential of the pure steel, in particular for the 3.5 % solution [12]. According to Leidheiser [15] the potential decrease in the beginning (i.e. the shifting of the potential in negative direction) of the epoxy-coated conventional low-carbon steel can be related to the entering of the moisture to the steel/coating boundary, followed by a chemical rearrangement in the border metal/oxide [15]. The fact, that the curves for one and three hours contact in solution, are almost the same (Fig.1) shows, that the processes of water penetration in the coating and the corrosion of steel surface become stable in one hour. This statement is confirmed from the dependence of the corrosion potential on time [12].

The anodic dissolution of iron in concentrated solutions of NaCl and FeCl₂ was studied in [4]. It was shown the formation of anodic film, induced by the precipitation of ferrous chloride on the electrode surface and the initiation of the film formation requires a supersaturation [4]. The iron corrosion is initiated by pits and spreads out in the form of corrosion product layers, one of which is poorly adherent. Concerning these immersion times, it was shown that the role of the occluded pits is negligible by comparison with the porous film effect. At the corrosion potential two diffusion processes are detected: the diffusion across the layer and the mass transport in the liquid phase. The degree of coupling between the two processes is dependent on the immersion time and the rotation rate [6]. The oxygen transport is produced not only in the liquid phase but also through porous layer of the corrosion products. The oxygen consumption

Fig. 1. Potentiodynamic polarization curves for epoxy-coated steel after 15 min (1), 1 h (2) and 3 h (3) contact in 3.5 % NaCl.

Fig. 2. Potentiodynamic polarization curves for epoxy-coated steel after 15 min (1) and 1 h (2) contact in 0.5 % NaCl.
occurs not only by electrochemical reduction but also by chemical oxidation of ferrous to ferric ions [7].

In 0.5 % NaCl solution (Fig. 2) the corrosion potential stays the same and the corrosion current grows slowly (compared to 3.5 % NaCl) with time after 1 hour immersion in the solution. As all other conditions are the same, such difference in the corrosion parameters for both concentrations might be related to the difference in the concentration of the two solutions and especially to the amount of the chloride ions and their influence on the corrosion parameters and behavior of the steel. The anodic polarization diagrams in 0.5 % solution clearly show fluctuations after an hour in the solution, which suggest oscillation behavior of the current at potentiostatic conditions.

Potentiostatic measurements

The potentiostatic measurements were conducted at each 100 mV in anodic direction, starting from the corrosion potential, according to the polarization curve. Some of the results are presented on Figs. 3 and 4. It can be seen, that at some conditions (depending on the defects, pores, solution concentration, etc.) the system shows periodical current oscillations at potentiostatic conditions at anodic potentials.

Current oscillations are seen in 3.5% solutions even without indications on the polarization curves (Fig.3, at 0.2 V). In 0.5 % solutions (Fig. 4) in the anodic range of potentials, at potentiostatic conditions, the current shows periodic oscillations with the time. The oscillations are of mixed type and are different in form, amplitude and period. At a given potential they change the amplitude while at the others they are stable. As the potential shifts in positive direction, the form and the period of the oscillations are changed, which indicates a strong dependence of the processes, provoking them, on the potential.

The instability on the anodic polarization curve and oscillations shows a presence of defects or pores in the coating, allowing the electrolyte to reach the steel surface. The appearance of the oscillations after an hour contact with the solutions shows the necessity of time for the processes, which provoke them.

It is known, that after the immersion of the coated metal in the solution, the water is the first one, which enter in the volume of the coating, before the ions of the electrolyte [16]. Therefore, at the very beginning of the corrosion process on the steel the chloride ions are absent. The presence of oscillation after an hour, their change with the potential growth, as well as the dependence on the solution concentration might be explained with the entering of chloride ions and a relation between the oscillations and the chloride ions content in the coating. The stabilization of the oscillations by amplitude and decrease of the period with the potential increase shows a strong influence of the electrical field on the rate of migration of the negative chloride ions in the coating and their influence on processes on the steel surface. The change in the character of the oscillations at very positive potentials may be related also with additional processes of anodic oxidation not only of the metal surface, but also of the components of the electrolyte.

In support of the assumption about the relation between the oscillations and the concentration of the chloride ions probably comes the results, published in [17, 18]. The authors found a close relation between the concentration of the chloride iron on the electrode surface at passive conditions and the form, frequency
and the amplitude of the oscillations. It is suggested, that the chloride ions do not enter in the passive film, without an availability of a sufficient driving force as a result of concentration gradient of the chloride ions on the surface. At a sufficiently high concentration gradient only a part of these ions enters in the passive film and produce destruction of the film [17, 18].

Li et al. [23] investigate the oscillatory electrodissolution of iron in neutral solutions of NaCl. They suppose a presence of inner non-pore layer and external pore salt film, formed on the electrode surface during the oscillatory processes. The oscillations with high frequency and small amplitude may be related to formation and dissolution of the inner layer and those with low frequency and large amplitude to the growth and removal of the outer porous salt film [23].

The oscillatory electrodissolution of the metal materials is a result of a complicated process, including surface reactions, film formation and dissolution and mass transfer.

In the case of organic coatings these reactions are getting more complicated because of difficulties in the diffusion of the reagents or products through the pores and defects in the coating and require further extensive research.
CONCLUSIONS

Epoxy-coated low carbon steel may exhibit current oscillations at potentiostatic anodic polarization in NaCl solutions. The oscillations are of different type, period and amplitude and are clearly expressed in the 0.5% solution.

An important result in this research is the possibility an epoxy coating to show an oscillatory behavior, which is very important for the needs of electrochemical, electronic and electrical technologies. The reasons for the oscillatory behavior are complex and require further extensive research.

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REFERENCES

A STUDY ON THE KINETICS OF THE ELECTRODEPOSITION OF Ni, Co AND Ni-Co ALLOY IN CITRATE ELECTROLYTE
PART 1. THE KINETIC STUDY
OF THE INDEPENDENT ELECTRODEPOSITION OF Ni AND Co

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ABSTRACT

The electrodeposition of Ni and Co was studied by electrochemical techniques in varying compositions of slightly acidic citrate electrolyte. Cyclic voltammetry and current transient measurements were used to characterize the initial stages of nucleation, growth mechanism and electrodeposition of Ni and Co. The voltammetry analysis showed that the electrodeposition of both Ni and Co occurs under diffusion-kinetic control associated with a typical nucleation process. The deposition of Ni is in one act of charge transfer with exchange of two electrons, the deposition of Co is a two-stage process of reduction of free cobalt ions to cobalt, and reduction of complex ions type CoCit\(^{-}\) to cobalt. The application of the method of chronoammetry proved that for cobalt the mechanism of nucleation is spontaneous, with three-dimensional nucleation and nuclei growth, while for nickel the slower progressive mechanism of nucleation is typical. The differences in the deposition mechanisms of the two metals is a possible explanation for their anomalous co-deposition in the electrolyte examined.

Keywords: electrodeposition kinetic, initial stages of nucleation, cyclic chronovoltammetry, chronoamperometry, nuclei growth.

INTRODUCTION

Over the past two decades there has been a growing interest in the applications of electrodeposited coatings of metals from the iron group (Ni, Co, and Fe) and their alloys for their unique magnetic, physical, mechanical, and thermophysical properties[1, 2].

The electrodeposition of Ni-Co alloys is classified as anomalous co-deposition which means that the less noble metal (Co) is preferentially deposited [10]. The disclosure of the reasons for anomalous co-deposition of Ni and Co in different electrolytes in many cases demands a combined application of several independent electrochemical methods and their diagnostic criteria [3, 5 - 10].

The electrochemical methods for preparation of metallic coatings and especially of the alloys are very attractive because of the high degree of control over the properties of the coatings while varying the experimental conditions [1 - 4]. To achieve this, a detailed knowledge on the mechanism of deposition of the metals both individually and in alloy is needed.

There are not enough data for the kinetics of independent deposition of Ni and Co in slightly acidic citrate electrolyte. The deposition kinetics of nanostructured Ni coating in sulphate electrolyte in presence of various organic additives was studied [5, 6] as well as in the typical Watts-bath [2, 7]. There are data for the kinetics of electrodeposition of Co in sulphate solutions [8, 9]. While the cyclic chronovoltammetry can give anotion
about the overall mechanism and kinetics of the occurring electrode processes [12], the chronoamperometric method [11] provides information about the initial stages of nucleation and the rate of nuclei growth, which can be used when searching the reasons for the anomalous co-deposition of the two metals in an alloy [5]. In this method the potential changes gradually from the equilibrium potential to potentials at which the metal begins depositing at a noticeable speed. Under these conditions, it is possible to compare the characteristics current-time (I - t) for potentials at which the main reaction does not occur, with potentials at which three-dimensional nuclei are formed and grow on an extrinsic substrate. The nucleation of the metal phase and the increase of the number of nuclei is usually illustrated with a few maxima in the I - t curves. The characteristic maxima indicate the mechanism of nucleation and the detention or the slow increase of the current up to a certain value suggest a three-dimensional growth of the nuclei [11].

The present study is aimed to obtaining some data about the general mechanism of independent deposition of Ni and Co in slightly acidic citrate electrolyte, as well as to obtain information about the initial stages of independent deposition of Ni and Co through application of the methods of cyclic voltammetry, chronoamperometry and chronopotentiometry.

EXPERIMENTAL

All electrochemical experiments were carried out in a thermostatic three-electrode cell without stirring. The working electrode was a copper disc with surface area 1 cm² and the platinum plate anode was about 30 times larger. All potentials were referred to the saturated calomel electrode (SCE). The solutions were prepared solving reagents of chemically pure substances in double-distilled water. The composition of the working electrolytes is shown in Table 1. The slightly acidic citrate electrolytes were brought to pH = 5.5 through addition of relevant quantities of sodium hydroxide and citric acid and all experiments were carried out at temperature of 20°C.

All experiments were carried out using computer controlled potentiostat type Wenking (Germany). The cyclic voltammograms were recorded in potential area from 0.2 V to -1.9 V (SCE) at scanning rate from 30 to 120 mV s⁻¹. The potentiostatic I - t dependencies and the galvanostatic E - t dependencies were recorded by rate equal to 1 s cm⁻² with respect to time.

RESULTS AND DISCUSSION

The method of cyclic voltammetry is used to define the area of potentials for reduction and to characterize the processes of deposition of Ni and Co. The characteristic voltammograms for deposition of Ni and Co recorded with scanning rates from 30 to 120 mV s⁻¹ in solutions 3 and 6, i.e. with concentration of Ni and Co 0.3 gmol dm⁻³ are shown in Fig. 1a, b.

There is a long initial polarization observed in the curves for independent deposition of Ni (Fig.1a) followed by a plateau of boundary current for Co (Fig.1b), whose value increases with the increase of the rate of potential scanning. With the increase of the rate of scanning, the plateau decreases and almost disappears at the highest value (Fig. 1a, curve 4). The kinetic of deposition of Ni corresponds to a combined control with predominantly activation nature of the polarization. The absence of anode branch is the proof for this finding. The plateau of boundary current is due to reaching the diffusion limitations at higher cathode potentials.

This conclusion corresponds to the data for the influence of the concentration of Ni on the course of the cathode polarization curves (Fig. 2a) from which it fol-
that the plateau of boundary current is more typical for the lower concentrations of Ni where obviously the diffusion limitations are achieved sooner.

The deposition curves of Co (Fig.1b) unlike those of Ni (Fig. 1a), have a pronounced cathode peak which increases with the increasing of potential scanning rate and the concentration of cobalt in the solution (Fig. 2b). The value of the peak current shifts to more cathodic potentials with the increase of the rate of scanning. There is not an identified oxidation peak in the working window of potentials when the curves turn scanning in anode direction. The appearance of the cyclic dependencies for deposition of Co evidences for the predominant diffusion limitations during its actual deposition (from -1.18 V to 1.30 V). This fact is supported by the observation that the observed peak increases with the increase of the concentration of Co (Fig. 2b). There is a retention of the current observed in the initial area of potentials of the deposition curves of cobalt, but as our subsequent observations indicate, there is no formation of cobalt coating within this area of potentials.

The chronovoltammetric examination also showed that the intersection of the cathode and anode branches of the curves is observed on the cathode sections that correspond to the potentials of nucleation: this is the area before the observed peaks, respectively plateaus for Ni. The voltammograms are analyzed based on Nicholson-Shain dependencies [12] and the developed diagnostic criteria of the method [13]. In Fig. 3a-d the dependencies \( i_p - v^{1/2} \) (Fig. 3a), \( i_p/v^{1/2} - v \) (Fig. 3b), \( (E_p - E_{p/2}) - v^{1/2} \) (Fig. 3c), and \( E_p - \log v \) (Fig. 3d) obtained from the chronovoltammograms are shown that satisfy the following equations [5, 12]:

\[
i_p = -0.496nFC_0 \left( \frac{\alpha n F}{RT} \right)^{1/2} D^{1/2} \sqrt{v}
\]

(1)

\[
E_p = K - \frac{2.3RT}{2\alpha n F \log v}
\]

(2)

The linear character of dependencies \( i_p - v^{1/2} \) (Fig. 3a),
and particularly the increase of the current in the peak with $v^{1/2}$, evidence that the deposition of Ni, Co is a diffusion controlled process. The application of the following diagnostic criteria specifies the degree of diffusion control and the interference on other stages in each case. Thus the practically weak dependence of $i_p/\sqrt{v}$ on $v$ (Fig. 3b) in the deposition of Ni, as well as the absence of anode branch in the cyclic voltammograms for Ni (Fig. 1a) and the shift of the potential in the peak/semi-peak in cathode direction (Fig. 3c, curve 1) prove the quasi-reversible nature (diffusion-activation control) of the deposition of Ni [13]. The dependencies in Fig. 3c also indicate that the control for deposition of Co is different from those of Ni. It corresponds to diffusion-controlled process with interference on the chemical stage preceding the reaction of discharge [13] that could possibly be the dissociation of the adsorbed citrate complexes of Co. The shift of the potential in the peak towards more negative values (Fig. 3c, curve 2) is a proof supporting the above suggestion.

In order to further clarify the mechanism of independent deposition and co-deposition of Ni and Co, the chronoammetric analysis was applied [11]. The typical time-current dependencies in compositions 3 and 6 in potentiostatic conditions are shown in Fig. 4a, b in a wide range of potentials applied from -0.850 V to -1.35 V. The same figure shows the processing of the curves in $I - t^{-1/2}$ coordinates (Fig. 4a*) and $I - t^{-3/2}$ coordinates (Fig. 5a, b) and this serves for the purpose of proving the growth mechanism of the nuclei formed, i.e. spontaneous in the first case and progressive in the second one.

It was found that there is neither deposition of the two metals nor any reactions associated with the background electrolyte at potentials more positive than -0.600 V and only charging the capacity of the double electric layer occurs. There is a well defined and recognizable maximum of current observed in the course of the chronoammograms recorded in electrolyte 1 for deposition of Ni (Fig. 4a), which is followed by an abrupt drop and subsequent retention, as the current follows the Cottrell equation that is valid in the case of diffusion control.
It can be said that this course proves the reduction of nickel ions occurring in one stage with transfer of two electrons under the reactions:

\[ \text{Ni}^{2+} + 2e^- \leftrightarrow \text{Ni} \]

\[ \text{NiCit}^- + 2e^- \leftrightarrow \text{Ni} + \text{Cit}^{3^-} \]

The deposition of Ni initiates at potentials above -0.950 V with the simultaneous evolution of hydrogen upon the reaction:

\[ 2\text{H}_2\text{O} + 2e^- \leftrightarrow \text{H}_2 + 2\text{OH}^- \]

which are evidenced by the time-current dependencies recorded additionally only in the background electrolyte. The course of the chronoammograms recorded in electrolyte 6 for deposition of Co (Fig. 6b) is quite typical. In the case of Co, there are two subsequent peaks of the current in the potential area from -1.0 V to 1.2 V, instead of one peak. The first one, i.e. for smaller values of time, is sharper and the decrease of current follows the Cotrell’s equation [14]. The second peak in the curves of Co evidences for a process of occurrence of both active nucleation and nuclei growth in conditions of diffusion limitations. The dependencies in Fig. 6b indicate that the deposition of Co occurs through a two-stage electron transfer as it has already been found for other electrolytes [8]. The first peak corresponds to reduction of the nearest free cobalt ions under the reaction:

\[ \text{Co}^{2+} + e^- \leftrightarrow \text{Co}^{3+}_{\text{ads}} \]

which is followed by a fast process of reduction of the monovalent ions to cobalt:

\[ \text{Co}^{3+}_{\text{ads}} + e^- \leftrightarrow \text{Co} \]

As a result of depletion of the electroactive form (Co\(^{2+}\)) in the layer near to the electrode, the current decreases with time. The process is entirely diffusion controlled. With time the diffusing complex ions of cobalt (CoCit) reach slower the electrode. Their delayed reduction is also associated with purely chemical processes that precede the reduction itself, and namely dissociation of the adsorbed complexes, for which the criteria of cyclic chronovoltammetry applied above indicated. Upon reaching higher cathode values of potential, the reduction of the citrate complexes to cobalt takes place:

\[ \text{CoCit}^- + 2e^- \leftrightarrow \text{Co} + \text{Cit}^{3^-} \]

The increase of current with time as a result of depletion of the complex ions of cobalt is smoother and is explained with the simultaneous growth mechanism of the nuclei formed. The suggestion that complex ions of Ni and Co are involved is supported by the previous investigations proving their shape and stability [15] that are also comparable with those in [16, 17]. It was found that in slightly acidic citrate electrolyte (pH = 5.5), nickel and cobalt present both as free metal ions (Ni\(^{2+}\) and Co\(^{2+}\)) and complex citrate ions mainly of the type NiCit and CoCit mainly with stability constants \(\text{lg}K_{\text{st(Ni)}} = 5.379\) and \(\text{lg}K_{\text{st(Co)}} = 4.38\).

The general conclusion suggested by the chronoammetric analysis is that the behavior of the curves in Fig. 5(a, b) evidences for a typical process of nucleation with three-dimensional growth of the nuclei at predominantly diffusion control on the part of the electroactive forms [11]. The critical time for nucleation, i.e. the time in which the current decreases, decreases with the increase of the cathode potential applied.

The method of chronoammetry provides clear diagnostic criteria to recognize the mechanism of nucleation. According to the theory developed by Scharifker-Hills [11], there are two boundary cases of nucleation with a diffusion controlled growth. At a high rate of nucleation all nuclei are formed spontaneously and the dependence time-current is described by:

\[
  i(t) = \frac{zFD^{1/2}c}{(\pi t)^{1/2}} \left[1 - \exp(-N\pi kD t)\right]
\]

(3)

where \(k = 8\pi C_o^n M/\rho\); \(D\) is diffusion coefficient; \(C_o^n\) is volumetric concentration of Ni\(^{2+}\) or Co\(^{2+}\); \(M\) is molar mass; \(\rho\) is density of the metal; \(N_o\) is the number of spots for nucleation. In this case the chronoammograms are linearized in coordinates \(I - t^{-1/2}\).

In the second case, i.e. at lower rate of nucleation, when the nuclei are formed continuously within the entire time window before reaching the area of overlapping with the diffusion limitation around the growing nuclei, we can speak about progressive (continuous) nucleation. In this case, the chronoammograms are linearized in coordinates \(I - t^{-3/2}\). The course of the current for progressive three-dimensional growth mechanism is described by the following equation:

\[
  i(t) = \frac{zFD^{1/2}c}{(\pi t)^{3/2}} \left[1 - \exp(-aN_k^o k^o D t^2 / 2)\right]
\]

(4)
where $k' = 4/3(8\pi C_\infty M/\rho)^{1/2}$.

The chronoammograms of Ni are linearized to a higher degree in coordinates $I - t^{-3/2}$ (Fig. 5a), which is indicative for a mechanism of progressive (continuous) nucleation. Unlike Ni, in the case of Co we can observe a better linearization of the chronoammograms.
in coordinates $I - t^{-1/2}$ (Fig. 4b*), which evidences for a mechanism of spontaneous nucleation that is super imposed onto the general diffusion controlled process of deposition of Co.

It is possible that the mentioned difference in the mechanisms of nuclei growth is due to the two-stage transfer of charge in the case of Co since the first stage has already localized the needed spots for crystal growth on the surface. The higher speed of nucleation in the case of Co through the mechanism of spontaneous nucleation can be a possible reason for its identified preferential (anomalous) deposition together with Ni. It also follows from the curves in Figs. 4 and 5 that with the increase of the potential applied the slope of dependencies $I - t^{-1/2}$ and $I - t^{-3/2}$ increases for both metals, which corresponds to the increase of the rate of nucleation.

The determination of the transition time as a function of current can provide additional information about the mechanism of interaction [14]. The course of the cathode potentiograms for Ni and Co is shown in Fig. 6a,b for solutions 3 (0,3M Ni) and 6 (0,3M Co), correspondingly.

The curves in Fig. 6a indicate that the cathode potentials for deposition of Ni shift smoothly to more negative potentials. In the case of Co (Fig. 6b), in the intermediate area of cathode potentials applied the dependencies $E - t$ follow the equation of Karauglanov [14], which means that the transition time is achieved decreasing with the increase of the current density. Thus the conclusion is proved that although being combined, the control of the process of Co deposition is diffusion to a higher extent than that of Ni. It is also proved that the mechanism of nucleation and nuclei growth of Co is faster than that of Ni.

**CONCLUSIONS**

The comparison of the dates from three electroanalytical methods shows the difference of the deposition kinetics and of the mechanisms of nucleation and crystal growth for Ni and Co in citrate electrolyte. The deposition of Ni occurs in one act of charge transfer with exchange of two electrons, and in the case of Co the deposition is a two-stage process of reduction of free cobalt ions to cobalt, and reduction of complex ions type $\text{CoCit}^-$ to cobalt. In the case of Co, there is a mechanism of spontaneous nucleation and three-dimensional growth, while in the case of Ni it comes to slower process of progressive (continuous) nucleation. The differences in the deposition mechanisms of the two metals is a possible explanation for their anomalous co-deposition in the electrolyte examined.

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ABSTRACT

In the paper the results from the study of the kinetic of joint electrodeposition of Ni and Co in Ni-Co alloy system are reported. It is found that the co-deposition of Ni and Co in Ni-Co alloy system in slightly acidic citrate electrolyte occurs under combined diffusion-kinetic control with a typical mechanism of nucleation similar to those in the case of Co. The application of the method of chronoammetry proved that the mechanism of nucleation for Ni-Co alloy is spontaneous with three-dimensional nucleation and nuclei growth. The difference in the independent deposition mechanisms of the two metals is a possible explanation for their anomalous co-deposition in the electrolyte examined. The anomalous co-deposition is more clearly noticeable in electrolytes with higher content of cobalt than nickel. The SEM-analysis proves that the alloys enriched in cobalt have crystallites with more even and rounded shape, which is expected in the case of spontaneous nucleation.

Keywords: electrodeposition mechanism, alloy system, cyclic chronovoltammetry, chronoammetry, nucleation, nuclei growth.

INTRODUCTION

The application of thin Ni-Co alloy films can be divided in three main categories: for decorative coatings purposes, for anti-corrosion protection in the industry [1, 2], and for highly functional coatings in various magnetic devices, especially in microsystems such as sensors, actuators, and memory devices [3, 4].

The electrodeposition of Ni-Co alloys is classified as anomalous co-deposition which means that the less noble metal (Co) is preferentially deposited [5 - 10]. This phenomenon is observed in sulphate [5, 10], sulfamate and chloride [6, 9], and citrate electrolytes [4], both with application of stationary current modes [5, 9, 10], and various pulse modes [6 - 8]. To explain this phenomenon, different reasons are found and reported, e.g. increased pH close to the electrode surface with formation of cobalt- and nickel hydroxides on the surface [8]; two-stage mechanism including adsorption of monovalent intermediate compounds and their reduction; underpotential deposition [9], and faster deposition kinetic of cobalt under diffusion control [10]. The most frequently cited model for anomalous co-deposition is based on the idea that the adsorbed forms of these metals include metallic mono-hydroxides Me(OH)ads+ obtained as intermediate product during the deposition. Under this mechanism, the anomalously high content of cobalt in the alloyed Ni-Co coating results from the preferential adsorption of Co(OH)ads to Ni(OH)ads on the cathode surface [8]. This conclusion is based on the comparison between the equilibrium constants for formation of the metal hydroxide ions Me(OH)+. The decrease of this value is in direction Fe(OH)+ > Co(OH)+ > Ni(OH)+. On the other hand, the comparison between the thermodynamic data for these constant indicates that the difference between their values is not large.
log \( K_{\text{FeOH}^-} \) = 4.5; log \( K_{\text{CoOH}^-} \) = 4.3; log \( K_{\text{NiOH}^-} \) = 4.1 [11]. The disclosure of the reasons for anomalous co-deposition of Ni and Co in different electrolytes in many cases demands a combined application of several independent electrochemical methods and their diagnostic criteria [5, 12 - 15].

The present study is aimed to obtaining some data about the mechanism of co-deposition of Ni and Co in slightly acidic citrate electrolyte through application of the method of cyclic chronovoltammetry, as well as to obtain information about the rate of nucleation on the initial stages of co-deposition of Ni and Co in Ni-Co alloy system through application of the methods of chronoammetry and chronopotentiometry. Our further goal is to clarify the specifics of the deposition of Ni and Co combining the data obtained with the results from the study on the composition and morphology of Ni-Co alloy with varying the content of cobalt and nickel in the electrolyte.

**EXPERIMENTAL**

All electrochemical experiments were carried out in a thermostatic three-electrode cell without stirring. The working electrode used was a copper disc with surface area 1 cm\(^2\), and the anode was a platinum plate with surface area almost 30 times larger than that of the cathode. All potentials were measured against a reference saturated calomel electrode (SCE). In order to compare the behavior of the two metals during electrodeposition with that of their co-deposition in Ni-Co alloy system, the solutions were prepared with different ratios Ni/Co (Table 1). The slightly acidic citrate electrolytes were brought to \( \text{pH} = 5.5 \) through addition of relevant quantities of sodium hydroxide and citric acid and all experiments were carried at temperature of 20\(^\circ\)C. The solutions were prepared solving reagents of chemically pure substances in double-distilled water.

All experiments were carried out using computer-controlled potentiocan type Wenking (Germany). The cyclic voltammograms were recorded in potential area from 0.2 V to -1.9 V (SCE) at scanning rate from 30 to 120 mV s\(^{-1}\). The potentiostatic I - t dependencies and the galvanostatic E - t dependencies were recorded at rate of potential scanning equal to 1 s cm\(^{-1}\) with respect to time. The examination of the morphology of Ni-Co alloys, as well as their composition (through EDSA analysis) was carried out using scanning electron microscope (SEM) with equipment of Oxford Instruments. JSM-6390-Jeol. The composition of the alloys was also examined using additional atomic-absorption analysis (AAA).

**RESULTS AND DISCUSSION**

The characteristic voltammograms for deposition of Ni-Co recorded with scanning rates from 30 to 120 mV s\(^{-1}\) in solution 1 (Table 1) are shown in Fig. 1a and in Fig. 1b - the polarization dependencies at \( v = 30 \text{ mV s}^{-1} \) in solutions with different ratios Ni/Co (Table 1).

In the deposition curves of Ni-Co alloy system (Fig. 1a) have a pronounced cathode peak which increases with the increase of potential scanning and the concentration of cobalt in the solution (Fig. 1b). The value of the peak current shifts to more cathode-like potentials with the increase of the rate of scanning. There is not an identified oxidation peak in the working window of potentials where the curves turn scanning in anode direction. The appearance of the cyclic dependencies evidences for the predominant diffusion limitations during its actual deposition of Ni-Co (from -1.2 V to 1.35 V). This fact is supported by the observation that the observed peak increases with the increase of the concentration of Co (Fig. 1b).

The deposition potentials of Ni-Co alloy system are shifted in a strongly negative direction in comparison with that for Co (-1.18 V for Co and -1.4 V for Ni-Co), which evidences for additional difficulties in the processes of nucleation and crystal growth during the co-

<table>
<thead>
<tr>
<th>№ of Solution (pH = 5.5)</th>
<th>( C_{\text{Co}^{2+}}^{\circ} )</th>
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deposition of the two metals. The chronovoltammetric examination also showed that the intersection of the cathode and anode branches of the curves is observed on the cathode sections that correspond to the potentials of nucleation. Fig. 2 a,b exhibits the comparison between the curves of independent deposition of Со and Ni and their co-deposition at two ratios in the solution (solutions 1 and 3 from Table 1), which indicates more clearly that in the total curve the total current is higher than the currents corresponding to the individual deposition of each metal.

Moreover, it is seen that in composition 1 (Fig. 2a), in which the content of the two metals is equal ((Ni/Co)_sol = 1), the discharge of Co-ions occurs at more positive potentials compared to that of Ni. The so called anomalous deposition of the two metals is observed. With the increase of the relative content of Ni in the solution compared to that of Co (Fig. 2b, composition 3), the effect of the preferential deposition of Co obviously weakens thus creating conditions for enrichment of the Ni alloy. It can also be seen that with the increase of the relative content of Ni, the peak of reduction of the Ni-Co alloy shifts to more positive potentials (Fig. 2b) and thus the potential of nucleation decreases with the increase of the ratio Ni/Co.

The proven mechanism of anomalous deposition of the two metals in compositions 1 and 3 is also confirmed by the identified influence of the potential and the ratio Ni/Co in the solution on the chemical content of Ni-Co alloy system, which is found through atomic absorption analysis (Fig. 3). It is seen that even when the relative content of Ni in the solution is three times higher (Fig. 3, curve 1) the content of Co in Ni-Co alloys is no less than 57 – 70 % mass, depending on the potential. The content of cobalt increases to 90 % mass when its content in the solution increases (Fig. 3, curve 3) and decreases to 78 % mass with the increase of the potential applied.

The voltammograms are analyzed based on Nicholson-Shain dependencies [17] and the developed diagnostic criteria of the method [16]. In Fig. 4 a-d the dependencies \( i_p - v^{1/2} \) (Fig. 4a); \( i_p/\sqrt{v} - v \) (Fig. 4b), \( (E_p - E_{p2}) - \sqrt{v} \) (Fig. 4c) and \( E_p - \log v \) (Fig. 4d).

The linear character of dependencies \( i_p - v^{1/2} \) (Fig. 4a), and particularly the increase of the current in the peak with \( v^{1/2} \), evidence that the deposition of Ni-Co system is a diffusion controlled process. According to the diagnostic criteria applied, the deposition kinetic of Ni-Co alloy is controlled to a greater extent by the
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followed by an abrupt drop and subsequent retention,
as the current follows the Cottrell equation that is valid
in the case of diffusion control.

The mentioned mechanisms for Ni and Co deposi-
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chronoammmograms of deposition of Ni-Co alloy system.

The general conclusion suggested by the chronoam-
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three-dimensional growth of the nuclei at predominantly
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[20]. The critical time for nucleation, i.e. the time in
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The method of chronoammetry provides clear diagnos-
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In order to further clarify the mechanism of co-dep-
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was applied. The typical time-current dependencies in
compositions 1 in potentiostatic conditions are shown in
Fig. 5a in a wide range of potentials applied from – 0.850
V to -1.35 V. The same figure shows the processing of
the curves in 1-t 1/2 coordinates (Fig. 5b).

It was found that there is neither deposition of the two
metals nor any reactions associated with the background
electrolyte at potentials more positive than -0.600 V and
only charging the capacity of the double electric layer
occurs. There is a well defined and recognizable maxi-

Fig. 3. Content of Ni-Co alloys (% mass Co) in depend-
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the general diffusion controlled process of deposition.
It is possible that the mentioned difference in the mechanisms of nuclei growth is due to the two-stage transfer of charge in the case of Co since the first stage has already localized the needed spots for crystal growth on the surface. The higher speed of nucleation in the case of Co through the mechanism of spontaneous nucleation can be a possible reason for its identified preferential (anomalous) deposition together with Ni. It also follows from the curves in Fig. 5 that with the increase of the potential applied the slope of dependencies $I - t^{-1/2}$ increases, which corresponds to the increase of the rate of nucleation.

Fig. 6 a,b displays the SEM images of Ni-Co alloy coating deposited at the same potential from electrolytes 3 (Fig. 6a) and 1 (Fig. 6b). The SEM images evidence that the alloys enriched in Ni (Fig. 6a) have larger crystals (about 500 nm) with idle-like shape of the crystallites. In the coatings enriched in Co (Fig. 6b), the crystallites formed are more rounded and smaller in dimension (about 300 nm), and their structure as a whole is smoother and more uniform in terms of morphology. This finding agrees with the theory [15, 16] proving that under the mechanism of spontaneous nucleation, which is more typical for Co and for Ni-Co, the crystallites shall be more uniform in shape and dimension.

CONCLUSIONS

The main conclusions that are imposed by this study are that the co-deposition of Ni and Co in Ni-Co alloy system becomes under combined diffusion-kinetic control with a typical mechanism of nucleation similar to those in the case of Co.

It was found that anomalous co-deposition of the metals occurs in slightly acidic citrate electrolytes, which can be explained with the different deposition kinetics and different mechanisms of nucleation and crystal growth for Ni and Co. With the increase of the relative content of Ni in the solution compared to that of Co, the effect of the preferential deposition of Co obviously weakens thus creating conditions for enrichment of the Ni alloy. The SEM-images prove that the crystallites in alloys enriched in Co have more even and rounded shape that agrees with the theory for the case of spontaneous nucleation.
REFERENCES


ABSTRACT

This work presents results of metallographic examination of the surface layers of grey cast iron, subjected to plasma bleaching. In the sintered layer are detected ledeburite structure, martensite, ferrite and graphite particles. It is shown that the pre-cast aluminum cladding surface increases the dispersion of carbide particles and the hardness of the melted layer.

Keywords: grey cast iron, microstructure, plasma fusion, bleaching, modifying aluminum, hardness.

INTRODUCTION

Grey cast iron is widely used for the manufacture of many parts in a variety of industries. From cast irons are made the most vital parts of a car - engine blocks, brake discs [1], cylinder liners diesel engines [2], piston rings, etc. [3]. The most frequently used unalloyed or low-alloyed grades of grey cast iron are with a lamellar graphite form.

The physical and mechanical properties of service parts made of cast iron are determined primarily by features of its microstructure. The main feature of the microstructure of the cast iron is the existence of a lamellar graphite mold. Flake graphite gives greater continuity of the metallic matrix. Therefore, grey cast iron has relatively low resistance values for time at relatively low rupture ductility. In addition, even modified, or doped grey cast badly resists abrasion and sliding wear when applying high contact loads. On the other hand, due to the plate-like shape of graphite in gray cast iron, it has low sensitivity to surface stress concentrators. In addition, grey cast iron has a high damping capacity (internal friction is 4 to 10 times higher than that of steel) and thus dampens vibrations well. So, in many cases it is expedient to produce grey cast iron core parts of automobiles, and the surface of the wear resistant materials to perform, for example, with a white cast iron alloy [4].

Widely reported in the literature is the possibility for hardening products for cast iron surface whitening during crystallization or in saturated surface diffusion with chromium, vanadium, or aluminum [5]. However, most of the known methods of whitening for the surface of cast irons require a number of additional technological measures, that are not in a position to guarantee the quality of the bleached layer without pores, graphite inclusions and cracks. There is also a significantly complicated and costly process of hardening. Studies of the possibility for bleaching grey iron with plasma remelting surface [6], show the high efficiency of this method, however, data on the possibility for additional alloying the surface layer of iron in the literature is not enough.

Whitening grey cast iron by surface melting induction, laser or other means, to ensure the formation of a surface layer of the structure, leads to a ledeburitic-martensitic composition with high hardness and wear resistance. The obtained continuous layer without large inclusions, cracks and roughness is satisfactory for difficult tasks.
The aim of this work is to study the possibility of fusion plasma for surface chill cast iron with lamellar graphite, and to characterize the microstructure and properties of cast iron after application of an aluminum underlayer and subsequent fusion plasma.

EXPERIMENTAL

Hardened layers were obtained without the additional cooling forced way, only relying on the heat sink into the metal. The starting temperature of the investigated irons was 20°C, after processing, it was raised to 80 - 120°C. Surface bleaching was made by remelting the cast iron surface by exposing it to the plasma jet. The influence of surface chill was assessed by measuring the hardness, microhardness and microstructure of the remelting zone, the transition zone and the heat affected zone.

RESULTS AND DISCUSSION

Grey cast iron has in the initial state a ferritic-pearlitic metal based plate and a graphite mold (Fig. 1).

After the plasma iron surface remelting, its hardness increased from 24 HRC to 52 HRC. The depth of the surface layer bleached was about 2 mm. The bleached layer has a dense structure, with no visible cracks and chips. The microstructure of the bleached area of the iron is shown in Fig. 2. It can be seen that it is a hypoeutectic white cast iron, in which there are no graphite particles. The metal substrate is an austenite-martensite composition in the axes of the dendrites. The microhardness of the austenite-martensite composition is 550 - 590 HV10. The dendrites do not have a clearly defined general direction of the growth axes of the first order. This means that the heat in this layer during crystallization, was very effective and was carried out both in the direction of the base metal and the atmosphere. The average dendritic parameter is 4 - 6 mm, which corresponds to approximately the crystallization rate in the direction of the axes of the dendrites of the first order of 1000°C s⁻¹. In the interdendritic space there is an eutectic cementite type, with microhardness 722 - 810 HV10.

In the lower layers of the molten layer there is a transition zone where are present both the structure characteristic for the base metal, the remelting zone and the intermediate products transformations, resulting from the rapid crystallization of liquid iron (Fig. 3).

Clearly visible are also the graphite plates that have not dissolved in the iron melt during the plasma treatment, due to the short exposure time. For the graphite plates, on both sides an adjacent cementite eutectic type, in which the carbide particles are arranged perpendicular to the surface of the graphite plates, is observed. We can assume that the transition zone has been formed during accelerated cooling of molten iron, heated to temperatures of a solid-liquid state. When it is not soluble, the graphite plate is the substrate on which the crystals of the carbide phase are grown. The metal based eutectic structure formed martensite and austenite. At some distance from graphite plates is located an area of high structure, having martensite and austenite. The integral microhardness of these areas is 440 - 480 HV10. In the deeper layers of the samples, described above, the...
composition is replaced by structures more typical for grey cast iron. The cooling rate at the surface remelting of pig iron at these depths is relatively low, so martensite meets troost-martensitic structures.

It is known [7], that introducing iron into aluminum in an amount of 10 – 17 % leads to a significant increase in its hardness and wear resistance, due to the formation of carbides of the type (Fe, Al) 3C. The doped surface layers of aluminum on the workpiece whiten at plasma remelting only at its preliminary application to the surface of the reinforcement. Using the method of plating, a flexible tool [8] for this purpose leads to obvious advantages, allowing to automate the process of applying aluminum and provides a constant thickness of the aluminum layer on the surface of the product.

The plasma remelting of cast iron clad aluminum method leads to an even greater increase in hardness, than plasma remelting without cladding. Hardness increases from 52 HRC to 62 HRC, and remelting zone microhardness increases up to 1000 - 1050 HV. The general type of structure, formed in the zone remelting is unchanged (Fig. 4). The bleached layer has a typical eutectic structure. The number of the eutectic components decreases, and the volume fraction, occupied by the dendrite arm, increases. Based on the substantial solubility of aluminum in α-iron at a temperature ranging from the melting point to room temperature (from 30 % to 8 % by mass), suggests that, while most of the aluminum is contained in the base metal. The dendritic structure in the zone of remelting the plasma surface is coated with aluminum at 4 - 6 microns. Obviously, the metal substrate is the refining zone and a minor amount of martensite austenite. Increasing the amount of martensite due to the action of aluminum has led to a sharp increase in the hardness of hardened layer up to 62 HRC.

CONCLUSIONS

Thus, prior to application of grey cast aluminum surface by plating a flexible instrument and subsequent remelting of the surface of the plasma, can significantly improve the hardness of the hardened layer, compared with the plasma remelting without coating with the aluminum layer. The quality of the hardened layer is much higher than in the bleaching iron, obtained by induction heating. In the zone of remelting, there are no pores and soluble graphite inclusions, which gives reason to recommend this as a very effective treatment for grey iron parts, working in conditions of intense friction, temperature and contact stresses.

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STUDY OF AXIAL FORCES WITH THE PURPOSE TO REALIZE A COMBINED PROCESS «HELICAL ROLLING-PRESSING»

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ABSTRACT

The key factor for practical realization of the combined process «helical rolling-pressing» is the axial force of the helical rolling, which should provide a continuous pressing in the matrix after the rolls. For the measurement of the maximum axial rolling force, which is actually the reserve of friction forces, a special strain gauge has been made. The work was carried out at a three-roll helical rolling mill “10-30” for the case of hot rolling of steel bars with diameters of 16 - 25 mm at a reduction of 6 % of diameter and a temperature of 1000°C. The results shown are of 24 tests.

Keywords: helical rolling, axial force, strain gauge, combined process.

INTRODUCTION

The usage of ultrafine-grain (UFG) and nanostructured (NS) metals and alloys as constructional and functional materials of the new generation promises huge advantages due to their properties. Different ways to obtain such materials with the use of intensive plastic deformation have been developed [1-2]. However, the industrial production of UFG and NS materials is still often interlinked with high expenditures of time and energy, restrictions of sizes, and, as a whole, low adaptability to manufacturing that reflects in their cost. Therefore, the development of new principles for using severe plastic deformation (SPD) for production of volumetric NS metals with perspective properties is an actual target.

It is known that during the helical rolling, owing to trajectory and speed features of the metal flow, the formation of UFG structure is also possible. However, owing to the same features the central part of the bar can remain not treated [7]. The combination of helical rolling and ECA pressing can eliminate this problem, thus providing the continuity of the process and a potentially better treatment of the structure, during the pass in comparison to the above described combined process. This idea is described in details in [8], however its realization is interlinked with difficulties of practical nature, caused by the complexity of the helical rolling process. The key factor is the value of the maximum axial force (that is, essentially, the reserve of friction forces) during helical rolling, which should be sufficient
for maintenance of continuous pressing in the matrix standing after the mill. Thus, owing to complexity of the process, experimental research of axial force maximum values distribution have high value for designing of the combined installation, with the purpose of accounting for the total influence of random factors, that is the very aim of this work.

The object in view is reached by the consecutive solution of following issues: experiment definition, designing and manufacturing of the measuring equipment, carrying out of the experiment and processing of its results.

EXPERIMENTAL

Measurements of axial force during helical rolling were repeatedly made by various authors [9 - 10] for the case of a pipe blank piece piercing into the sleeve and had the target of the optimization of the mandrel form and the piercing process as a whole. However, measurements of the arising axial force for the case of full compulsory braking of the bar in mill rolls of this type, have not been carried out.

For assessment of the demanded data about the maximum axial effort, a decision was made regarding carrying out of the experiment in 3 sequences with 8 experiments in each, with one influencing factor - the ratio between rolls diameter (D_y) and the diameter of blank piece (D_0), accordingly using different values of the factor for each sequence. Such assessment will allow to collect the statistical material for estimation of the maximum axial force, along all the product mix of the mill. Besides this, the use of a relative indicator (D_y/D_0) as the factor will allow the expansion of the database of experimental data in the future at the expense of experiments for other mills with the same type of calibration and adjustment of rolls.

The experiment was carried out at the mill of radial-displacement rolling (RDR) “10-30”, designed by National Research Technological University “Moscow Institute of Steel and Alloys” (Russia), as the one providing the demanded structure of the bar after rolling [7, 11]. For the experiment initial profiles with diameters: 16 mm, 20 mm and 25 mm, as the most typical for mill product mix, have been chosen. The ratio between the diameter of the conical rolls (71 mm) and the diameter of the blank piece (D_y/D_0), as well as the initial (D_0) and the final dimensions (D_1) of bars, by sequences of experiments, are given in Table 1.

The percentage reduction (ε, %) for all cases is assumed to be constant, and equal to 6 % of diameter, as convenient for mill adjustment, as well as due to the fear of possible damaging of rolls and camp structure under high load.

Round hot rolled bars (GOST 2590-88) with length of 300 mm were used as blank pieces for the experiment, with diameters according to Table 1. Steel grade St3 (0,14 - 0,22 % C) as one of the most globally widespread constructional material was chosen as the material for blank pieces. The temperature of the bars heating up was defined at the level of 1000°С, which was the average value of the temperature for heat treatment of this class of steel. The distance from the deformation region to the measuring plate corresponded to the prospective distance to the matrix during the combined process and was equal to 100 mm.

The scheme for carrying out of the experiment for measurement of the maximum axial force is shown on Fig. 1. The methodology of the experiment is as follows. Bars for experiments with length of 300 mm, with diameters according to Table 1, in sets of 2 pieces are loaded into the tubular furnace, warmed up to 1000°С with staying of 16 - 30 minutes, depending on the section and arrangement of the blank pieces. After this, the bars in turns are put into the mill rolls. In the process of rolling the bar (1), moving forward, touches the measuring plate (3) with fixed edges and bends it elastically, under the influence of axial force (F). Plate deformation

<table>
<thead>
<tr>
<th>Sequence of experiments</th>
<th>D_y/D_0</th>
<th>D_0, mm</th>
<th>D_1, mm</th>
<th>Number of experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2,8</td>
<td>25</td>
<td>23,5</td>
<td>8</td>
</tr>
<tr>
<td>II</td>
<td>3,6</td>
<td>20</td>
<td>18,8</td>
<td>8</td>
</tr>
<tr>
<td>III</td>
<td>4,4</td>
<td>16</td>
<td>15</td>
<td>8</td>
</tr>
</tbody>
</table>
is perceived by resistive strain sensors (7) pasted on it and registered by a strain sensor station in the form of an effort schedule. The peak value of the loading is registered in the table of results.

In addition to the mill RDR “10-30”, the equipment involved in the experiment, includes the following: a tubular furnace Nabertherm R120/1000/13 (Nabertherm GmbH, Germany); a strain sensor station ZET-017-T8 (“ETMS” CJSC, Russia); a measuring plate with resistive strain gauge sensors TKFO1-2-200 (“ETMS” CJSC, Russia); a laptop for control of the strain sensor station and signals recording.

The use of a plate with fixed edges (beam scheme) as a measurement device, is caused by the features of the mill design, which is not intended for piercing of blank pieces, and therefore is complicated, unlike in the application of ready decisions (serial load cells) [9-11]. Besides this, such a scheme was chosen owing to the greatest linearity of measurements, less dependence on the point of force application [13], better security of the resistive strain sensors, both from temperature and from mechanical damages, simplicity and convenience of realization. The steel 5ХВ2С (alloyed spring steel) after tempering was chosen as the material of the measuring plate, as capable to endure considerable elastic deformation. The dimensions of the plate were calculated with a condition for achievement of deformation in the places of the resistive strain gauge sensors pasting, equal to the maximum admissible deformation of chosen resistive strain gauge sensors (2 %) after the force of 100 kN that is more than 2.5 times greater than the expected peak force. Plate edges, realising the beam scheme, lean against thick-wall brackets (4), connected to the front frame of the rolling mill adjusting bolts (6).

Thus, the measuring plate with four resistive strain gauge sensors, connected into the bridge scheme and providing thermal compensation, was developed and manufactured. Resistive strain gauge sensors were pasted using a special glue Z70 (Hottinger Baldwin Messtechnik GmbH, Germany). The scheme of pasting and connection of the resistive strain gauge sensors is shown on Fig. 2.

Resistive strain sensors are pasted symmetrically in the middle of the distance between the centre of plate and support points. Measuring (active) resistive strain sensors ($R^A$) are pasted along the plate, compensatory sensors ($R^K$) - across it, thus perceiving only the temperature disturbance. During the connection into the bridge scheme, measuring ($R^A$) and compensatory ($R^K$) elements alternate. Such connection provides the increase.

![Fig. 1. Scheme of maximum axial force measurement carrying out. (1 - bar; 2 – rolls, 3 - measuring plates, 4 – brackets, 5 – frame, 6 - adjusting bolts, 7 - resistive strain sensors, F - axial force).](image1)

![Fig. 2. Scheme of resistive strain gauge sensors pasting and connection to the measuring plate. a) Scheme of resistive strain gauge sensors pasting; b) Scheme of resistive strain gauge sensors connection (E - feeding of bridge; $e_0$ - output voltage).](image2)
in sensitivity of the scheme during its protection against temperature distortions [13]. The scheme receives a feed of 5V direct current from the strain sensor station. Signal recording is made with frequency of digitization of 1 kHz. The measuring plate was calibrated at the torsion and tensile testing machine MI-40KU (Ukraine) in a mode of compression testing, as per methodology, minimizing the influence of the hysteresis. The essence of calibration is the composition of the dependence connecting the electric voltage in the scheme and the bending force, applied to the plate. This dependence should have a linear character. For carrying out of the calibration the plate was consistently loaded with force with the step of 5 kN in a range from zero to 35 kN. The corresponding values of the voltage in the scheme under loading and after its removal, were fixed. With the view of hysteresis reduction and accuracy increase, 3 passes on the specified range of forces – upwards, downwards and upwards were carried out, or 42 measurements in total (including measurements of zero values).

The data received in the process of calibration tests were statistically processed, and a regression equation was developed on their basis, connecting the force applied to the plate \( F_i, N \) with the voltage \( U_i, mV \) in the scheme. The equation looks like: \( F_i = -3631.2 U_i + 10122 \). The ratio of determination \( R^2 = 0.99998 \); the standard error of measurements attributed to the value of the working range of plate measurements (40 kN) based on results from 42 tests was less than 0.2 %. The received data were uploaded into the program of measurements registration and processing of the strain sensor station ZET-017-T8 for the possibility of signal recording in the form of the force trend. After the experiment little random control loadings were made, in which the deviation of values did not exceed the value specified above, which confirmed the accuracy and the stability of the work of the measuring plate.

### RESULTS AND DISCUSSION

All steps of the experiment have passed in the normal mode. At the moment of the visible bend achievement of the bar resting against the plate, the mill drive engines were synchronously stopped to make possible the taking out of the bar from the stand without interfering with mill settings. The general view of the experimental installation and the bar, taken out after rolling, are shown on Fig. 3. On Fig. 3a the bend of the measuring plate under the influence of the axial force is clearly seen. On Fig. 3b in the bottom part of the bar there are roll marks seen, characterizing the deformations region.

Force trends fixed by the strain sensor station are generally similar and have the same distinctive sections. As an illustration of this, Fig. 4 shows the trends of tests II-3 and II-6, fixed by strain sensor station. At the first section there is a sharp (during approximately 0.15 sec) increasing of the force, with some delay closer to the peak. At this stage, there is a bend of the plate under the influence of axial movement of the bar and a small

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**Table 2. Statistical characteristics of experiments.**

<table>
<thead>
<tr>
<th>Statistical parameter</th>
<th>Experiments sequence/ ( (D_v / D_0) )</th>
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<tbody>
<tr>
<td></td>
<td>I / 2,8</td>
</tr>
<tr>
<td>( F_{\text{ave}} N )</td>
<td>35 541</td>
</tr>
<tr>
<td>( F_{\text{max}} N )</td>
<td>39 394</td>
</tr>
<tr>
<td>( F_{\text{min}} N )</td>
<td>31 077</td>
</tr>
<tr>
<td>( F_{st} N )</td>
<td>2 402</td>
</tr>
</tbody>
</table>

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Fig. 3. Carrying out of the experiment. a) carrying out of the experiment (moment of rolls stoppage); b) bar after the test 1-7.
deformation of the head end of the bar. The shape of this section of the trend comes close to a parabola shape. Then there is a bend of the bar, accompanied by decreasing of the force by one third and a smooth alignment of the force decreasing, probably connected with the start of rolls sliding. Thus, it is important to notice, that at the last stage, the bar leans not only against the plate, but also against the part of the front frame, because at this stage it is generally strongly bent.

The moment of the stoppage of the drives is clearly visible at the trends in the form of a short negative spike to the right of the peak. As it was shown by the experiments, the moment of the drives stoppage does not influence the qualitative and the quantitative picture of the force changing in practice. The results of each sequence of experiments have been checked for presence of gross errors by Student’s t-test, and then statistical characteristics have been calculated for each sequence: arithmetic average ($F_{\text{ave}}$), maximum ($F_{\text{max}}$) and minimum ($F_{\text{min}}$) values, standard deviation ($F_{\text{st}}$). The listed characteristics are shown in Table 2. Values of the force in all experiments are shown graphically on Fig. 5.

CONCLUSIONS

The equation $F = -4.78(D_L/D_b)^2 + 25.05(D_L/D_b) + 2.89$, characterizing the dependence of maximum axial force at helical rolling from the ratio between the rolls diameter and the diameter of blank piece with constant reduction $\varepsilon = 6\%$ (shown in dotted line) has been obtained. The ratio of determination was equal to $R^2 = 0.92$. 

Fig. 4. Force trends for tests II-3 (a) and II-6 (b).

Fig. 5. Values of maximum axial force.
From the data it is possible to draw the conclusion that during the rolling of thicker profiles essentially a high disorder of values of forces is observed, that can be possibly explained by the increased influence of the following factors - features of internal and contact friction at the blank piece, its rheology, features of the deforming tool calibration.

The measured values of the axial force (up to 38 kN) evidence the principal possibility of the combined process of rolling-pressing realization with high values of the angles at the joint of the channels of the ECA-matrix (140° - 150°). It was established that after reaching of the force peak, there is a blank piece bend, thus, during the realization of the combined process, the main danger here is not in the lack of force, but in the possibility of a blank piece bend between the rolls and the matrix. Besides that, the value of the force can be raised a little by using of notched rolls at maximum reduction. The obtained results are comparable to results of research on similar profiles piercing forces on three-roll mills [9-10].

The results of this study can be used for the optimization of the process of continuous blank pieces piercing into the sleeve, and as results containing data on the reserve of axial force (friction forces) of the helical rolling.

REFERENCES

Short Communication

BREAKDOWN BEHAVIOUR DURING REANODIZATION
OF THICK POROUS ANODIC ALUMINA IN AQUEOUS
AND NON-AQUEOUS SOLUTIONS

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ABSTRACT

A comparative study towards reanodization of thick (22 µm) porous anodic alumina coatings in aqueous and non-aqueous electrolyte solutions is performed. The kinetics of pore-filling and breakdown characteristics during reanodization demonstrate unanticipated development such as some persistence in voltage growth in aqueous environment and extremely sharp voltage drop at breakdown threshold in non-aqueous one. These findings could be most probably assigned to the irregular structure and complicated phase composition of thick porous coatings.

Keywords: anodic aluminium oxide, reanodization, breakdown voltage.

EXPERIMENTAL

The kinetics of pore-filling and breakdown behavior during re-anodization of porous anodic oxide films on aluminium are studied in two different (aqueous and non-aqueous) electrolytes - aqueous borate electrolyte (ABE) and ammonium salycilate in dimethylformamide (0.1M AS/DMF). Porous films are formed in 15 % sulfuric acid solution at current density 5x10^{-3} A cm^{-2} for 180 min. Under these conditions porous layers with a thickness of approximately 22 µm are formed [1]. The re-anodization is carried out at current density 1x10^{-3} A cm^{-2} for 1 hour. All studies were performed at room temperature. All these electrochemical procedures took place using two-electrode cell of working and auxiliary (Pt grid) electrodes, and a home-made high voltage galvanostat (600 V, 0.5 A). The formation voltage was controlled and recorded on a precision multimeter (Mastech MS 8050) along with a PC-based data acquisition system.

RESULTS AND DISCUSSION

As a result of these studies a series of re-anodization kinetic \(U(t)\)-curves are produced and are characterized with good reproducibility. An example of re-anodization curves derived using various electrolytes is presented in Fig. 1. It is interesting to note that in the kinetic curves shown, some peculiarities could be observed as well. In re-anodization in ABE, persistence in the values of voltage for a sizable period of time after reaching 150 V is observed. The emergence of breakdowns begins in about 3000 s which is quite unexpected. On the other hand, the curve recorded by pore-filling in 0.1M AS/DMF shows sharp voltage drop of approximately 600
Fig. 1. Kinetic curves of pore-filling of porous matrices formed in 15% sulfuric acid solution at current density 5.0 mA cm\(^{-2}\) for 180 min. Reanodization was carried out at current density 1 mA cm\(^{-2}\) for 1 h.

volts at the first breakdown, compared to only 100 V in 1M AS/DMF [2]. Furthermore, comparing both curves a significant difference within the breakdown oscillations’ amplitude is obvious.

**CONCLUSIONS**

A series of re-anodization kinetic \(U(t)\)-curves is derived and they demonstrate very good reproducibility. The special features observed in the kinetic \(U(t)\)-curves for both electrolyte solutions are probably due to the large thickness of porous matrix, suggesting some peculiarities in the structure and phase composition of the porous part of the film. Furthermore, tenfold lower concentration of AS/DMF solution reveals a significant effect on the first breakdown as well.

**REFERENCES**


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Results and the discussion provided should be clear and concise.

Conclusions
The main conclusions of the study have to be presented in a short Conclusions section.

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