XRD-XRF-ICP-GC Analytical System in Carboniferous Claystones and Mudstones Monitoring for the Non-Soil Reclamation of Coal Mine Waste Dumps (Silesian Coal Basin in Poland)

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Abstract: - Examination of wastes to evaluate their usefulness for utilization needs applying modern chemical testing methods. The XRD-XRF-ICP-GC set of test methods constitutes an integrated testing system enabling to conduct ecochemical examination of carboniferous claystones and mudstones. As far as the problem of time-consuming operations is concerned, the offered system of chemical testing in the form of an integrated XRD-XRF-ICP-GC assembly fits in a market-oriented field of activity of accredited chemical laboratories. Within a reasonable period of time, it allows to obtain information about mineralogical and chemical properties of carboniferous claystones and mudstones. It provides the full range of information beginning from mineral composition (XRD) through chemical composition including the number of elements and organic compounds (XRF-ICP-GC) up to the contents relating to the amounts of ingredients both organic and inorganic in the leaching tests (ICP-GC). The XRD-XRF-ICP-GC testing system proves to be of particular importance in obtaining reliable results enabling to perform precise assessment (from ecochemical point of view) of carboniferous claystones and mudstones to evaluate their usefulness for utilization in non-soil reclamation of coal mine waste dumps.

Key-Words: monitoring, analytical system, claystones, mudstones, non-soil reclamation,

1 Introduction

The physical-chemical testing of coal mine waste and carboniferous claystones and mudstones for their ecochemical assessment constitutes an element of environmental monitoring. The monitoring of carboniferous claystones and mudstones are one of the subsystems of complex environmental monitoring comprising determination of the conditions and forecasts relating to hazards to environment of their use in the non-soil reclamation of mine waste dumps.

In Poland problem of coal wastes utilization is one of the most important tasks in environmental protection. In Polish coal mining produced ca. 35,000,000 tons/year of coal wastes. This refers to carboniferous claystones and mudstones, in particular its physical and chemical properties and possibilities of utilization [1,2,3 and 4]. Since the amount of coal waste used for industrial purposes in Poland is not very high, and large quantities are removed to waste dumps, the biological reclamation of the dumps is essential. For both financial reasons and implementation ease, non-soil reclamation is more and more frequently applied.

2 Monitoring of caboniferous claystones and mudstones

2.1 Monitoring system

The necessity of carboniferous claystones and mudstones monitoring results from a framework program of monitoring the activity of mining facilities in the natural environment. Such programs are components of environment impact assessment of hard coal deposits exploitation. Monitoring of the waste produced, transported and dumped by a coal mine is an element of activities connected with coal waste management and

utilization, performed by the mines. The following are the principal tasks of coal waste monitoring:

- qualitative and quantitative assessment;
- assessment of waste dumps and their impact on environment;
- verification of waste management efficiency;
- stimulation of development of waste-free technologies ("cleaner production").

Implementation of the above tasks may be based on a specific Quality Waste Monitoring Program (QWMP). Apart from the quantity record, such a program should contain data for physical-chemical assessment, as well as data on mechanical properties of carboniferous claystones and mudstones. Monitoring of carboniferous claystones and mudstones have been incorporated in a Claystones Monitoring (CM) sub-program, presented by Fig. 1 in form of a diagram.

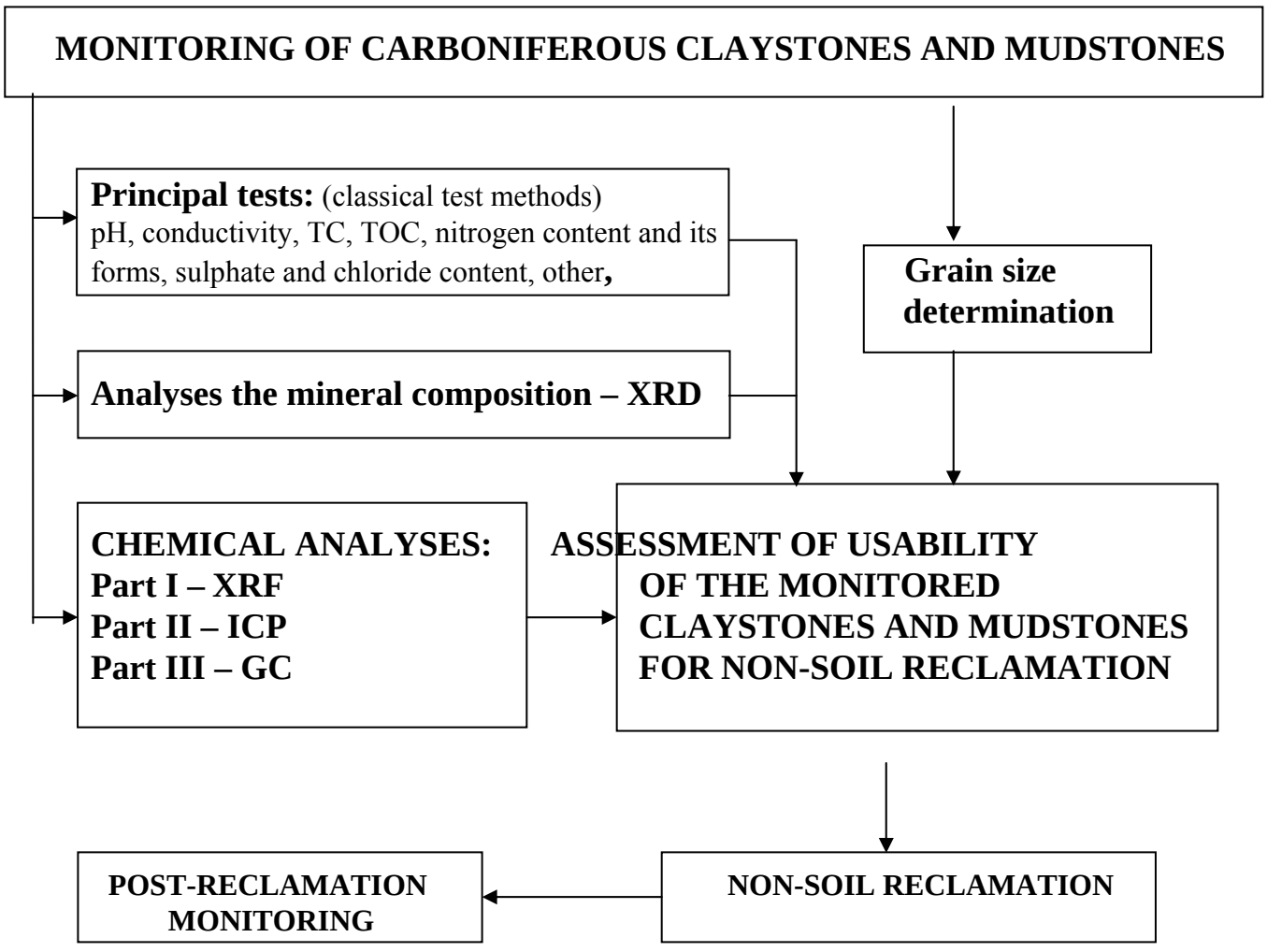

Fig. 1. Schema of carboniferous claystones and mudstones researches in monitoring system

2.2 Claystones and mudstones monitoring for non-soil reclamation

The prognosis for chances of biological non-soil reclamation of coal mine waste dumps may be based on monitoring clayey components of waste. To draw conclusions concerning the scope of activities connected with improvement and making up reclamation work one needs, apart from local monitoring results, also the results of specialized tests. This type of monitoring is focused mainly on the surface layer of the dump and plant material used for reclamation (Table 1).

Table 1. Results of the mineral composition monitorring of carboniferous claystones and mudstones used for building up the waste dump in the near-surface part.

Components	Claystones n=20	Mudstones n=12
Clays minerals		
Average in %	56.5	47.5
Range in %	38 - 76	34 - 60
Standard dev. in %	10.5	8.5
Carbonate minerals		
Average in %	0.7	1.2
Range in %	0 - 5	0 - 5
Standard dev. in %	1.5	1.8

The tests in carboniferous claystones and mudstones of clayey components and carbonates concentrate mostly on assessment of buffering ability [2]. Determination of other components activated in water aims at identifying both the components which are favorable as well as noxious to the growth of plants used for non-soil reclamation. Monitoring in this scope is also connected with determining the doses of fertilizers necessary for appropriate plant growth.

3.3 Assessment of the monitored claystones and mudstones suitability for non-soil reclamation

The carboniferous claystones reaction is an important parameter for determination of its suitability for non-soil reclamation. This refers both to the initial reaction, that is material into which plants are introduced (pH in H_2O), as well as the reaction after some time has lapsed. The time prognosis based on the initial reaction measured in water is not quite favorable against the buffering ability balance (Fig. 2)

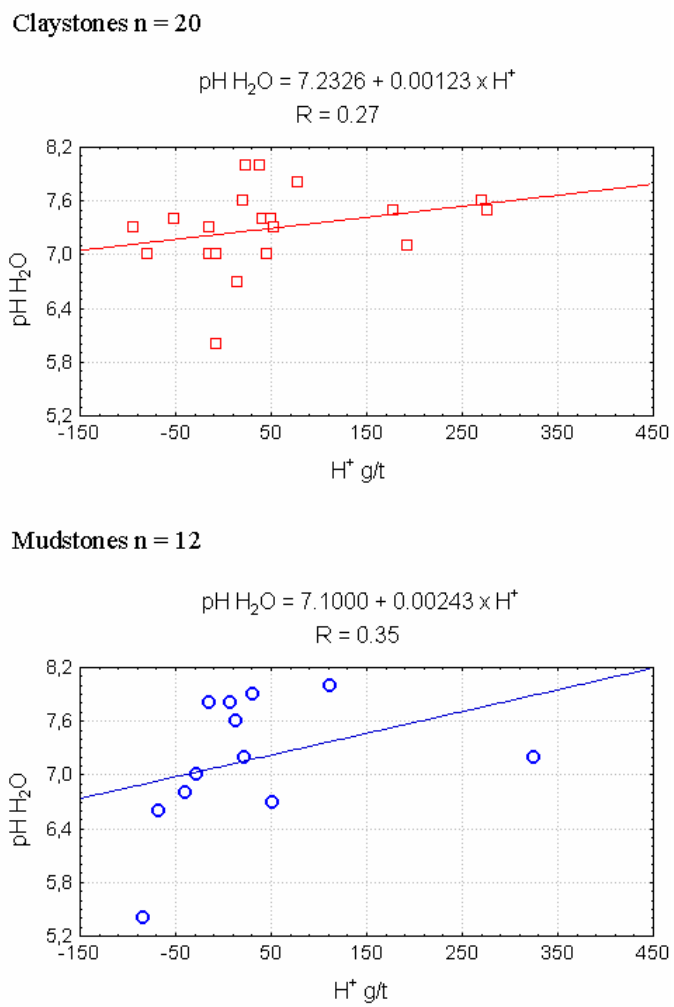

Fig. 2. Environment buffering ability in relation to pH measured in H_2O.

A much better prognosis of changes in the environment reaction can be obtained by correlating the buffering ability of the claystones and mudstones environment and its reaction measured in 30% H_2O_2 after 24 hours of activation (Fig. 3).

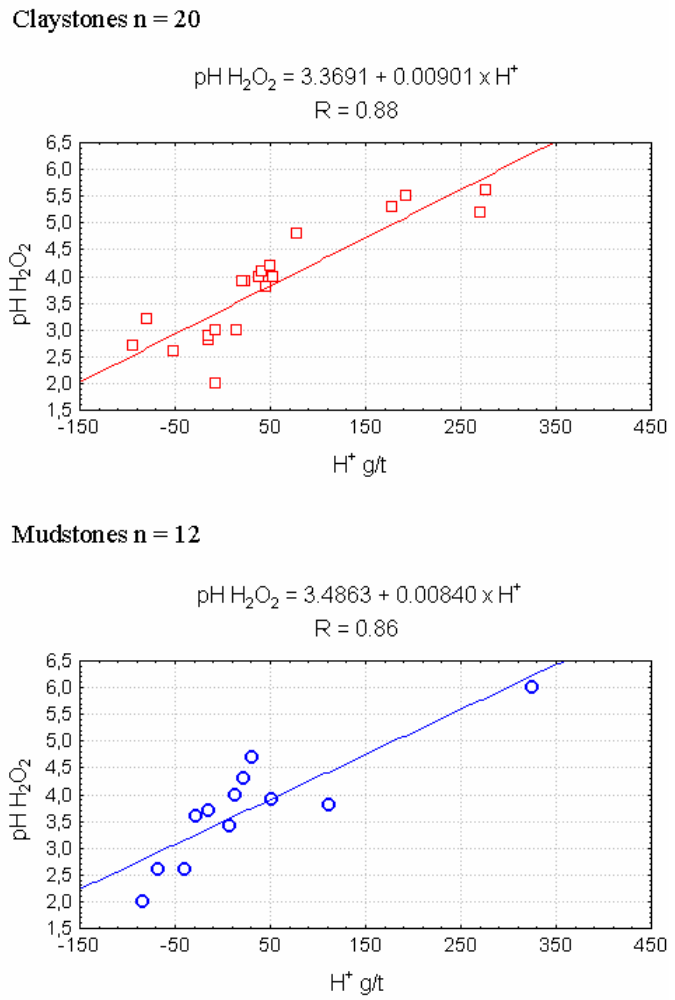

Fig. 3. Environment buffering ability in relation to pH measured in H_2O_2.

4 Analytical methods in monitoring of caboniferous claystones

Executing the investigation within ecochemical assessment of carboniferous claystones needs a reliable integrated testing system. The measuring equipment applied for this should limit the time of conduction the tests and have positive (saving) economic aspect. One of the systems is the one proposed in the testing scheme, i.e. XRD-XRF-ICP-GC. Such a set of methods for conducting carboniferous claystones surveys is used in the Central Mining Institute in the Department of Environmental Monitoring.

4.1 X-ray Diffraction Spectrometry (XRD)

Mineralogical investigation of carboniferous claystones is performed using the diffractometer: X'Pert Philips – radiation CuK_α and CoK_α. The tests are conducted in collaboration with the Department of Mineralogy, Faculty of Earth Sciences, University of Silesia. The interpretation of the diffractograms is based on the data from the files: PDF-2 Philips and ASTM. Quantitative determination is made using standardization methods [5, 6 and 7]. Results of the mineral composition monitoring of carboniferous claystones and mudstones are presented in Table 1.

4.2 X-ray Fluorescence Spectrometry (XRF)

The XRF method is applied for determining the following compounds in carboniferous claystones and mudstones: SO_2, TiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O and P_2O_5. Calibration curves are drawn on the basis of standard samples for which the concentration of analyzed compounds is known [1 and 8]. Results of the chemical composition monitoring of carboniferous waste are presented in Table 2.

Table 2. Main components of coal wastes by XRF method [1].

n = 61	Range in %	Average in %
SiO_2	11.98 - 85.38	56.38
TiO_2	0.19 - 1.17	0.88
Al_2O_3	3.71 - 30.33	21.05
Fe_2O_3	4.34 - 77.60	9.02
CaO	0.51 - 51.27	3.57
MgO	0.17 - 4.22	2.71
Na_2O	0.33 - 7.00	0.89
K_2O	0.23 - 4.03	2.89
SO_3	0.14 - 8.29	1.26
P_2O_5	0.03 - 0.77	0.26

4.3 Inductively Coupled Plasma (ICP)

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is applied for chemical investigation relating to leaching tests from the carboniferous claystones and mudstones. The ICP method, apart from the mentioned determination of trace elements serves to determine many constituents in leaching tests and investigate the speciation of metals [9 and 10].

ICP spectrometer Perkin Elmer Optima 3000DV is used in these researches. Scott's spray chamber together with cross-flow or cone-spray nebulizers is used to determine metal contents.

Preparation of samples for testing, selection of analytic lines, time of analysis and method of calibration have been prepared on the basis of both the experience gathered in the CMI's Department of Environmental Monitoring and literature data [1,11 and 12].

4.4 Gas Chromatography (GC)

The researches concerning organic substances in coal wastes are conducted by GC method. The monitoring was reduces to PAH and i.e., the compounds that may be dangerous for environment. Moreover the frequency of researches was also reduced because of the economic aspect. In the Department of Environmental Monitoring CMI the monitoring determinations are made according to Polish standards and EPA methods.

5 Summary

Monitoring is an important element for determining and forecasting changes in the environment of coal waste dumps at the stage of preparing for biological reclamation and after its completion. Monitoring of carboniferous claystones and mudstones aimed at its utilization for biological non-soil reclamation is of particular importance.

The testing system based on analytic XRD-XRF-ICP-GC methods and supplemented with some extra-instrumental test methods enables to carry out fast and competent ecochemical assessments of the carboniferous claystones and mudstones. In respect of time consumption, the proposed system of chemical investigation within an integrated XRD-XRF-ICP-GC system, is a pro-economic element of performance of accredited chemical laboratories. It enables to obtain, in a short time period, the information on mineralogical and chemical properties of carboniferous claystones and mudstones.

This refers to the full scope of information, beginning from mineral composition, through chemical composition including the amounts of elements and heavy metals (XRF/ICP) up to the contents relating to the amount of ingredients and metals in extracts (ICP) and organic contaminants (GC).

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