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Examinations carried out for the substantiating of the further utilization and deposition of slags/flue ashes resulting from the combustion of lignite deposits in North Hungary

Theses of the doctorial dissertation
to attain the Ph.D degree

Place of research work:

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1. PRELIMINARIES AND OBJECT OF THE RESEARCH

The lignite deposits of North Hungary are situated at the foot of the mountains Mátra and Bükk. In these two regions operate the two largest lignite opencast mines of Hungary, the products of which are utilized almost in 100% ratio for energetic purposes at the power station of the Mátrai Erőmű Co. in Visonta.

In the course of my investigations I examined the solid-grain combustion products issuing from this power station. I was looking for the possibility of their utilization as their sale could mean some surplus receipts for my working place, the Mátrai Erőmű Co. The quantity of the refuse to be deposed could be diminished, whereby transport and handling charges could be saved. Moreover smaller waste deposits would require less expenditure on landscape recultivation, and in addition to economical advantages, it would further the lessening of the load of environment.

Until the time of the erection of flue ash-separator equipments (1986), the major part of the solid components had been apt to escape with the flue-gas from the combustion space into the ambient atmosphere. Nowadays, following the modernization, the major part of the refuse of about yearly one and a half megaton is being dumped onto the deposits installed in the immediate vicinity of the power station. According to my opinion, the arising solid refuse could be utilized in many an industrial and agricultural field, which is technically solvable, furthering thereby the lessening of using up of other, more valuable materials, or even their total replacement.

The basis of every material utilization is the knowledge of all those properties of the material to be utilized, which are of importance in the given field of application and are qualitatively regulated.

Taking the above-mentioned suggestions into consideration, I tried to collect all those application fields, in which the solid combustion products arising from the burning of the lignite of North-Hungary could be utilized. I looked for the qualitative requirements on basis of which it could be known, whether the analyzed material would be suitable for use in the given field. I endeavoured to define the most significant properties, grouping them according to their usability. In addition to determining the factual features and comparing them to the qualitative requirements

I looked about for application fields and possibilities, which, later on, could render help to other researchers in their investigations of similar aspect.

From among the large application possibilities, I did not examine the possibilities of agricultural amelioration and chemical industrial utilization. Neither did examine nor mention in my dissertation the utilization possibilities of the gypsum produced in the flue-gas desulphurizer equipment put up at the time of my research. I was solely looking for solutions regarding the utilization of slag/flue ash mixtures for the production of grained composites. But even within this application field, I paid greater attention to the special field of building construction and civil engineering. This was because, on the one hand, the examination of all the application possibilities would have been beyond my power, regarding energy, time demand and examination costs and, on the other hand, it was apparently the building industry in the field of which these products could be widely utilized. Moreover, the marketability of the slag/flue ash being given in this field, its sale would be most promising in regard to the quantity produced.

Utilization possibilities of slag/flue ash mixtures for the production of grained composites:

1. As granular additives to composites
   a) as fillings without binding agents (for dams, fillings, stabilized earth roads)
   b) as filling material (f.i. into polymer materials)
   c) as additives to concretes and similar composites
   d) as additives to meliorate the pompingability of concretes and pulps
2. As slightly hydraulic binding agents
   a) as hydraulic cement complements
   b) as universal binding agents

The produced solid-grained combustion products or their mixtures can be used in the above mentioned application fields, solely if they fulfil the relating qualitative requirements, regarding the:

- grain-size distribution
- grain density and hollowness
- loss of ignition
- clay-mud content
- purity (f.i. SO_4^{2-}, Cl^-, organic impurities etc.)
- disperseability
- radioactivity
- toxic material content

Using slag/flue ash mixtures as slightly hydraulic binding agents, the chemical properties are even more important, in addition to the above already mentioned properties.

The most important characteristics of chemical compositions are:

a) the acidity / alkaline nature
b) the magnitude of the hydraulic modulus
c) the purity: SO_4^{2-} and Cl^- ion content

In the first phase of my work I wished to analyze, first of all, those of the above mentioned examinations, concerning which experiments and measurements have already been made previously. I collected the previously made studies containing the results of those examinations, which to repeat is unneeded. I was looking for the application possibilities of the solid-corned combustion products produced at the power station “Mátra”, comparing their properties with the requirements as regards their utilization in a given application field.

In the second phase of my work, I dealt with the characteristics of slag/flue-ash mixtures piled up since more than ten years on the deposits, and with the influence of these deposits on the ground water.

In the following, I wish to sum up the refuse components, analyzed in the course of my investigations. The residual corned solid combustion products are separated into two parts already in the combustion chamber. The solid-state grained material falling due to gravity from the combustion chamber is the slag.

The greater part (about 90%) of the residual grained solid combustion product leaves the combustion chamber together with the gas fume. The solid-state grained materials remaining in the gas fume current egressing from the combustion chamber are the flue ashes. The direction of the flow of the gas fume egressing from the furnace changes, when avoiding the single technological elements in the gas fume tunnel at several places. The importance of two of the said technological elements, namely the so called

ECO and Ljungström air heaters, is to be stressed as having one of the most important functions, id est the flue ash separation. In these places, one part of the flue ash is separated from the gas fume. The here separated flue ashes are the so-called ECO and Ljungström flue ashes. The small, close-grained solid combustion products, remaining henceforward in the gas fume, get into the electrical flue ash separating system. The material separated here is the so called filtered flue ash.

The main elements and targets of my investigations, are as follows:

- To find the optimal sampling site, where to determine the properties of the slag/flue ash mixture produced at the power station, on the basis of lignite samples. The knowledge gained will chiefly be of help to other investigators in their further work in this field.

- To examine the grain-size distribution (as being one of the most important properties of all solid-grained material mixtures) of all the solid-state impurities getting into the gas fume in the course of the combustion of lignite. I had a try at approximating the empirical partition function with a theoretical approximating function. I was in search of continuous, also theoretically justifiable partition functions, which would fully characterize the different flue ash fractions separated at several places during the technologic process of the power station. We can, in knowledge of the measuring results of the single measuring points characterize the given flue ash assortments with one single, continuous, also theoretically justifiable partition function. My aim is, furthermore, to determine the statistical characteristics of the grain-size distribution, on basis of which it could be decided, whether the produced combustion products could, in compliance with the respective standards and prescriptions, be utilized or not.

- To examine the density of the agglomerates containing the given grain-size fractions, comparing the ratio between smaller and larger grains within the given grain fraction to the distribution regarded as ideal for the purposes of the building industry. On this does namely depend the usability of the flue ash for the production of concretes and similarly made composites, and the cement quantity being necessary to it.

- To examine the degree of the breaking-up of the solid-grained slag collected from under the combustion chamber, separating from the fume flow while being transported through the pipeline to the deposit. I compared the grain-size distribution of the slag samples collected directly at their production place with the grain-size distribution of the slag samples collected from the deposit. I examined, furthermore, the formal properties of slag and flue ash grains forming grain aggregations. If it can be proved that the slag grains will crack up to a high degree during their transport, this could hinder their usability as load-bearing material without their pre-treatment.

- To analyze the mineral composition and hydraulic binding capacity of the flue ash samples on the basis of their chemical composition. I compared the values got with the values prescribed in the requirements set for Portland cements. Relying upon these statements can it be decided, whether the produced flue ash materials are applicable to replace cement, or can solely be used as additives.

- To execute an environmental effect analysis on the basis of the examination of the spatial and chronological order of the taken water samples collected from the environment of the deposits, serving to ascertain whether the pollution from the deposits could get into the ground-waters and water layers or not.

2. THE RESEARCH METHOD USED

The elaboration of my dissertation is founded upon the investigational and professional work of several years (theoretical activity, study of professional literature, departmental research activity at the university, analysis of the experimental results and examinations, putting to use the experience gained in the course of foreign study-tours and practice). Luckily for me, I encounter the problems raised in my dissertation also day-to-day in my work at the power station.

The processing of the collected samples and all the got results were determining in my investigations. The samples being at my disposal are unequivocally characteristic of the quantity and quality of the total produced and deposed solid-state refuse.

While working on my dissertation, I was always in contact with the teachers of the Department of Mining and Geotechnics of the Institute of Geotechnology and Space Informatics of the University of Miskolc as well as with the specialists of the Mátrai Erőmű Co. I was given every aid necessary for my investigations and help in the evaluation of the got results.

3. THE NEW RESULTS OF MY INVESTIGATIONS

The main results and statements of my investigations can be summarized in the following short theses:

3.1 The optimal sampling points

The lignite production, product transportation and storage system of the Mátrai Erőmű Ltd. constitutes a time-dependent network, with many sources and branches, forming an open looped (non-closed) production cycle. The got products originating from different product sources appear collectively first in

the coal-storage courtyard, so that the representative samples for the prediction of the qualitative properties of the ashes can only be sampled there.

This statement can render help to further works based on the analysis of lignite-samples

3.2 Checking the data of wet screening analysis

I approximated the empirical grain-size distribution function of 25 different flue ash samples, by the help of regression estimation of tenth degree, with a lognormal distribution function. The Kolmogorov-test has verified this distribution hypothesis for all the samples at a reliability level of 0,80. With this function I have given a distribution function, by the help of which one can draw up the characteristic grain-size distribution diagram of a given flue ash assortment for all three flue ash sorts immediately.

3.2/a ECO-type flue ashes

The expected average value of the lognormal grain-size distributions of the flue ash samples type ECO, adapted to the empirical grain-size distribution function, amounted to 334,9 μm, while the average value of the deviations was 233,9 μm. The average coefficient of irregularity, which determines the compactibility was 3,3. These values are characteristic of middling compressible materials.

3.2/b Ljungström-type flue ashes

The expected average value of the lognormal grain-size distributions of the flue ash samples type Ljungström, adapted to the empirical grain-size distribution function, amounted to 347 μm, while the average value of the deviations was 353 μm. The average coefficient of irregularity was 3,4. The flue ashes type Ljungström also belong to the middling compressible materials.

3.2/c The so called “filtered flue ashes”

The expected average value of the lognormal grain-size distributions of the flue ash samples type “filtered flue ashes”, adapted to the empirical grain-size distribution, amounted to 184 μm, while the average value of the deviations was 162 μm. The average coefficient of irregularity was 3. The so-called “filtered flue ashes” are in the neighbourhood of the lowest limit of the category characteristic of the middling compressible materials.

3.3 Compactness test

Comparing the grain-size distribution of the flue ash samples to the Fuller-curve held characteristic of concrete and mortar materials and, regarding the requirements set, known as being ideal for dry mixtures, I was convinced that the flue ash aggregates examined by me are not conform to these requirements. Concerning flue ash aggregates type ECO and Ljungström, the ratio of the finer grain aggregates (smaller than the average conventional value) does not reach the value needed. The grain-size of the so-called “filtered flue ashes” is so small that the grains deviate from the ideal admitted grain-size both in the range of the small and the large grain-size.

It can be stated, that concrete products made solely of these materials do not fully meet the requirements of concretes class I. and class II. defined for the building industry.

But in cases, when in a solid grain-mixture the ratio of grains, the size of which is similar to that of the flue ashes produced at the power station “Mátra”, will have to be raised, in interest of the ideal grain distribution, the product got thereby can be well used as filling materials.

3.4 Analysis of the chemical composition

From the chemical (oxidic) composition of the 88 flue ash samples being at my disposal, it was easy to diagnose that the samples are of an acidic character, and that their hydraulic modulus belongs to the range of 0,028-0,976, as opposed to the optimal range of 1,7-2,3, owing to which, the flue ashes cannot concrete hydraulically, not even if all the other conditions of their concreting are fulfilled. On the basis of their sulphate content, I determined also the purity degree of the flue ashes produced in our power station, according to the requirements of the cement industry.

On the basis of the analysis of the chemical composition, the following facts can be stated:

1. All the examined samples are of an acidic character, so that these flue ashes are solely as an admixture able to establish a chemical bond.

2. The sulphate content of the samples, regarding the purity needed in cement industry, is too high, in consequence of which, the flue ashes produced in our power station are acutely corrosive in character.

3. The binding capacity of the samples being is my disposal are, due to the low hydraulic modulus, not able to approach the binding capacity of Portland cements.

4. Due to the low CaO-content, no chemical bond can be generated in a sufficient degree on the deposits. Thus, in case of their drying out, the deposits have to be watered to prevent dust formation, while after being filled up, they must be covered.

3.5 The breakage of the slag

Comparing the grain-size of seven slag samples collected at the pulp deposit with the grain-size of the slag samples collected at the power station, it can be stated that the grain-size of the samples collected at the pulp deposit is considerably smaller than the other. This contraction in size results from the breakage of the slag during its hydraulic transport. The greater part of the grains forming the slag is cavernous.

The mixtures in the deposits are no more liable to collapse, and can thus be used as grained admixtures

The slag produced at the power station is because of its low load-bearing capacity unfit for the preparation of normal concretes for the building industry.

3.6 The analysis of water samples collected from sites close to the deposits.

Comparing the results of the oxidic analysis of water samples collected from water-quality observation wells and several other dewatering wells bored close to the slag/flue ash deposits of the power station, with the results of the oxidic analysis of the water samples collected from artesian wells and drainage drift galleries worked up before the formation of the deposits had been brought about (1967), it can be stated, that no considerable quantity of pollution can infiltrate from the deposits into the environment. It was proved by former studies that neither toxic nor heavy metal pollution could be found in the environment of the power station. This being so, I did not occupy myself with this problem. I did analyze, however, the solution iron, sulphate-ion and calcium-ion content as well as the hardness of the ground of the environment.
Concerning several water quality observation wells, it had been assumed that the pollution could have infiltrated from the deposit into the well. Though this assumption might indicate the possibility of leakage in the environment of the

wells, it, nevertheless, can be disregarded as being not dangerous to health.

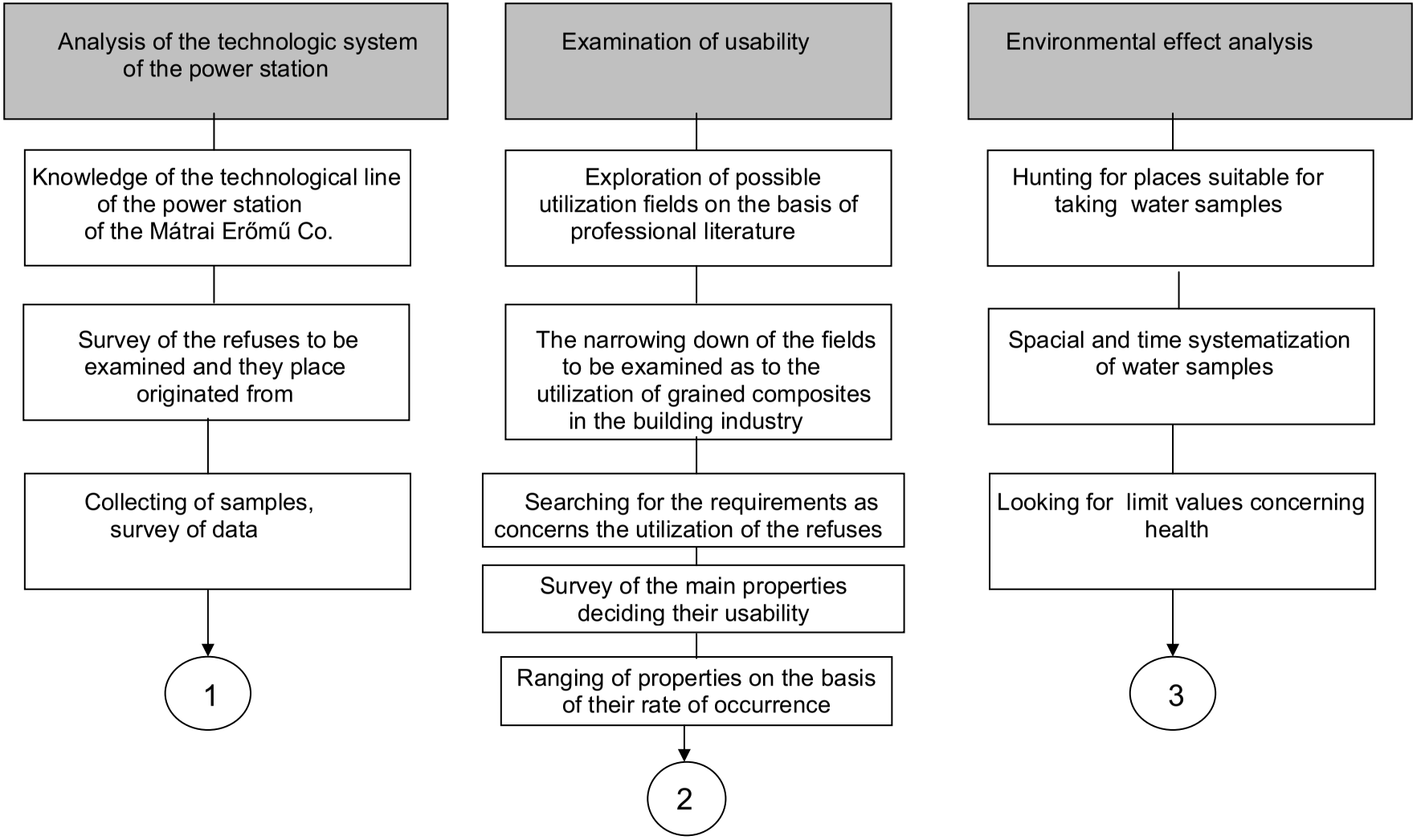
3.7 The generally valid method of the analysis

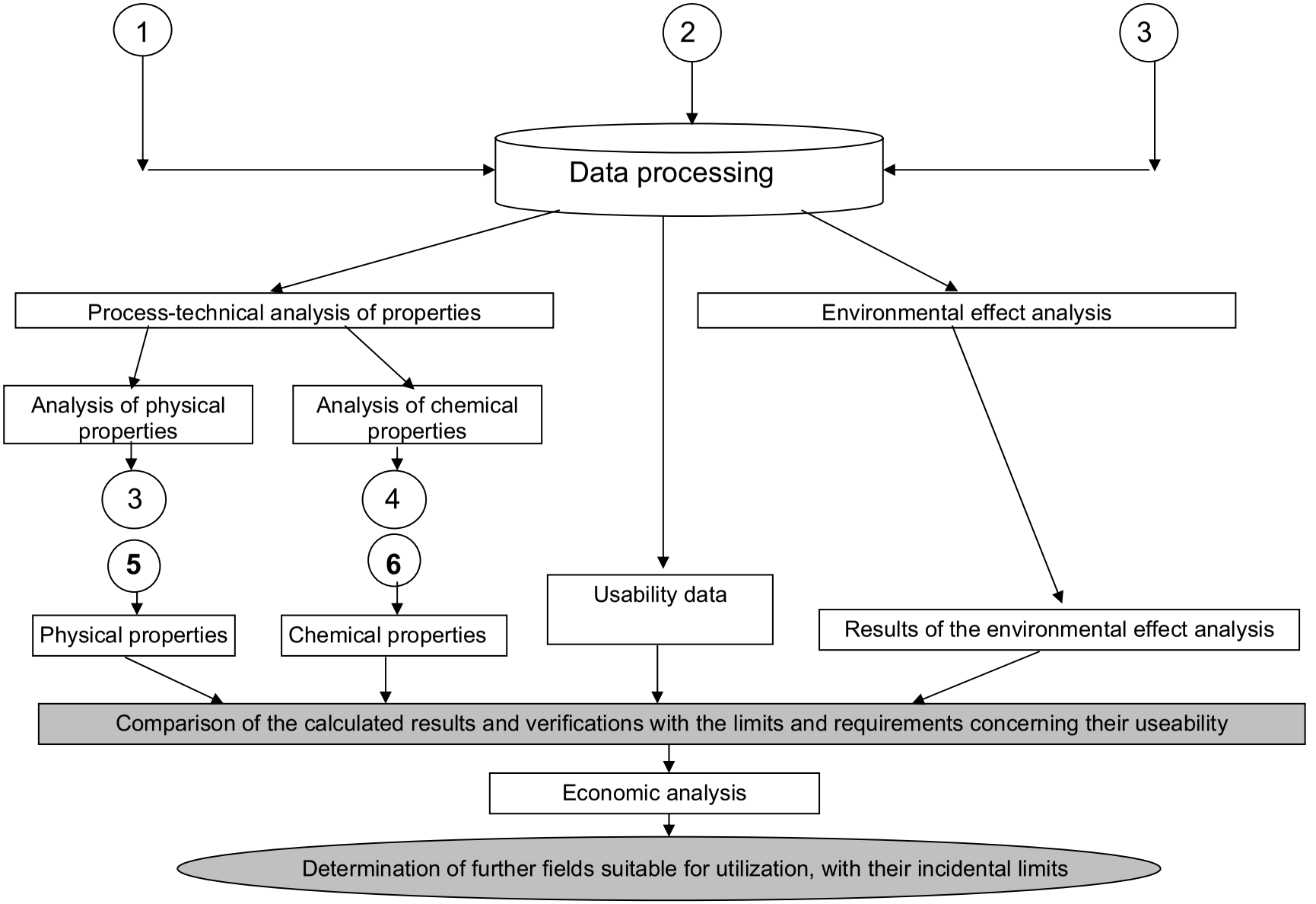
In the course of my research work, I elaborated a method of analysis, built up on a logically interdependent system, the elements of which are based on experimental facts. The results and statements of the examinations regarding the usability, disposability and workability of the produced refuses are of universal validity and generally applicable for all the power stations working according to the similar technological system as the Mátrai Erőmű Co.

I used the testing method known from processing techniques for the determination of the important properties as regards the utilization of the refuses. I then supplemented this method with statistical and mathematical methods.

I illustrated the building-up of the analyzing method with a flow-process diagram.

Method of the analysis

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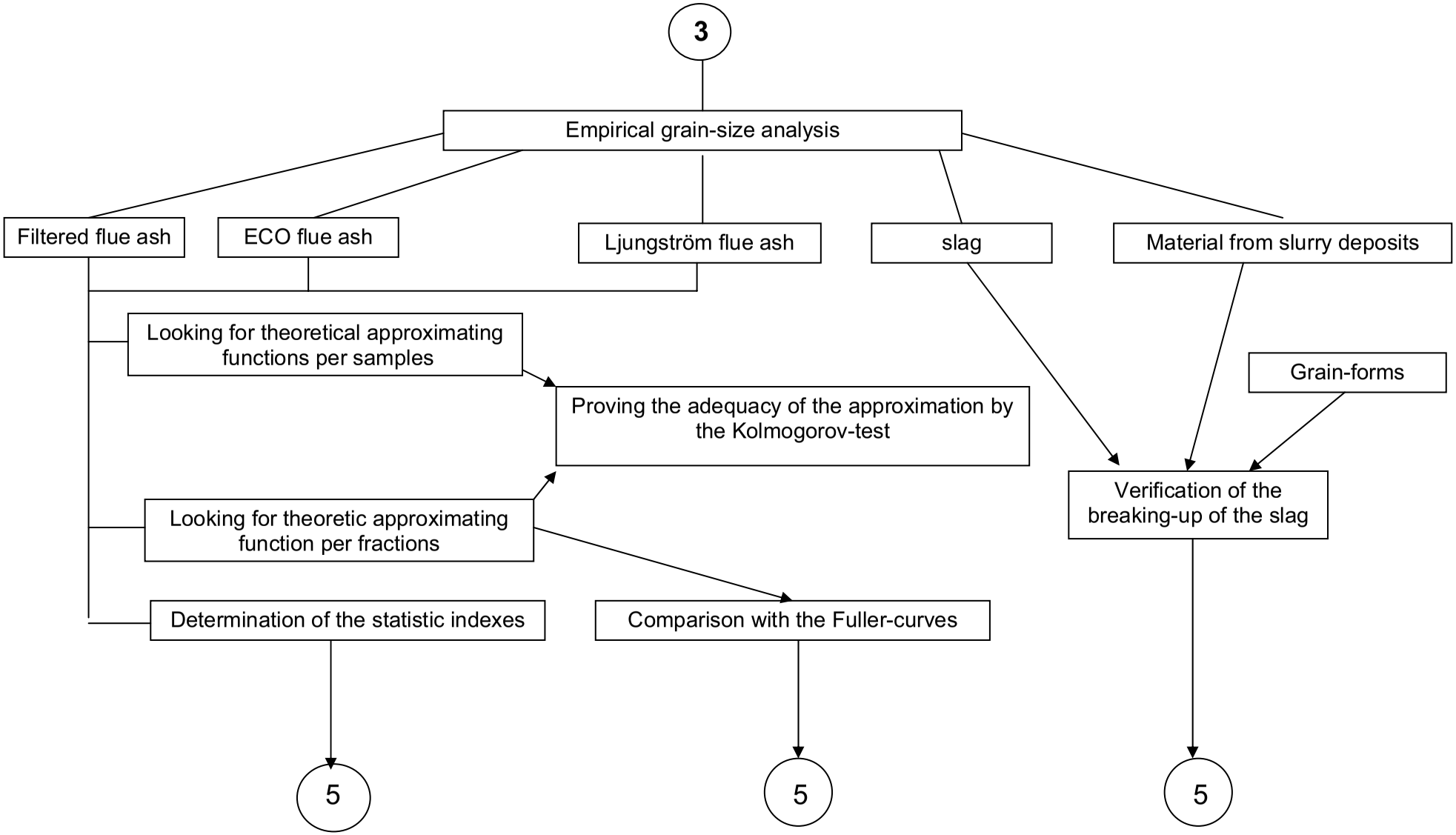
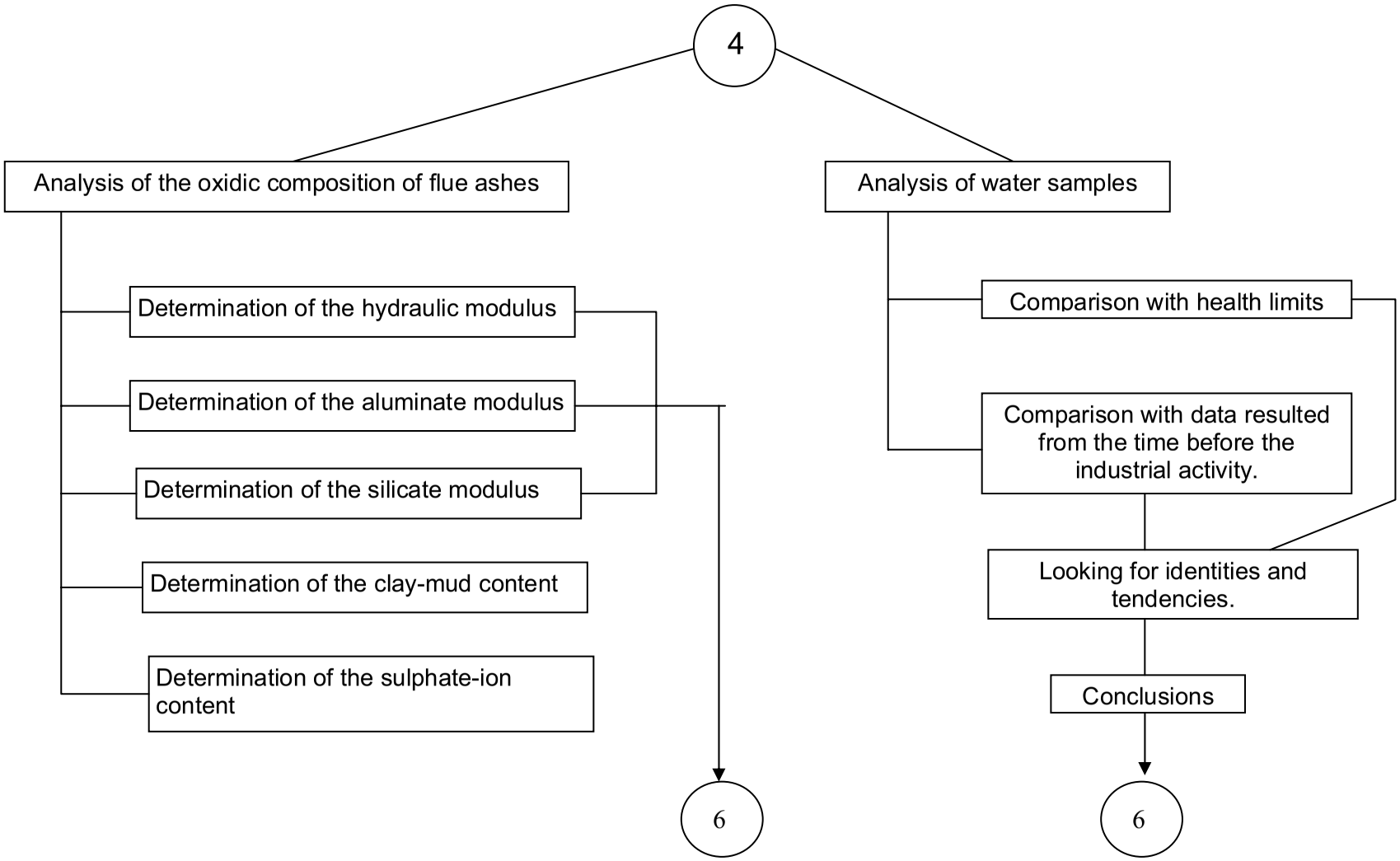
2
3
Data processing
Process-technical analysis of properties
Environmental effect analysis
Analysis of physical properties
Analysis of chemical properties
3
4
5
6
Usability data
Physical properties
Chemical properties
Results of the environmental effect analysis
Comparison of the calculated results and verifications with the limits and requirements concerning their useability
Economic analysis
Determination of further fields suitable for utilization, with their incidental limits


3
Empirical grain-size analysis
Filtered flue ash
ECO flue ash
Ljungström flue ash
slag
Material from slurry deposits
Looking for theoretical approximating functions per samples
Proving the adequacy of the approximation by the Kolmogorov-test
Grain-forms
Verification of the breaking-up of the slag
Looking for theoretic approximating function per fractions
Determination of the statistic indexes
Comparison with the Fuller-curves
5
5
5


4
Analysis of the oxidic composition of flue ashes
Analysis of water samples
Determination of the hydraulic modulus
Determination of the aluminate modulus
Determination of the silicate modulus
Determination of the clay-mud content
Determination of the sulphate-ion content
Comparison with health limits
Comparison with data resulted from the time before the industrial activity.
Looking for identities and tendencies.
Conclusions
6
6

3.8 Economical estimation

After executing the technical examinations, I economically estimated the attainable reduction of costs, if certain utilization possibilities were realized.

I estimated the transfer costs onto the deposits of the refuses produced at the power station, their stockpiling costs and the costs of landscape architecture after the elimination of the deposits.

The result of my estimations was that, in addition to the incomes of sales a cost reduction of yearly about 120 Ft/ton could be attained.

4. The utilization of the research results

In the course of my research work, I always kept the utilization of greatest extent to the fore as regards the solid-grained combustion products produced at the power station. Profit can be derived not only from the sale of the refuse, but also owing to the lessening of the costs of waste-disposal and by easing the load of environment. In the first years of my research work I had been member of a team, which had succeeded in replacing the so called thin liquid slag-flue ash deposing technology with the consistent slag-flue ash deposing technology, the latter being more beneficial to the environment.

After the realization of the up-to-date technology of disposal, I was chiefly occupied with the usability of the slag/flue ash refuses, and most intensively with the utilization of grain composites. In this field of utilization, the utilizable refuse quantity is commensurable with the total produced quantity. The produced combustion products can be utilized in the following main fields:

As grained aggregates:

- For road and bank building
  - slag materials are unusable
  - slag/flue ash mixtures are usable

- As filling materials for asphalt mixtures:
  - The usage of slag products, ECO- and Ljungström flue ash materials is inadmissible
  - The usage of filtered flue ash materials is in their original production state fully admissible

- For composites made on the principle of concretes:
  - slag products are unusable
  - flue ash products can be used, depending on their purity and lay-mud content

- As aggregates to meliorate the pompingability:
  - The filtered flue ash products are up to the grain-size of 160 μm respectively, 250 μm usable. All in all 70-80% of the total produced flue ash products.

- As slightly hydraulic binding agent:
  - The filtered flue ash products can be used in their milled form (maximum admissible grain-size is 50 μm, and a mixture ratio of maximum 35%).

- As binding agent, for road building:
  - The filter-flue ash products can be used after being milled

The utilization of the possibilities detailed in my dissertation and shortly summarized in this résumé can mean considerable advantages for the Mátrai Erőmű CO. and other power stations using a similar technological process in the sale of flue ashes separated in the power station and of materials being deposed on the slurry deposits.

Thus also the deposition costs, the space demand of the deposits, and the load of the environment can be reduced by the salvaging. The developed, generally valid methods can be useful also for other organizations dealing with similar problems.

I do hope, I could contribute to the endeavour to further the utilization of the refuse produced in coal-fed power stations. My effort was to help the protection of environment and the work of the organizations being interested in this theme.

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