

characterized by spectroscopic methods. This compound can be used in the synthesis of thermally stable polymers or as precursors for the production of medicines.

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A STUDY OF THE CHEMICAL FORMS OF COBALT AND COOPER IN ASH FROM BIOMASS

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ABSTRACT

The total content of metals in combustion waste do not indicate the actual hazard to the environment, it is necessary to establish chemical speciation and their mobility. Individual fractions of metals can be separated and evaluated by performing a sequential extraction. The sequential extraction provides data on the concentration of individual fractions of elements in ash, on the degrees of their mobility and also on potential bioavailability. The sequential extraction of industrial ash from biomass from power station in Arłamów (Poland) has been performed, in accordance with the five-step Tessier procedure, including preliminary leaching of ash with

distilled water and digesting of ash in HNO₃/HClO₄ mixture after the fourth step of extraction. The content of Co and Cu was marked in the following fractions, defined as: 1) soluble in water, 2) exchangeable, 3) soluble in acids, 4) oxide, 5) pseudosulfide, 6) residual. The results of the analyses of chemical fractions of metals were compared to the total contents of Co and Cu in the studied ash from single-step mineralization process. The concentrations of metals were determined by the flame atomic absorption method (FAAS).

KEYWORDS

ash, biomass, chemical speciation, heavy metal, FAAS

INTRODUCTION

Until recently, the power industry in Poland was mainly based on burning hard coal and brown coal. In recent years, the power stations have implemented energy collection systems from renewable sources by using biomass as fuel, co-combustion with coal or combustion independently. Usually, for energy purposes, one uses woody biomass (wood scraps, shavings, chips, sawdust), animal production waste and biogas [1]. Biomass, as compared to coal, has the same element composition, the differences occur in the quantity of individual elements and chemical compounds. Different quantitative composition translates to different conditions of ignition and combustion. During the process of biomass combustion the ash formation percentage is significantly lower (2 - 6%) than during the process of coal combustion (about 22%). The amount of combustion by-products depend on the type of biomass being burned [2]. Ash from biomass combustion is a new class of combustion waste. There are articles on that subject in literature but these articles do not allow to present the full characteristics of such ash. It is known that such ash contain higher levels of CaO, MgO, Na₂O, K₂O, P₂O₅ and lower levels of SiO₂, Al₂O₃ and TiO₂ with respect to the coal ashes. Moreover, such ash shows the contents of glass phase and also lower softening temperatures (750 - 1000°C) and melting temperatures regarding coal ash. The data regarding the content of heavy metals in ashes from biomass, their chemical speciation and eventual bioavailability is fragmentary, therefore it is hard to predict their eventual influence on natural environment [3-5]

Cobalt and copper commonly occur in plant and animal organisms. High concentration of these elements impair human homeostasis, can lead to blood coagulation impairment, liver damage or gastrointestinal disorders [6-7]. Short- and long-term storage of ashes from biomass combustion can lead to excessive emission of these metals to the environment, polluting natural ecosystems.

Sequential extraction allows the simulation of natural and also anthropogenically changed environmental conditions. By performing subsequent extractions with the use of solutions with increasing aggression, it is possible to evaluate the potential mobility and bioavailability of metals [8].

The aim of the work was analysis chemical fractions of cobalt and copper in industrial ash from biomass combustion using sequential extraction.

MATERIALS AND METHODS**REAGENTS AND SOLUTIONS**

All chemicals and reagents were of analytical grade or higher purity and were obtained from POCH and Chempur, Poland. The solutions were prepared by dissolving appropriate compounds in doubledistilled water from the Water Purification System (SolPure 7 POLL LAB, Poland). Standard solutions were prepared from standard solutions for atomic absorption (Sigma-Aldrich Chemie GmbH, Switzerland) – the concentrations of all metals in standard solutions were the same and equals 1000 µg·cm⁻³ in 1% of HNO₃. Working standard solutions containing Co and Cu were prepared by serial dilution of the appropriately of standard solution for atomic absorption

PREPARATION OF SAMPLES

The object of the research was the ash from the power station in Arłamów, being the product of combustion of wood chips. The ash has been dried at room temperature for 14 days until to get air-dry state, and then it was triturated consecutively in ceramic and agate mortar. Such prepared ash had been stored in a hermetically closed container (PE) and used for laboratory research.

SEQUENTIAL EXTRACTION PROCEDURE

The process of sequential extraction of ash has been performed in accordance with the five-step Tessier procedure [9], including preliminary leaching of ash with distilled water and digesting of ash in HNO₃/HClO₄ mixture after the fourth step of extraction [10-11] (Figure 1). Research was performed on three (n = 3) parallel samples.

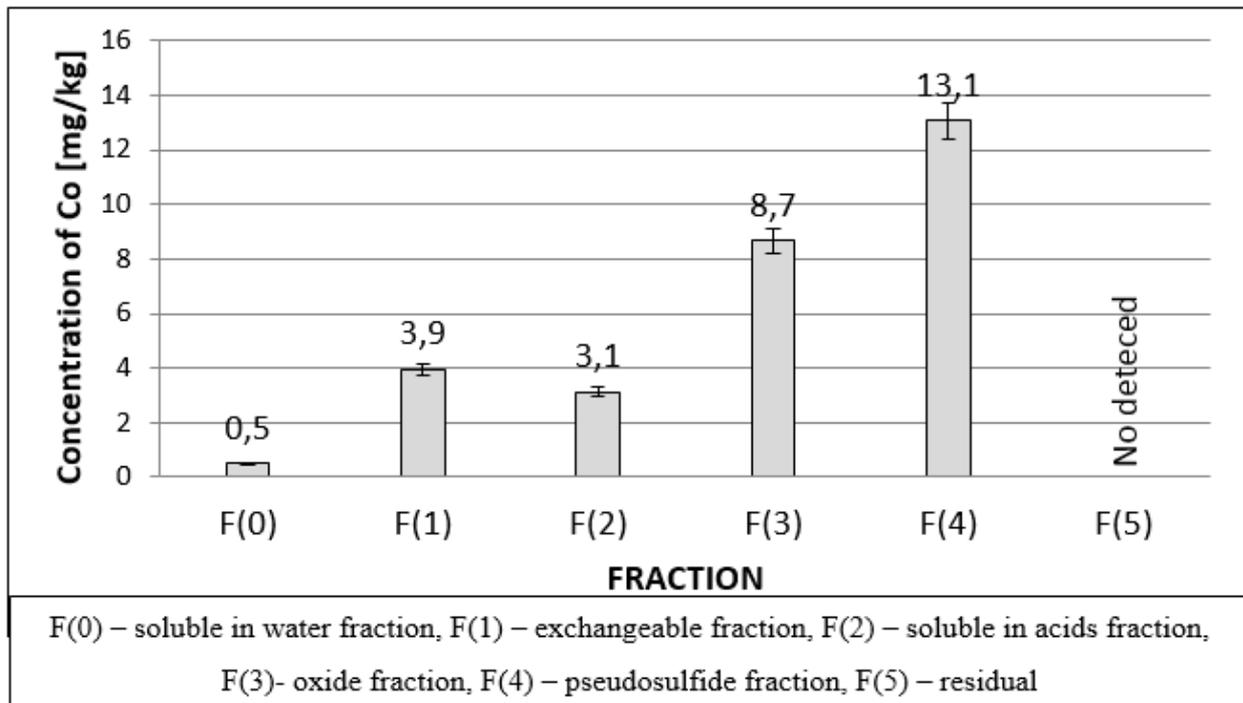


Figure 2 - The content of cobalt [mg/kg] in the samples of ash from biomass

In case of copper, has no been detected chemical forms Cu in soluble in water fraction. The dominant content of this metal has been identified in pseudosulfide fraction (42,3 mg/kg) and oxide fraction (44,2 mg/kg). The content Cu in other fractions constitute: exchangeable – 0,87 mg/kg, soluble in acids – 0,52 mg/kg and residual – 16,6 mg/kg (Figure 3).

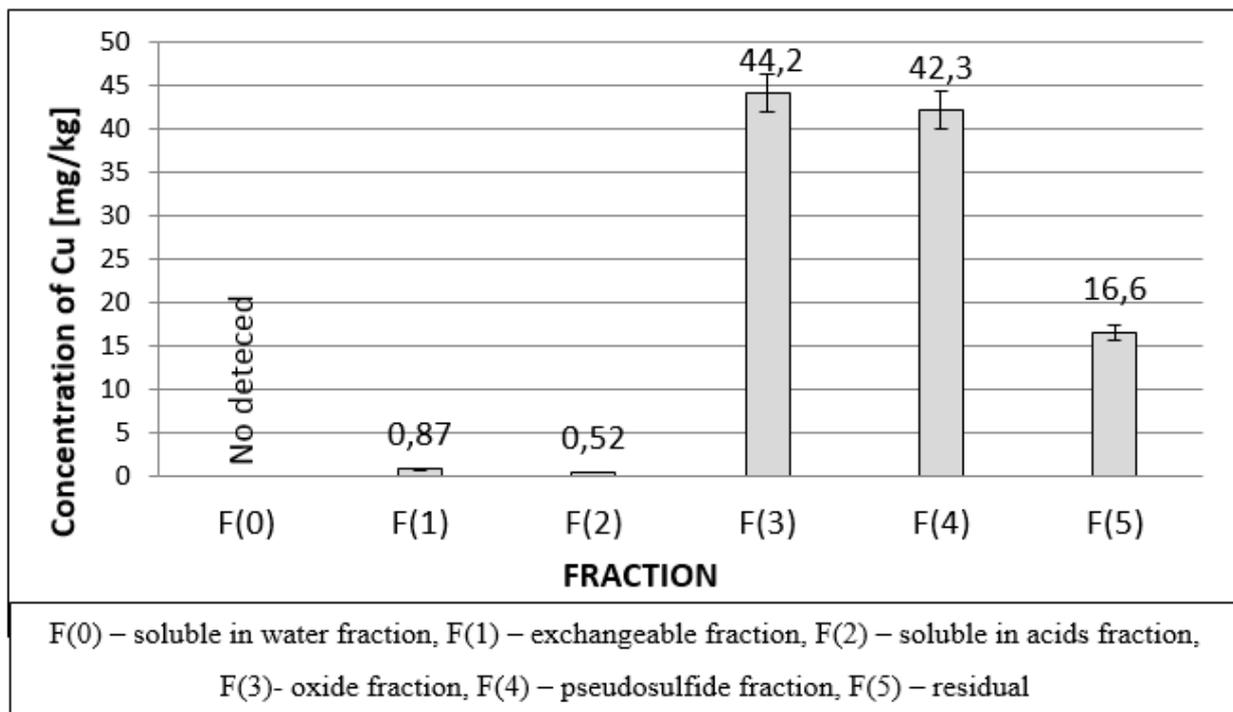


Figure 3 - The content of copper [mg/kg] in the samples of ash from biomass

The study fractions in the ash due to the increase content metals form ranks:

for **cobalt**: residual < soluble in water < soluble in acids < exchangeable < oxide < pseudosulfide

for **copper**: soluble in water < soluble in acids < exchangeable < residual < pseudosulfide < oxide

THE CHARACTERISTIC OF THE MOBILE FRACTION OF STUDY METALS

The analyse of the chemical fractions in ash allows to evaluate mobility and bioavailability studied metals in environmental conditions. The mobile forms Co and Cu are present in soluble in water, exchangeable (pH = 7) and soluble in acids (pH = 5) fractions. Metals contained in other fractions can only get through to the natural environment in specific conditions, that is, using more aggressive extractants (oxide and pseudosulfide fractions) or with the use of micro-organisms (pseudosulfide

fraction and residual). The conducted analysis indicates that mobile Co and Cu fractions in environmental conditions, that is, soluble in water, soluble in magnesium chloride and in acetate buffer, constitute in total 7,58 mg/kg (Co) and 1,38 mg/kg (Cu). The content of mobile forms of these metals with respect to their total content in ash, respectively Co (27 mg/kg), Cu (107 mg/kg) amounts to 25,9% (Co) and 1,32% (Cu) (Figure 4).

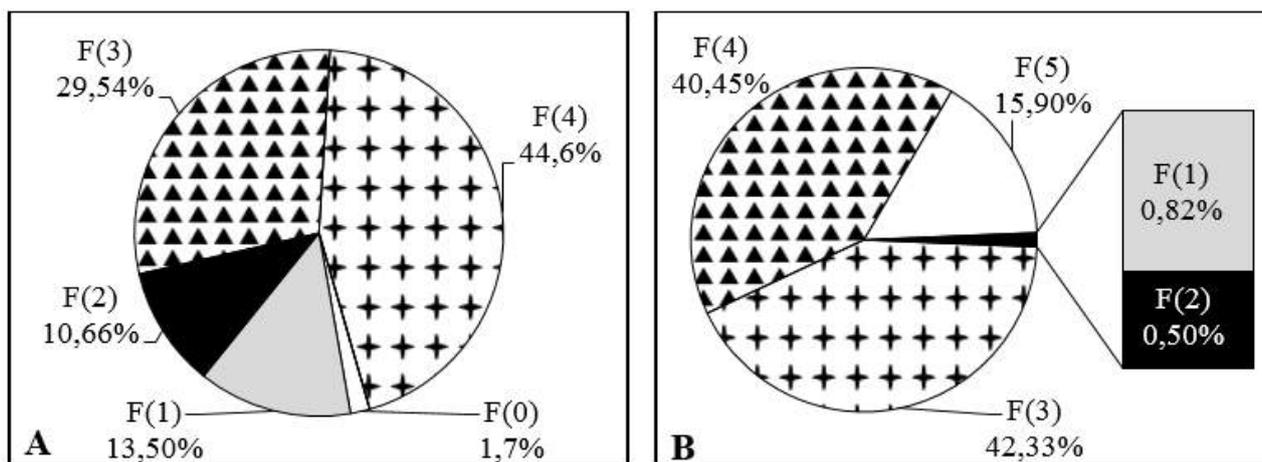


Figure 4 – The mobile fractions of cobalt (A) and copper (B) in industrial ash from biomass

MASS BALANCE

The mass balance allows to verify the obtained analytic results. The mass balance has been conducted by comparing the total content of metals in ash with the contents sum of individual metals in particular ash fractions, analyzed in solutions that emerged from sequential extraction. It has been established that the absolute result differences for the analyzed metals amount to: Co– 2,7 mg/kg; Cu – 2,9 mg/kg. Relative errors, calculated as a quotient of the absolute error and the exact value, amount to 9% (Co) and 2% (Cu).

CONCLUSIONS

A quantitative analysis of industrial ash from biomass combustion has been conducted regarding the total content and chemical speciation of Co and Cu. It has been established that the total content of metals in industrial ash amounts to 27 mg/kg (Co) and 107 mg/kg (Cu). Mobile fractions of the analyzed metals, which can undergo the leaching process to groundwater in environmental conditions, amount to: 25,9 % (Co) and 1,3 % (Cu) of their total content in ash.

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