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Assessment of the chemical, microbiological and toxicological aspects of post-processing water from underground coal gasification

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ABSTRACT

The purpose of this paper is to provide a comprehensive characterisation (including chemical, microbiological and toxicological parameters) of water after the underground coal gasification (UCG) process. This is the first report in which these parameters were analysed together to assess the environmental risk of the water generated during the simulation of the underground coal gasification (UCG) process performed by the Central Mining Institute (Poland). Chemical analysis of the water indicated many hazardous chemical compounds, including benzene, toluene, ethylbenzene, xylene, phenols and polycyclic aromatic hydrocarbons (PAHs). Additionally, large quantities of inorganic compounds from the coal and ashes produced during the volatilisation process were noted. Due to the presence of refractory and inhibitory compounds in the post-processing water samples, the microbiological and toxicological analyses revealed the high toxicity of the UCG post-processing water. Among the tested microorganisms, mesophilic, thermophilic, psychrophilic, spore-forming, anaerobic and S-oxidizing bacteria were identified. However, the number of detected microorganisms was very low. The psychrophilic bacteria dominated among tested bacteria. There were no fungi or *Actinomycetes* in any of the water samples. Preliminary study revealed that hydrocarbon-oxidizing bacteria were metabolically active in the water samples.

The samples were very toxic to the biotests, with the TU_{50} reaching 262. None of biotests was the most sensitive to all samples. Cytotoxicity and genotoxicity testing of the water samples in *Vicia* uncovered strong cytotoxic and clastogenic effects. Furthermore, TUNEL indicated that all of the water samples caused sporadic DNA fragmentation in the nuclei of the roots.

1. Introduction

Underground coal gasification (UCG) is currently regarded as a promising alternative method of obtaining energy from coal (Chen et al., 2011; Eftekhari et al., 2012; Liu et al., 2011; Prabu and Jayanti, 2012; Stańczyk et al., 2012). Intensified research on the UCG process began in the 1930s in the former Soviet Union. Large-scale studies were also carried out in the United States in the 1970s and 1980s (Shafirovich and Varma, 2009). In Europe, UCG process research was conducted from 1982 to 1999 (Wiatowski et al., 2012). At present, wide research in the field of UCG processing continues in China and Australia (Kapusta and Stańczyk, 2011; Liu et al., 2007, 2009; Yang, 2007; Yang et al., 2008). In 2007, studies were resumed in Europe, through the HUGE Project (Hydrogen Oriented Underground Coal Gasification for Europe, 2007–2010), coordinated by the Central Mining Institute in Poland. The UCG process is based on the direct injection of a gasifying agent to the ignited coal seam followed by collection of a gas product at the surface (Kapusta and Stańczyk, 2011). Post-processing water is generated both during the UCG process and after its completion. During the reactor operation time, post-processing water mainly derives from condensates separated during gas collection and treatment. After the termination of the process, condensates are mostly separated from the warm and humid gas coming out of the post-reaction zone and mine water flowing into the post-reaction zone. During UCG, a number of

Abbreviations: UCG, underground coal gasification; PAHs, polycyclic aromatic hydrocarbons; TU, toxic units; BTEX, benzene, toluene, ethylbenzene, xylene; EC, effective concentration; BOD-5, five days biochemical oxygen demand; COD, chemical oxygen demand; EC_{20}, threshold toxicity; EC_{50}, median toxicity; LC, lethal dose

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heterogeneous and homogenous reactions take place (Kapusta and Stańczyk, 2011; Yang et al., 2008) that contaminate UCG post-processing water with hazardous chemicals, such as organic aromatic compounds, including benzene, toluene, ethylbenzene, xylene, phenols and polycyclic aromatic hydrocarbons (PAHs). Additionally, large quantities of heavy metals can be released from coal tars and ashes produced in the volatilisation process, which is favoured by the high temperature of the process and the presence of numerous chemicals (Humenick and Fletcher Matox, 1978; Liu et al., 2006, 2007; Stuermer et al., 1982; Yang, 2009).

UCG post-processing water resembles coke wastewater, in terms of their physico-chemical compositions (Kim et al., 2008), and both are subject to legal regulations related to their removal and treatment. Water Framework Directive 2000/60/EC, article 16 (Directive 2000/60/EC, 2000) contains a list of priority hazardous substances, some of which were identified in the UCG post-processing water (benzene, naphthalene, PAHs and heavy metals).

Although the problem of water pollution generated during UCG has been described, no full analysis of post-processing water has been performed, not only in terms of its physico-chemical characteristics but also in terms of the toxicological and microbiological characteristics. Microbiological and toxicological studies are very relevant for environmental risk assessment and developing effective methods to treat the contaminated water. The only attempt at toxicity analysis was described by DeGraeve (1980). The authors described bioassays which were used to determine the toxicity of the untreated condenser water from the Hanna-3 UCG experiment (Wyoming, USA) and its major toxic constituents (phenol, ammonia, and phenol and ammonia mixture) to fathead minnows (*Pimephales promelas*), rainbow trout (*Salmo gairdneri*) and *Daphnia pulicaria* (DeGraeve, 1980). Their study results indicated a very high toxicity of the samples that ranged from LC_{50}=0.1 to 0.18 percent, depending on the assay.

Whole-sample toxicity programmes have been promoted since the 1970s in the USA. With the implementation of the Water Framework Directive, the use of biotests in Europe is expected to increase significantly (Wahdia and Thompson, 2007). There are no EU regulations on the application of the bioassays for monitoring effluents. However, in some countries, bioassays are utilised for effluent control (Direct Toxicity Assessment and Special Waste Regulations in UK; Wahdia and Thompson, 2007).

Due to the complexity of effluents, a battery of bioassays should be applied for toxicity screening. Organisms from different taxonomic groups should be chosen for the battery. According to Pessala et al. (2004), the combination of tests should be selected individually for each sample type. Pollumaa et al. (2004) proposed bioassays with luminescent bacteria, protozoa, crustaceans and algae for evaluating the toxicity of oil-shale industry solid wastes polluted with heavy metals and hydrocarbons. In our project, a battery of six bioassays was applied, comprising bacterial, protozoan, crustacean and plant assays. No single bioassay was found to be most sensitive for all of the samples. Luminescent bacteria are very sensitive to simple organics with EC_{50} values in the range of 0.1 to 10 mg/L (Kaiser and Palabrica, 1991). However, the toxicity effects of nonpolar (e.g., hydrocarbons and their hydrophobic derivatives) and polar toxins (e.g., phenols), are additive and depend on the lipophilicity of the compounds. Further, Spirotox with *Spirostomum ambiguum* is much more sensitive than the bacteria to heavy metals (Nałęcz-Jawecki and Sawicki, 1998), but is less sensitive to organics.

Of note, the effluents contain thousands of compounds and only a small fraction are identified chemically. Blum et al. (2011) suggested monitoring heterocyclic compounds, as they are typical constituents of coal tars, their aqueous solubilities are several times higher than those of PAH and BTEX, and their toxicity is high.

Nakajima et al. (2013) monitored the toxicity of effluents obtained from hydrothermally treated coals. Their results suggested that the increased toxicity in *Daphnia magna* assays was caused by lower molecular weight compounds (phenols) formed during the treatment. Borrely et al. (2004) applied biotests with daphnia and luminescent bacteria to study the detoxification of effluents with an electron beam accelerator and found that in some cases the toxicity increased due to the formation of hydrogen peroxide.

The aim of this study was to carry out a comprehensive characterisation of post-processing water samples, which were collected during a UCG experiment performed by the Central Mining Institute in Poland. The assays included chemical, microbiological and toxicological analyses.

2. Materials and methods

2.1. Design of the UCG experiment

The experiment was carried out on a UCG pilot plant. The experimental installation enables simulation of the UCG process *in ex situ* conditions. Black coal from the Wieczorek coal mine was used. Selected parameters of used coal are shown in Table S1. The UCG process experiment was conducted for a period of 96 h. During the first 48 h of the process, oxygen was used as a gasifying agent. Oxygen flow to the reaction zone was constant and was 4 m^3/h. Between 48 and 82 h after the initiation of the process, a significant deterioration occurred in the quality of the produced gas (stream flow ratio 6 m^3/h). Due to this deterioration, after 82 h, the process was carried out with air enriched by oxygen (oxygen content 44 vol%). A simplified scheme of the experiment installation is presented in Fig. S1.

2.2. Post-processing water sampling

The post-processing water samples were collected at three steps of the UCG simulation experiment, e.g., after 12 h (Sample I), 48 h (Sample II) and 72 h (Sample III). The purpose of this sampling procedure was to determine if the relevant phase of the process has a significant influence on the wastewater composition. For the microbiological analysis, the water samples were collected in sterilised 1-L polyethylene flasks. The samples were transported to the laboratory for chemical, toxicological and microbiological assays, which were performed immediately.

2.3. Chemical analyses

Chemical analyses of the water samples were conducted in the Laboratory of Water and Sewage Analysis of Główny Instytut Górnictwa (Central Mining Institute). The samples were filtered to remove coal tars and other undissolved residues. The inorganic contaminants (such an ammonia, nitrogen, free and bound cyanides, sulphates, B, Cr, Ti, Pb, Fe, Cd, Cu) and organic pollutants (phenols, BTEX and PAHs) were measured. The chemical analyses were carried out according to standard analytical methods. To determine pH and conductivity, potentiometry methods were used according to PN-90/C-04540.01 and PN-EN 27888:1999 standards. Ammonia nitrogen was determined by Flow Injection Analysis (FIA) with gaseous diffusion and spectrophotometric detection (according to PN-EN ISO 11732:2007). The sulphates were determined by a gravimetric method after precipitation with barium. Free- and bound- cyanides and phenolics were determined by Segment Flow Analysis (SFA) with spectrophotometric detection (PN-EN ISO 14403:2004; PN-EN ISO 14402:2004). Boron and other metals (Cr, Zn, Cd, Cu, Mo, Ni, Pb, and Ti) were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (PB-07.22v.2.0). The BOD-5 and COD indices were determined by electrochemical and spectrophotometric methods (PN-EN 1899-1:2002; PN-EN 1899-2:2002; PB-07.26v.1.10). For the determination of BTEX compounds, gas chromatography coupled with a mass spectrometer (GC–MS) was used (Agilent Technologies 7890A). To determine the levels of 15 polycyclic aromatic hydrocarbons, solid phase extraction (SPE) high-performance liquid chromatography (HPLC) on Supelclean ENVI-C18 cartridges was carried out using the Agilent Technologies HPLC 1200 Series system.

2.4. Toxicological analysis

Organisms differ in their sensitivity to various groups of chemicals. Thus the battery of six bioassays, testing for both acute toxicity and chronic toxicity, comprising bacterial, protozoan, crustacean and plant assays were chosen. The following commercially available tests were used for the ecotoxicological assays: