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Humans - Valuable Resource for Foundry Industry Development

Split, June 16th – 18th, 2021

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PREFACE

Knowledge is becoming an increasingly important resource for economic development. The Republic of Croatia is facing the challenges of the world economy, with the aim to meet certain requirements in shaping the education system. Ensuring the quality assurance of the education system is just one of the requirements set up as a continuous mission of University of Zagreb Faculty of Metallurgy and other co-organizers from the high-education. As the level of education of the population affects the progress of the economy, it is extremely important for the Republic of Croatia to increase the ratio of highly educated persons. In recent years, the ratio of the highly educated population of the Republic of Croatia has been growing, but in comparison with Europe, Croatia is still lagging behind. In order to increase the share of highly educated persons, it is necessary to invest in the quality of education, both in higher education and in secondary and primary education. This would increase awareness of the importance of education, which would ultimately result in an increase in the ratio of highly educated and competent professionals.

Metal industry as a base branch represents an important factor contributing to the economic potential of each country. Current market development as well as technical and economic objective, the production of high-quality, low-cost and environmentally friendly casting, requires application of recent and advanced materials, as well as production technologies, followed and supported by understanding of production process. The metal industry has been recognized as a "driving subdivision" of economy development.

Until the recession and deepening of the economic crisis in Croatia, companies operated stably, focused on streamlining production, investing in technology and employee's education, increasing product quality and productivity, developing innovation and fighting for the market. The recession and economic crisis have slowed the strengthening of this economic activity. In order to overcome and mitigate the negative results caused by falling orders and reduced production, companies have developed new production programs and sought new customers and markets in order to maintain good positions within their market niches. Taking into account the growing need of large (global) producers for small series products, it is assumed that it will build a network of suppliers in which Croatian producers can be included. Small quantities are sufficient to employ their production capacities, and with a skilled workforce and new market opportunities, the growth of existing companies is expected, as well as the establishment of new ones. By investing in modern equipment and production certification, metal producers indicate a desire for growth. The main features of Croatian industry are stable product quality and reliability in accordance with EU standards, while on the other hand it is important to invest in available professional workforce, targeted support of scientific institutions, good production infrastructure with emphasis on modern technologies and transport links to the world.

Despite the recognizability and importance of the profession, the profession is underestimated by the amount of the average net monthly salary per employee in legal entities. The gross value added of the product is also indicative. Since the Croatian market is too small for significant production growth, companies in the observed activity primarily direct their production capacities to EU countries, which also means increasing the level of productivity of assets and labor. Competitiveness can be based exclusively on modern technology, efficient production processes but also on a highly skilled workforce. All this requires investment in infrastructure and educational study programs that should strive to acquire primarily practical knowledge and skills with an emphasis on the development and application of modern materials and technologies, in order to change this status of the Republic of Croatia.

Therefore, the motto of the ***19th International Foundrymen Conference*** is focused to the **HUMANS** as a **valuable resource for foundry industry development**. Human resources have an unavoidable role in scientific, technological and practical aspects concerning research, development and application of casting technology with the common perspective – increase of competitiveness.

Special attention will be focused towards the competitiveness ability of foundries, improvement of materials features and casting technologies, environmental protection as well as subjects connected to the application of castings.

During this Conference 49 papers will be presented in hybrid mode (online and in situ) due to pandemia of COVID-19 virus. In this Conference scientists from 14 countries (Australia, Austria, Bosnia and Herzegovina, Croatia, Czech Republic, India, Kosovo, Poland, Romania, Spain, Serbia, Slovenia, Slovakia, United States of America) recognized the importance to be a part of this scientific event. Book of Abstracts of the 19th International Foundrymen Conference includes summaries of the papers. The Proceedings book consists of papers *in extenso* published in electronic format (USB). Full length papers have undergone the international review procedure, done by eminent experts from corresponding fields, but have not undergone linguistic proof reading. Sequence of papers in Proceedings book has been done by category of papers in following order: plenary lectures, invited lectures, oral and poster presentation, and inside the category alphabetically by the first author's surname.

Within the Conference Student section is organized. This is an opportunity for industry to meet and recruit human resources as a main potential for business development. Coexistence of material science and sustainable technology in economic growth represent a knowledge transfer between small and medium enterprises' (SMEs´), industry and higher education institutions. Higher education at the Faculty of Metallurgy (HEI), conceived through the program and the learning outcomes, is based, inter alia, on promoting students' scientific and research work on applied topics, enabling ambitious and creative young people to become independent problem solvers, developing and supporting their curiosity, analytics and communication: **Graduates like the labour market needs!**

This occasion represents an opportunity to discuss and increase the mutual collaboration between HEIs' and industry with the aim of information exchange related to advanced experience in foundry processes and technologies, gaining the new experience in presentation and / or teaching methods and techniques within lifelong learning process.

The organizers of the Conference would like to thank all participants, reviewers, sponsors, auspices, media coverage and all those who have contributed to this Conference in any way.

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CONTENTS

19th INTERNATIONAL FOUNDRYMEN CONFERENCE
Humans - Valuable Resource for Foundry Industry Development
Split, June 16th-18th, 2021
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CHEMICAL LEACHING OF SUBBITUMINOUS COAL FROM THE BOGOVINA - EAST FIELD (BOGOVINA BASIN, SERBIA) USING HYDROCHLORIC ACID

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Poster presentation
Original scientific paper

Abstract

All over the world, huge amounts of coal are available and it is utilized in large quantities for different purposes. The coal combustion causes environmental problems, such as the release of toxic metals and other pollutants into wastewaters, emission of noxious gases, produce of ash dumps, etc. One of the solutions for the reduction of environment pollution, caused by coal combustion, is demineralization and desulphurization of coal. In that sense, treatment of coal by different chemical reagents becomes important. A subbituminous coal, used in this study was taken from the Bogovina - East field (Lower Miocene ≈ 20-16 Ma) of the Bogovina Basin, which is located in Eastern Serbia. The sample was selected based on the previous studies of Bogovina - East field which indicated a high amount of sulphur, relatively high percent of mineral matter and considerably amount of liptinites for humic coal, which represent the most reactive maceral group. The aim of the study was an attempt to reduce the amount of ash and sulphur in coal, keeping the organic matter unaltered as possible, using simple and cheap method e.g. treatment with hydrochloric acid (HCl). Ash and total sulphur content was determined before and after HCl leaching. In addition characteristics of initial and treated coal were tracked by X-ray diffraction (XRD) analysis and Fourier-transform infrared (FTIR) spectroscopy. The obtained results showed that the high percentage of deashing (≈ 80 %) was achieved with cheap hydrochloric acid. XRD analysis of ash before and after sample treatment provides more information about mineral phases in coal and effects of chemical leaching. FTIR analysis indicates almost no changes in structure of coal organic matter after treatment by HCl, which is important for further coal usage (e.g. combustion). On the other hand, the applied chemical leaching with HCl had low impact on the sulphur content in Bogovina coal (desulphurization percentage ≈ 8 %). Therefore, in future research other reagents for efficient desulphurization should be investigated.

Keywords: *coal, acid, demineralization*

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INTRODUCTION

Coal may be defined as a sedimentary rock containing usually less than 50 % of mineral matter [1]. Coal is composed of organic, combustible phase and inorganic, mineral matter [1]. The inorganic mineral matter of coal can have various forms such as: coal discrete crystalline particles, amorphous mineral parts, inorganic elements chemically bonded to the organic phase and compounds dissolved in water absorbed by the coal pores [2]. Complex organic matter of coal is mainly composed of insoluble part (kerogen), whereas content of soluble (extractable) organic matter (bitumen) is commonly less than 5 %.

During the consumption of coal, i.e. coal combustion, byproducts that have damaging environmental effects are released. One of the ultimate environmental "culprits" in coal is sulphur. During coal combustion, sulphur causes gases, SO_2 and SO_3 to be released into the atmosphere together with ash and soot [3, 4]. In addition, the higher sulphur content in coal is considered to be harmful because sulphuric gases can cause corrosion and other consequences that require more frequent equipment maintenance [4].

Therefore investigations concerning demineralization (deashing) and desulphurization of coal have the substantial importance. These processes can be carried out by physical treatment, chemical treatment and microbial treatment [5].

For bioleaching of coal, in order to decrease the amount of sulphur, different microorganisms are used. In study of Mishra et al. (2018) [3] lignite was treated with *Leptospirillum ferriphilum* resulting in percent of desulphurization of 56 %, whereas small amounts of added surfactant, Span 80 decreased sulphur content for 61 %. The studies of coal desulphurization were conducted also with cultures of *A. ferrooxidans*, *A. thiooxidans*, *Sulfolobus acidocaldarius*, *Pseudomonas putida* and *Pseudomonas aeruginosa* [4].

Physical treatment of coal such as electrostatic separation resulted in decrease of ash content from 43 % to 18 % [6].

Chemical treatment for producing cleaner coal could be carried out by using acid solutions, alkali solutions, combine treatment of coal with acids and alkalis, oxidizing agents, chelating agents, and stepwise washing by acids [5]. In one of the studies, the removal of 70% of the organic sulphur was achieved when hydroiodic acid was applied as a single reagent. Applying of coal stepwise acid leaching (HCl and HNO_3) resulted in the ash and sulphur content decrease from 7.9 % to 0.6 % and from 2.6 % to 1.4 %, respectively [7]. An important oxidizing agent for chemical treatment of coal is H_2O_2. In study of Vasilakos and Clinton [8], 90 % of pyritic sulphur was removed from coal using H_2O_2/H_2SO_4 solution. Use of alkali solutions (5 % NaOH) decreased ash content from 28.2 % to 1.6 %, and from 7.0 % to 0.9 % in two studied coals samples [9]. The combined acid and alkali solutions for leaching coal were also applied for coal demineralization. Treatment of coal with NaOH followed by acid solution leaching under the pressure, resulted in demineralization percent of 90 % [10].

Results of coal leaching depend on coal composition, particle size, reaction time, temperature, and reagent (solution) concentration.

MATERIALS AND METHODS

A subbituminous coal, used in this study was taken from the Bogovina - East field (Lower Miocene ≈ 20-16 Ma) of the Bogovina Basin (Eastern Serbia). The sample was selected based on the previous studies [11] of Bogovina - East field which indicated high amount of sulphur,

relatively high percent of mineral matter and considerably amount of liptinites for humic coal, which represent the most reactive maceral group.

The sample was air-dried and ground to the particle size < 200 μm. Initial coal sample was characterized by a standard proximate analysis method. Proximate analysis included determination of analytical moisture, volatile matter, ash and fixed carbon. The analysis was performed according to ASTM-D-3172 standard. The results are shown in table 1, along with total sulphur content, which was determined by the Eschka method.

The coal sample was treated with hydrochloric acid (10 % solution) in a glass beaker for 30 minutes at three different reaction temperatures, while stirred at 250 rpm. Experiments were performed at 30 ^{o}C (A-1), 60 ^{o}C (A-2), and 90 ^{o}C (A-3). At the end of the reaction period the treated mixture was vacuum filtered. After filtration, the treated coal was washed with hot distilled water (until pH=7) and firstly was dried at room temperature, then was dried at 105 ^{o}C.

X-ray diffraction (XRD) analysis was used to determine and monitoring the mineral composition of the samples' ashes. Prior to XRD analysis, samples were subjected to low temperature ashing (LTA) process. XRD analysis was carried out on a Philips X-ray diffractometer model PW-1710.

Fourier-transform infrared (FTIR) analysis of untreated and treated coal samples was performed on a Thermo Fisher Scientific Nicolet IS-50. Recording was done by ATR (Attenuated Total Reflectance) technique in the range from 4000 cm^{-1} to 400 cm^{-1}, and 32 scans at resolution 4.

Table 1. Characteristics of initial Bogovina coal sample

Parameter	Content (wt. %)	
Moisture	16.82	Proximate analysis of coal sample
Volatile meters	38.44	
Ash	17.52	
Fixed carbon	27.22	
Total sulphur	6.03	

RESULTS AND DISCUSSION

The results of the acid leaching of coal sample at different temperatures are presented in Table 2.

Table 2. Ash and total sulphur content in initial coal and leached coal samples after treatment by HCl solution (10 %) at different temperatures for 30 minutes

Sample	Temperature (^{o}C)	Content of ash in sample (wt. %)	Content of total sulphur in sample (wt. %)
Initial coal sample	/	17.52	6.03
A-1	30	3.65	5.58
A-2	60	3.62	5.51
A-3	90	3.68	5.53

The content of ash decreased significantly (≈ 80 %) by HCl treatment, while the content of total sulphur decreased only slightly (≈ 8 %). The obtained results (Table 2) indicate that temperature does not affect deashing and desulphurization of Bogovina coal by HCl. Ash and sulphur removal slightly increased by heating from 30 °C – 60 °C, and then insignificantly decreased in the temperature range 60 °C – 90 °C. The optimal temperature for both processes is 60 °C. Negligible impact of HCl on desulfurization, associated by absence of pyrite in XRD spectrum of coal sample (Figure 1a) may imply that majority of sulphur is associated with organic matter. Therefore, other reagents for desulphurization of Bogovina coal should be investigated. Deashing efficiency at 30 °C (7.46 %) and 60 °C (8.62 %) was rather similar, and consequently, energy consumption for heating from 30°C to 60°C in such case is not reasonable.

Changes in qualitative composition of mineral matter caused by chemical leaching are followed by XRD, performed on LTA of the initial and treated coal (Figure 1). LTA of initial Bogovina coal dominates by amorphous matter, whereas other constituents are quartz (Q), olivine (O), calcite (C) anhydrite (A), mica (M) and unidentified phase (U) (Figure 1a). Amorphous matter also dominates in LTA of leached coal (Figure 1b). As expected, treatment with HCl resulted in removal of calcite, anhydrite and mica, as well as unidentified phase. Scarce distribution of minerals in LTA of leached coal, represented mostly by resistant quartz, is consistent with efficient deashing (≈ 80 %). In addition to quartz, the coal residues obtained by HCl treatment contains low amount of olivine (Figure 1b), which is also relatively prone to acidic dissolution resulted from ion-exchange reaction between Mg^{2+}/Fe^{2+} ions and H^+ ions [12].

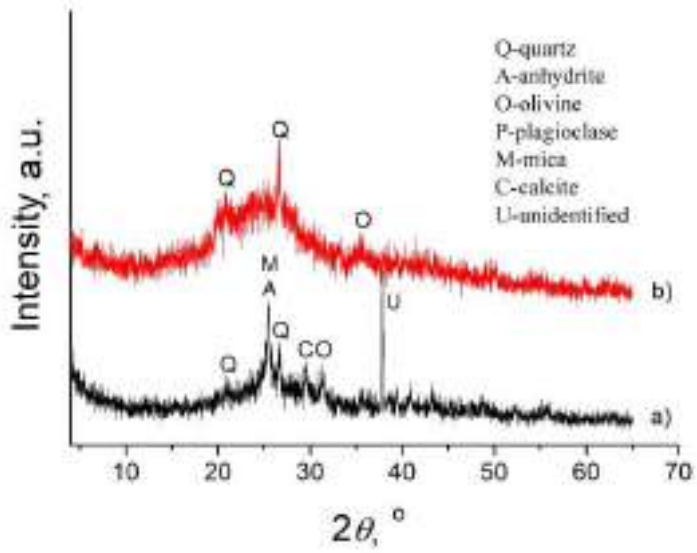

Figure 1. XRD spectra of (a) initial Bogovina coal sample and (b) coal sample after leaching with 10 % HCl at 60 °C (A-2)

FTIR spectra indicate almost no change in structure of coal organic matter caused by HCl treatment (Figure 2) that is important for further utilization of coal (e.g. combustion).

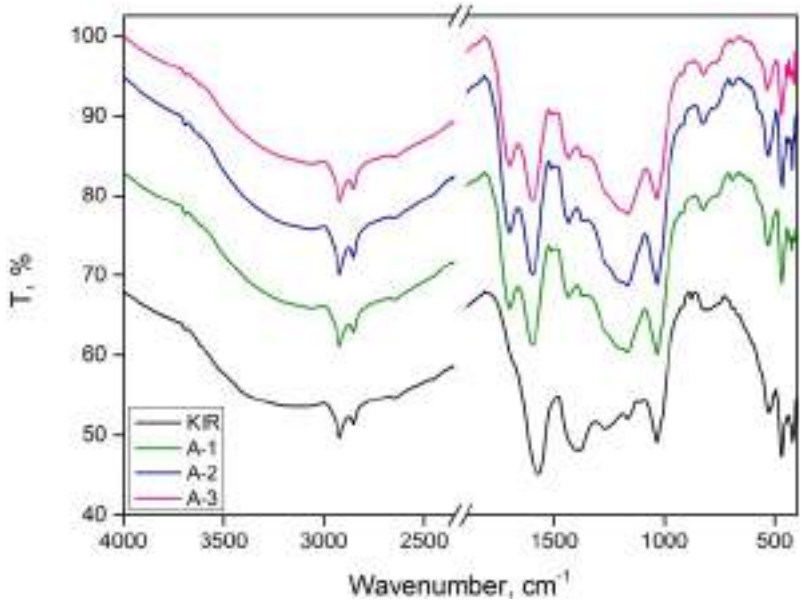

Figure 2. FTIR spectra of initial coal sample (KIR) and treated coal samples (A-1 – A-3)

CONCLUSIONS

The current study concerns an investigation of demineralization (deashing) and desulphurization of Lower Miocene subbituminous coal originating from the Bogovina - East field (Bogovina Basin, Eastern Serbia) by treatment with 10 % HCl solution at different temperatures (30 ^{o}C, 60 ^{o}C and 90 ^{o}C) for 30 minutes. The content of ash decreased significantly (≈ 80 %) by HCl treatment, while the content of total sulphur decreased only slightly (≈ 8 %). Therefore in future research other reagents for desulphurization should be investigated. The obtained results indicate that temperature does not affect deashing and desulphurization of Bogovina coal by HCl. XRD data showed that by acidic leaching with HCl complete removal of calcite, anhydrite and mica from LTA of the initial coal is achieved, resulting in very scarce distribution of minerals in LTA of the treated coal, represented by resistant quartz and low amount of olivine, only. The FTIR spectra signify that the structure of coal organic matter did not changed substantially after HCl treatment. Accordingly, we can assume that the calorific value of coal remained unaltered after used acidic leaching.

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